Biodiesel Fuel Standards

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Abstract: Two major specifications establishing the quality requirements for biodiesel fuels are the ASTM D 6751 in the USA and the EN 14214 in Europe. This paper includes a summary of these standards, compares the US and EU specifications and test methods, and discusses the underlying issues. A summary of biodiesel standards in selected other countries is also provided.

- Biodiesel Specifications
- Properties and Testing
- Appendix A: Other Countries

Biodiesel Specifications

Development of biodiesel standards started in the 1990's, to support the increasing use of biodiesel and its blends as automotive fuels. The American Society for Testing of Materials (ASTM) adopted a provisional specification PS121 for biodiesel in 1999. The final *ASTM D 6751* standard was adopted in 2002 [ASTM 2002]. In Europe, *EN 14214* biodiesel standard (based on former DIN 51606) was finalized in October 2003. The US and EU standards have international significance; they are usually the starting point for biodiesel specifications developed in other countries (see Appendix A).

Approaches to standards for biodiesel differ. In the USA, ASTM D 6751 establishes specifications for a *biodiesel blend stock* for middle distillate fuels. While the specification was written for B100, it is not intended for neat biodiesel used as automotive fuel. Rather, it is for the biodiesel component that is to be blended with grades 1-D and 2-D diesel fuels as defined by ASTM D 975 to give biodiesel/diesel fuel blends. While no standards for biodiesel/diesel fuel blends have yet been published by ASTM, ASTM D 975 could potentially be modified to allow up to 5% biodiesel, as levels up to 5% have minimal impact on the blended fuel's properties. For higher level blends up to B20, a stand alone specification will likely be needed [Howell 2005].

In Europe, EN 14214 establishes specifications for fatty acid methyl esters for diesel engines. In contrast to ASTM D 6751, B100 that meets this standard could be used unblended in a diesel engine (if the engine has been adapted to operate on B100) or blended with diesel fuel to produce a blend in accordance with EN 590, the European diesel fuel specification. Blends up to 5% of Fatty Acid Methyl Ester (FAME) are allowed in diesel fuel defined by EN 590.

Biodiesel specifications and test methods according to ASTM D 6751 and EN 14214 are compared with those of petrodiesel in Table 1. Both ASTM D 6751 and EN 14214 establish specifications for key fuel properties for biodiesel—the former for biodiesel blend component, the latter for both blend stock and neat biodiesel automotive fuel. EN 590 establishes specifications for blends of biodiesel and diesel fuel with 5% or less biodiesel.

Table 1
US and EU Biodiesel Specifications

Property	ASTM D975-04c		ASTM D6751-03a		EN 590:2004		EN 14214:2003	
Flash point, min	No 1D 38°C No 2D 52°C	D93	130°C	D93	55°C	EN 22719	120°C	prEN ISO 3679
Water & sediment, max	0.05% vol	D2709	0.05% vol	D2709				
Water, max					200 mg/kg	EN ISO 12937	500 mg/kg	EN ISO 12937
Total contamination, max					24 mg/kg	EN 12662	24 mg/kg	EN 12662
Distillation temperature (% vol recovered)	90%: 1D <288°C 2D 282-338°C	D86	90%: <360°C	D1160	65%: >250°C 85%: <350°C	EN ISO 3405		
Kinematic viscosity	1D 1.3-2.4 mm^2/s 2D 1.9-4.1 mm^2/s	D445	1.9-6.0 mm^2/s	D445	2.0-4.5 mm^2/s	EN ISO 3104	3.5-5.0 mm^2/s	EN ISO 3104

Property	**ASTM D975-04c**		**ASTM D6751-03a**		**EN 590:2004**		**EN 14214:2003**	
Density					820-845 kg/m^3	EN ISO 3675 EN ISO 12185	860-900 kg/m^3	EN ISO 3675 EN ISO 12185
Ester content					< 5% FAME	EN 14078	> 96.5%	EN 14103
Ash, max	0.01% wt	D482			0.01% wt	EN ISO 6245		
Sulfated Ash, max			0.020% wt	D874			0.02% wt	ISO 3987
Sulfur, max (by weight)	1D and 2D: S15 15 ppm S500 0.05% S5000 0.5%	D5453 D2622	Two grades: S15 15 ppm S500 0.05%	D5453	Two grades: 50 mg/kg 10 mg/kg	EN ISO 14596 EN ISO 8754 EN ISO 24269	10 mg/kg	prEN ISO 20846 prEN ISO 20884
Copper strip corrosion	< No 3	D130	< No 3	D130	class 1	EN ISO 2160	class 1	EN ISO 2160
Cetane number, min	40	D613	47	D613	51.0	EN ISO 5165	51.0	EN ISO 5165
Cetane index, min					46.0	EN ISO 4264		
One of: - cetane index - aromaticity	 > 40 < 35% vol	 D976 D1319						
PAH, max					11% wt	IP 391 EN 12916		
Operability, one of: - cloud point - LTFT/CFPP	Regional requirements	D2500 D4539 D6371						
Cloud point			report	D2500	Location & season dependant	EN 23015		
CFPP					Location & season dependant	EN 116	Location & season dependant	EN 116
Carbon residue, max	1D: 0.15% wt 2D: 0.35% wt	D524	0.050% wt	D4530	0.30% wt	EN ISO 10370	0.30% wt	EN ISO 10370
Acid number, max			0.80 mg KOH/g	D664			0.50 mg KOH/g	EN 14104
Oxidation stability					< 25 g/m^3	EN ISO 12205	> 6.0 hrs	EN 14112
Iodine value							< 120	EN 14111
Linolenic acid methyl ester							< 12.0% wt	EN 14103
Polyunstatured methyl esters							< 1% wt	No method specified
Methanol							< 0.20% wt	EN 14110
Monoglycerides, diglycerides & triglycerides							MG <0.8% wt DG <0.2% wt TG <0.2% wt	EN 14105
Group I metals (Na + K)							< 5.0 mg/kg	EN 14108 EN 14109
Group II metals (Ca + Mg)							< 5.0 mg/kg	EN 14538
Free glycerin, max			0.020% wt	D6584			0.02% wt	EN 14105 EN 14106
Total glycerin, max			0.240% wt	D6584			0.25% wt	EN 14105

Property	ASTM D975-04c		ASTM D6751-03a		EN 590:2004		EN 14214:2003	
Phosphorous, max			0.001% wt	D4951			10 mg/kg	EN 14107
Lubricity	< 520 µm	D6079			< 460 µm	ISO 12156-1		

The US specification, ASTM D 6751, defines biodiesel as mono-alkyl esters of long chain fatty acids derived from vegetable oils and animal fats. The type of alcohol used is not specified. Thus mono-alkyl esters could be produced with any alcohol (methanol, ethanol, etc.) so long as it meets the detailed requirements outlined in the fuel specification. By requiring that the fuel be mono-alkyl esters of long chain fatty acids, other components, with the exception of additives, would inherently be excluded.

The European biodiesel specification, EN 14214, is more restrictive and applies only to mono-alkyl esters made with *methanol*, fatty acid methyl esters (FAME). The minimum ester content is specified at 96.5%. The addition of components that are not fatty acid methyl esters—other than additives—is not allowed.

Properties and Testing

Flash Point

This property is commonly used to assess the tendency of a material to form a combustible mixture in air. As a fuel sample is heated, the partial pressure of fuel vapor above the liquid surface will rise and eventually a combustible mixture of fuel vapor and air will form. The flash point temperature is intended to approximate the minimum temperature at which such a combustible mixture will form. However, it should be kept in mind that flash point temperature values are a function of the apparatus, sample, and operational procedures used for their determination. Correlation with other methods and with situations encountered in the field cannot always be guaranteed.

There are minimum limits set for this property to meet legal requirements and safety precautions for fuel handling and storage. The value for biodiesel is set much higher than that for diesel fuel because for biodiesel, flash point is also used to limit any un-reacted alcohol left over from the fuel production process.

For ASTM D 6751, the flash point of biodiesel is intended to be 100°C minimum but because of the high variability of the test method, the minimum flash point temperature has been set to 130°C to ensure that the minimum of 100°C will be met. A flash point of 100°C will be exceeded only if the alcohol content of the fuel is less than 0.18% to 0.22% [Van Gerpen 1997]. Typical flash points of biodiesel are over 160°C.

Flash point in ASTM D 6751 is determined by the Pensky-Martens closed cup method (ASTM D 93). While other methods can be used, this is the referee method that is to be used to resolve any disputes. This method uses a covered brass cup with at least 75 ml of sample inside. The temperature of the sample is monitored with a thermometer and the sample is heated and stirred at specified rates. An ignition source is directed into the test cup at regular intervals until a flash is detected. The Pensky-Martens test is a dynamic test method and the vapor above the sample may not be at the same temperature as the sample. The precision of this test method is very dependant on the rate of temperature increase of the sample. Variations in the thermal conductivity of the sample being tested can affect the result and it may not always be possible to obtain the required precision.

EN 14214 has a minimum flash point specification of 120°C. The test method used for flash point in EN 14214 is the *rapid equilibrium closed cup method*, ISO 3679. This test method uses a much smaller 2 ml sample and is an equilibrium method where the sample and vapor are at the same temperature. Round Robin testing in Europe determined that the rapid equilibrium closed cup method with a thermal detection device was better suited for determining the flash point of FAME contaminated with traces of methanol [ISO 2002]. The poor visibility of the methanol flame was claimed to be the source of difficulty with the Pensky-Martens method [Prankl 2000].

EN 14214 does not rely exclusively on flash point for limiting the methanol content, but includes a separate maximum limit for methanol of 0.20% mass.

While it may appear that the ASTM flash point requirement is higher than that in the European standard, the test methods used in these two standards differ significantly and this sort of comparison should not be made, especially since the difference is close within the precision limits of the test methods.

Water and Sediment

Water and sediment in fuel can be major sources of contamination. Water especially can cause corrosion and support microbiological growth. It is important that water and sediment be kept to a minimum. Water contamination can occur in numerous places of the fuel handling chain. While fuel may be water free as it leaves the production facility, it can pick up water as it passes through the distribution and storage system.

Normally water can exist in fuel as either free water or dissolved in solution. With free water, there is a distinctive boundary between the fuel and water phases. The amount of water that a fuel can hold in solution depends on the fuel. Petroleum diesel fuels reach saturation at values typically less than 60 ppm, while B100 can reach saturation at levels as high as 1500 ppm. The solubility of water in blends of biodiesel and petroleum diesel does not scale linearly. The solubility of water in B20 is equivalent to that for petroleum diesel fuel; typically less than 60 ppm [Van Gerpen 1997]. It is therefore possible when blending a diesel fuel and a biodiesel, neither of which has any free water, to end up with a fuel blend that has free water.

The specification for biodiesel, ASTM D 6751, and the specification for diesel fuel, ASTM D 975, allow up to 500 ppm by volume of water and sediment. The method used to measure this, ASTM D 2709, centrifuges a sample for 10 minutes. The water and sediment settle to the bottom of the centrifuge tube and the combined total is read off the graduations on the tube. This method can only account for free water and sediment and is adequate for fuels where the solubility of water is much less than the specified maximum limit for water and sediment. This is the case for diesel fuel. As the solubility of water increases above the maximum allowable limit, as is the case with biodiesel, care needs to be taken to ensure that any blends with petroleum diesel do not result in a water and sediment content that is unacceptable.

If proper fuel handling procedures and good workmanship practices have been followed and little free water is present in either fuel, it is possible for blends up to B20 to contain less than 500 ppm of free water even if starting with fuels that are saturated with water. This is illustrated in Table 2 [STM 2003], which shows data for different blends of diesel fuel and biodiesel made from three different types of fat. The water analysis in this case was done with Karl Fischer titration and is the total of free water and dissolved water. Even the B100 from animal fat that contained over 1500 mg/kg total water resulted in a B20 blend with 350 mg/kg water. In this case, the resulting free water will be below the maximum acceptable value of 500 ppm by volume.

Table 2

Example Total Free and Dissolved Water (mg/kg)

	Vegetable Oil	**Used Cooking Oil**	**Animal Fat**
Diesel	43	43	43
B5	79	50	119
B20	189	71	350
B100	776	185	1581

The European biodiesel standard, EN 14214, has separate specifications for water and total contamination. The limit on water is 500 mg/kg but unlike the limit for ASTM D 6751, it is the total of free water and bound water measured using Karl Fischer titration. Total contamination is set at 24 mg/kg and is determined by the sediment that is left after filtering a sample of the fuel.

Kinematic Viscosity

Viscosity is important to diesel engines because it can affect the operation of the fuel injection equipment and the development of the fuel spray. For some engines, a minimum viscosity specification helps prevent power loss due to injection pump and injector leakage and is one requirement for sufficient fuel system component lubrication. Maximum viscosity however is limited by engine design, size and fuel injection equipment size. Fuels with high viscosity tend to form larger droplets on injection into the cylinder, which can result in poor combustion and increased emissions. High viscosity fuels can also increase fuel system component stresses and can result in higher wear rates and/or component failure [Bayer 2002].

Biodiesel (ASTM D 6751) has an allowable range on viscosity of 1.9 to 6.0 mm^2/s. The upper limit is higher than the upper limit of 4.1 mm^2/s for No. 2 Diesel fuel defined by ASTM D 975. Blending biodiesel into No. 2 Diesel fuel that has a viscosity near its upper limit can result in a final blend with a viscosity that exceeds 4.1 mm^2/s.

Kinematic viscosity for biodiesel is determined with a calibrated glass capillary viscometer (ASTM D 445). The time for a fixed volume of liquid to flow under gravity through the capillary of the viscometer maintained at a temperature of 40°C is measured. The kinematic viscosity is the product of the measured time and the calibration constant of the viscometer.

EN 14214 differs in the range of allowable viscosity. FAME that meets EN 14214 must have a viscosity between 3.5 to 5.0 mm^2/s. Most common fats used to produce biodiesel in both North America and Europe produce methyl esters with viscosity in the range of 3.5 to 5.0 mm^2/s. Some tropical oils that contain short chain fatty acids such as coconut oil, will result in methyl esters that are significantly less viscous than this range but would fall into the range allowed by ASTM D 6751.

Ash/Sulfated Ash

Ash forming materials may be present in fuel as abrasive solids and soluble metallic soaps. In biodiesel, unreacted catalyst from the fuel production process may also be present. Abrasive solids and unreacted catalyst can result in excessive wear of the fuel injection equipment, the piston and piston rings and can contribute to engine deposits. Soluble metallic soaps have little impact on wear but can contribute to fuel filter plugging and engine deposits.

The standard test method for ash in petroleum products that do not contain ash-forming additives is ASTM D 482. In these products, any ash forming materials would be considered as unwanted impurities. A sample of the fuel is placed in a crucible, ignited and allowed to burn in air until only ash and carbon remain. The residue is then heated to 775°C to remove carbonaceous material. The mass of residue left after the removal of the carbonaceous material and normalized by the mass of the original sample is the reported test result. Some of the ash forming materials contained in the original fuel sample can react with oxygen in the air to form oxides. As a result, the final residue can have a higher mass than the original ash forming materials in the fuel sample.

Both the ASTM and European biodiesel standard uses the sulfated ash test method to measure this property (designated as ASTM D 874 by ASTM). In this test, the sample is ignited and burned until only ash and carbon remain. After cooling, the residue is treated with sulfuric acid and heated at 775°C until the carbon oxidation is complete, cooled, retreated with sulfuric acid and heated again at 775°C to a constant weight. This test method is used in cases where significant loss of ash forming material would result during the removal of carbonaceous material with ASTM D 482. This is the case with oxides of the alkaline metals found in the catalyst used in the biodiesel production process. Oxides of these metals evaporate around 550°C. When phosphorous is absent, alkaline metals such as sodium, potassium, barium and calcium are converted to their sulfates by treating with sulfuric acid. These sulfates have a higher boiling point than the oxides of these metals and therefore losses are minimized. As with the oxidized ash test (ASTM D 482), the residue remaining after the test can be higher than the original ash forming impurities found in the original sample. Sulfates formed from these impurities tend to be heavier than their respective oxides. This is reflected in the maximum allowable limit of 0.020 wt% for sulfated ash in biodiesel specification, ASTM D 6751. The corresponding limit for oxidized ash in diesel fuel, ASTM D 975, is 0.010 wt%.

The sulfated ash test, ASTM D 874, was originally developed for determining ash forming metallic constituents in lubricating oils and additives. It worked well with the older lubricating oil additive technology (barium, calcium, zinc and phosphorous) for which it was originally developed. Newer lubricating oil additives contain multiple metallic and non-metallic compounds and have additional elements such as magnesium and boron that affect the test results and have made this test method less reliable for its original intended purpose. Ash forming elements in biodiesel are fewer than those encountered in current lubricating oils technology and the concerns over the reliability of the sulfated ash test may not apply to biodiesel.

Phosphorous is one of the elements that is known to significantly interfere with the sulfated ash test. It remains partially or wholly in the sulfated ash as metal phosphates. This will generally not be a concern for finished biodiesel that meets the

0.001% wt phosphorous limit. Phosphorous concentrations above 0.001% wt are needed before the sulfated ash test is significantly affected [Mittelbach 1996].

Sulfur

Starting in 2006, on-road fuels for diesel engines in North America must have less than 15 ppm mass of sulfur. The sulfur requirements for many non-road applications will be higher at 500 ppm mass (starting in 2007) but will eventually be aligned with the on-road requirements. ASTM D 6751 defines two different grades of biodiesel; S15 with a sulfur level less than or equal to 15 ppm and a S500 grade with a sulfur level less than or equal to 500 ppm. While most biodiesel fuels can easily meet the S15 grade requirement, some produced from animal fats cannot and may therefore not be suitable for blends used as on-road fuel.

In Europe, diesel fuel must have less than 50 ppm sulfur starting in 2005 and 10 ppm starting in 2009. The current maximum limit of sulfur in biodiesel meeting EN 14214 is 10 ppm.

While other test methods are used to measure sulfur in fuel, ASTM D 5453 is the referee method for fuels with less than 15 ppm sulfur. In this test, a sample of the fuel is inserted into a high temperature combustion tube having an oxygen rich atmosphere. Fuel sulfur is oxidized to sulfur dioxide. Water produced during the sample combustion is removed and the combustion gases are then exposed to ultraviolet light at a wavelength that excites the sulfur dioxide. As the excited sulfur dioxide returns to its stable state, it emits photons which are detected by a photo-multiplier tube. The resulting signal is a measure of the sulfur in the sample.

Copper Strip Corrosion

This test is a measure of possible problems that could be encountered with the interaction of the fuel with copper and brass or bronze fuel system components. It was originally developed to determine the relative corrosiveness of reactive sulfur compounds present in refined petroleum products. The effect of these compounds varies with chemical composition and does not necessarily correlate with sulfur concentration.

In the test method, ASTM D 130, a polished copper strip is immersed in a specified quantity of fuel sample. For both diesel fuel (ASTM D 975) and biodiesel (ASTM D 6751) the sample is then held at 50°C for 3 hours. At the end of this time period, the sample is removed, washed and compared with the ASTM Copper Strip Corrosion Standards. Acids or sulfur containing compounds can tarnish the copper strip, thus indicating potential corrosion problems. The acceptable ASTM rating for both diesel fuel and biodiesel is a No. 3 or better. This rating would be achieved with a dark tarnish on the copper strip. Any signs of corrosion on the copper strip would designate it as a No. 4 and would be unacceptable.

EN 14214 is more restrictive on the copper strip corrosion test. The acceptable rating is No. 1 which requires that only slight tarnishing of the copper strip occur during the test.

Cetane Number

Cetane number is a measure of the ignition quality of a fuel used in compression ignition engines. It can have an impact on combustion quality and emissions. Biodiesel fuels generally have higher cetane numbers than diesel fuels. This is reflected by the fact that the minimum requirement for ASTM D 6751 biodiesel is 47 while that for ASTM D 975 diesel fuel is 40. The corresponding lower limit for cetane number in EN 14214 is 51.0, which is the same as that required for European diesel fuel specified in EN 590.

The only method currently acceptable for cetane number compliance determination for ASTM fuel standards is ASTM 613. In this test, the cetane number is determined by comparing its combustion characteristics with those for blends of reference fuels of known cetane number. Testing is done in a special cetane rating engine under standard operating conditions. The engine is operated with the sample whose cetane number is being determined and the compression ratio in this engine is varied with a hand wheel until a specific ignition delay is achieved. Two reference fuels are then used that have cetane numbers that bracket the expected cetane number of the sample fuel. The compression ratio for each of these is adjusted to give the same specified ignition delay. The cetane number of the sample is obtained by interpolation of the hand wheel readings and the cetane numbers of the bracketing reference fuels.

Because ASTM D 613 is a relatively expensive test, cetane index calculations (ASTM D 976 and ASTM D 4737) have been developed to estimate the cetane number for diesel fuel. These are based on fuel density and distillation characteristics of diesel fuel and may not be used for biodiesel or biodiesel blends. There is currently no substantiating data to support the calculation of cetane index for fuels containing biodiesel.

Low Temperature Operability Tests

Low temperature operability of fuel is critical in cold climates. Biodiesel generally has poorer low temperature operability than petroleum fuels and extra care needs to be taken at colder temperatures to ensure trouble free operation.

The oldest and most conservative measure of low temperature operability is *cloud point* (ASTM D 2500). This test measures the temperature at which a cloud or a haze of wax crystals starts to appear in the fuel under the test conditions. It is applicable to light colored fuels. These crystals can collect in filters and eventually lead to blockage of the fuel system. Flow improvers, additives that can improve low temperature operability, do not affect cloud point but are used in diesel fuel to prevent agglomeration of these crystals and thus avoiding to some extent, the possibility of filter blockage. Cloud point is the most conservative test and is most appropriate for applications that can not tolerate much risk. ASTM D 3117, the Wax Appearance Point test, measures a similar property for dark-colored fuels.

The Pour Point Test (ASTM D 97) is another test that is commonly referred to. It measures the lowest temperature at which a product is fluid. Although this is the lowest temperature of a petroleum product's utility for certain applications, it over predicts the low temperature operability of most products and is therefore of limited usefulness.

For many applications, the actual low temperature operability limit will fall somewhere between the cloud point and the pour point. Several tests have been developed to try and predict this. The Low Temperature Flow Test (LTFT), ASTM D 4539 estimates the filterability of diesel fuels at low temperatures. It was introduced in the early 1980's and was designed to correlate with the most severe and one of the most common fuel delivery systems used in North American heavy duty trucks at the time. The test indicates the minimum temperature at which a fresh 200 ml sample can flow through a 17 mm filter in less than 60 seconds. In a 1981 CRC study [CRC 1983][CRC 1983a], it was found that cloud point and LTFT predicted the performance of base fuels well but that the LTFT was better able to predict the low temperature operability of fuels with flow improvers. No independent data has been published to determine the applicability of this test to newer vehicles and fuels.

The Cold Filter Plugging Point (CFPP), ASTM D 6371, is another low temperature operability test. It correlates well with European light duty trucks except when the fuel system contains a paper filter exposed to the weather or if the CFPP temperature is more than 12°C lower than the cloud point. In this test, a cooled 20 ml sample is drawn through a 45 mm screen and then allowed to flow back for further cooling. Testing continues until the amount of wax crystals that have separated out of solution are sufficient to prevent the fuel from flowing through the screen in under 60 seconds. This method over predicted cold weather operability of North American vehicles tested in the CRC study.

The biodiesel specification, ASTM D 6751, only requires that the cloud point be reported. It is then up to the user to determine the appropriate actions that need to be taken to ensure trouble free operation. The diesel fuel specification, ASTM D 975, offers further guidance on low temperature operability. A study by the Biodiesel Cold Flow Blending Consortium can provide further guidance for blending low level blends of biodiesel in cold weather [NBB 2005].

EN 14214 handles low temperature operability differently from ASTM 6751. While no specific requirements are applied to FAME, EN 14214 outlines CFPP values that automotive diesel fuel must meet for summer and winter grades.

Carbon Residue

The term carbon residue—when used in the context of a fuel property—refers to the carbonaceous residue formed during the evaporation and pyrolysis of a fuel under specific test conditions. Carbon residue tests are intended to give a measure of the tendency of a fuel to form carbon deposits under conditions where volatile fuel components evaporate quickly such as in the combustion chamber. Although the results of carbon residue tests are not directly related to engine deposits, this property is considered an indication of the carbon deposit forming tendency of petroleum diesel fuels. It is known that non-volatile coke forming compounds that were not adequately separated during distillation and other refinery processes can contribute to engine deposits if they end up in diesel fuel.

The compounds that affect carbon residue test results in biodiesel are very different from those in diesel fuel. The carbon residue content of biodiesel shows a strong correlation with free fatty acids, glycerides, soaps, inorganic impurities, polymers, additives like pour point depressants, and the content of higher unsaturated fatty acids [Prankl 2000]. It is not known if a correlation exists between carbon residue values in biodiesel and engine deposits.

For ASTM D 975 diesel fuel, carbon residue measurement is carried out only on the highest boiling fraction of the fuel. The sample to be tested is distilled, and the final 10% residual of distillation is used for testing. Biodiesel, on the other hand, has a very narrow distillation range so achieving this 10% residual is more difficult. Biodiesel carbon residue for ASTM D 6751 is determined on the full sample and then the calculation is executed as if it were the 10% residual.

Diesel fuel carbon residue is determined with the *Ramsbottom Carbon Residue* test method, ASTM D 524. This test is intended for relatively non-volatile petroleum products which partially decompose on heating in air. A sample is placed in a flask with a capillary opening at the top, which provides some measure of protection against decomposition in the presence of air. The flask is then quickly heated in a furnace maintained at approximately 550°C. After all the volatile material has evaporated, the remaining heavy residue undergoes cracking and coking reactions. Further decomposition or oxidation can also occur due to the possibility of air entering the flask through the capillary opening. After the flask has been held in the furnace for a specified period of time it is removed and cooled in a desiccator. The mass of residue remaining in the flask determines the carbon residue.

Biodiesel is much more prone to partial decomposition as it is heated in the presence of air than is diesel fuel. The *Micro Method*, ASTM D 4530, is therefore used as the referee method to determine the carbon residue of biodiesel. The sample is heated in a glass vial to 500°C in an inert nitrogen atmosphere. The volatile material is swept away and the remainder of the sample undergoes reactions that form a residue. The mass of residue remaining in the flask determines the carbon residue test result.

The limits for diesel fuel in ASTM D 975 are 0.15% mass for No. 1 diesel and 0.35% mass for No. 2 diesel. These limits are specified on the carbon residue in the 10% distillation residue and not in the whole fuel sample. The compounds most likely to form carbon residue will be concentrated in this distillation residue. The corresponding carbon residue limit in ASTM D 6751 for biodiesel is 0.050% mass. The limit for biodiesel is based not on the 10% distillation residue but on a 100% sample. However, ASTM D 6751 specifies that the calculation of carbon residue is carried out as if it were the 10% residual. To see the implication of this, it is helpful to examine the equations used for determining the carbon residue.

The Ramsbottom carbon residue test method for diesel fuel (ASTM D 524) gives:

(1)% Carbon Residue = 100 × (mass of carbon residue/mass of sample)

For diesel fuel, the mass of sample is the mass of 10% distillation residue used for the test and the reported carbon residue is the % mass of carbon residue in this 10% distillation residue. The 0.35% limit on No. 2 diesel fuel would be achieved with 0.0035 g carbon residue/g of the 10% distillation residue.

The biodiesel carbon residue calculation is carried out as if it were the 10% residual. The applicable equation from the Micro Method carbon residue test used for biodiesel (ASTM D 4530-93) is:

(2)% Carbon Residue = 100 × (mass of carbon residue/mass of 10% residue) × E

where E is the ratio of the mass of the sample in the flask after distillation over the mass of the sample in the flask before distillation. Since no distillation actually is carried out, ASTM D 6751 requires that a constant value of 20/200 is to be used for E and that the calculation be carried out as though the sample being tested were the 10% distillation residue. The value used for “mass of 10% residue” in this equation is then the mass of 100% sample used to determine the carbon residue. The 0.050% limit for biodiesel would then be achieved with 0.0050 g carbon residue/g of sample (from Equation (2): 100 × (0.0050/1) × (20/200) = 0.050%).

This difference between diesel fuel and biodiesel is actually much larger than the respective values of 0.0035 g/g and 0.0050 g/g suggest, because the value for diesel fuel is the mass of carbon residue per unit mass of 10% distillation residue, while that for biodiesel is the mass of carbon residue per mass of un-distilled sample. Since volatile fuel components do not produce solid residues, the same absolute mass of carbon residue is determined for a given fuel in tests with the 10%

distillation residue and with the un-distilled sample. To convert the diesel fuel carbon residue to a value based on the whole un-distilled sample, it would need to be multiplied by the ratio of mass of the 10% distillation residue and the mass of the whole sample. Assuming that the density of light- and heavy-boiling hydrocarbon fractions is similar, this will be about 0.1. The 0.035% carbon residue No. 2 diesel fuel, when expressed on the same basis as that for biodiesel (i.e. per unit mass of un-distilled sample) would be approximately 0.00035 g carbon residue/g of sample. Thus, after accounting for the differences in calculation procedures, the carbon residue limit of ASTM biodiesel is actually more than 10 times larger than that for ASTM diesel fuel. The inclusion of E = 20/200 in the calculation for biodiesel artificially reduces the resulting carbon residue value by a factor of 10.

The reader should be cautioned not to conclude that biodiesel is more prone to forming engine deposits. As was noted earlier, the carbon residue test was developed as an indication of the coking tendency of petroleum products. There is no indication that the carbon residue forming compounds of biodiesel—such as free fatty acids or glycerides—contribute to engine deposits. These impurities in biodiesel may contribute to *fuel system* deposits, but this is not the deposit type that the carbon residue test was originally developed for. In summary, it is not clear whether the carbon residue test when applied to biodiesel has any relevance to determining engine deposit tendency. Rather, the carbon residue test when applied to biodiesel is better thought of as another method to detect unwanted impurities.

EN 14214 requires that the carbon residue determination for biodiesel be carried out on the 10% distillation residue as is done for diesel fuel. The 10% distillation residue is obtained using vacuum distillation (ASTM D 1160) to avoid cracking reactions in the biodiesel. Round robin testing in Europe found that carrying out the carbon residue test on a 100% sample resulted in poor reproducibility. Carbon residue determination on the 10% distillation residue was reported to give better results [Prankl 2000][BLT 1999]. The upper limit of 0.30% mass on the 10% distillation residue specified in EN 14214 is the same as that for diesel fuel specified in EN 590.

Ash forming compounds or non-volatile additives in the fuel will add to the carbon residue value and they will be included as part of the total carbon residue test result. For example, alkyl nitrate cetane improvers in the fuel will result in a higher carbon residue test result. However, these additives are not known to cause engine deposits. Carbon residue test results on fuels with significant amounts of these cetane improvers or other ash forming additives will give erroneously high carbon residue. In these cases, carbon residue test results are only valid for the base fuel before the addition of fuel additives.

Acid Number

The acid number property is a measure of the concentration of acid in the fuel. Its units of mg KOH/g reflect the method used to determine this property. A sample of the fuel is titrated with a strong base until the acids are neutralized. The amount of strong base, expressed as mg KOH/g of fuel needed to neutralize the acid is the acid number.

A number of factors can influence the acid number of biodiesel. Free fatty acids that were not fully removed during the fuel processing and acids formed during fuel degradation are two important contributing factors to biodiesel acid number. Biodiesel with a high acid number have been correlated with increased fuel system deposits and increased the risk of corrosion.

The referee method for acid number for ASTM D 6751 biodiesel is ASTM D 664, Acid Number of Petroleum Products by Potentiometric Titration. This test suitable for all fuels including dark colored ones. In this test, a fuel sample is dissolved in a mixture of toluene and propan-2-ol containing a small amount of water. The mixture is then titrated potentiometrically with alcoholic potassium hydroxide. The test is applicable for the determination of acids with dissociation constants in water greater than 10^{-9}. Salts will also react if their hydrolysis constants are larger than 10^{-9}.

The acid number limit for ASTM D 6751 biodiesel is 0.80 mg KOH/g. There is no acid number limit for ASTM D 975 diesel fuel. EN 14214 has a limit of 0.50 mg KOH/g limit.

Glycerin

It is important to ensure that the biodiesel has low levels of free glycerin (glycerol) and total glycerin. Free glycerin is a major byproduct of biodiesel production and is separated from the alkyl esters during the production process. It is however possible for small amounts to remain in the fuel. Bound glycerin is the molecular structure that forms the backbone of the triglyceride molecules from which biodiesel is produced. Total glycerin is the sum of free glycerin and bound glycerin.

Excess free glycerin can build up in storage and fuel tanks, cause injector deposits or clog filters. Excess total glycerin can result from the incomplete conversion of oil or fat into alkyl esters. This can also lead to injector fouling, the formation of deposits at injection nozzles, pistons and valves and it can result in poor low temperature operability.

ASTM D 6584 is the test method used to determine free and total glycerin. In this method, the sample to be analyzed and two internal standards are trimethylsilyated (a reaction in which a substance is converted into a form having trimethylsilyl, -$Si(CH_3)_3$, substituents) and then analyzed by gas chromatography. Mono-, di- and triglycerides are determined by comparing to monoolein, diolein and triolein standards. The bound glycerin is calculated by multiplying each of mono-, di- and triglycerides by conversion factors that represent the glycerin portion of each of these compounds. The actual equation used to calculate mass fraction of total glycerin is:

(3)$m = m_0 + 0.2591 \cdot m_1 + 0.1488 \cdot m_2 + 0.1044 \cdot m_3$

Where:
m - mass fraction of total glycerin
m_0 - mass fraction of free glycerin
m_1 - mass fraction of monoglycerides
m_2 - mass fraction of diglycerides
m_3 - mass fraction of triglycerides

The method on which ASTM D 6548 is based, the Plank method, was developed to obtain group separation of glycercol, mono-, di- and triglycerides typically occurring in methyl esters made from rapeseed oil (RME). Vegetable oil methyl esters with fatty acid compositions or chain lengths similar to RME such as those made from sunflower, soy and used frying oil can be analyzed without any changes. The method however is not applicable to methyl esters from oils that have significant lauric oils (methyl laurate) such as coconut and palm kernel oil without modification. Superimposition of peaks of long chain fatty acid methyl esters and short chain monoglycerides on the chromatogram can lead to significant error [Plank 1995].

The presence of trace quantities of volatile compounds such as solvents used as carriers for additives and hydrocarbons from tanks or pipelines can cause interference in the determination of free glycerol with the Plank method [Bondioli 2005].

The current limits on free and total glycerin in ASTM D 6751 are 0.020% mass and 0.240% mass respectively. While the solubility of free glycerin can be as high as 0.14% mass, well above the allowable limit, it can be almost entirely removed if proper processing steps are taken. Water washing for example is one way to achieve very low levels of free glycerin [Van Gerpen 1997]. The current level for total glycerin is near the limit where the bound glycerin portion would begin to adversely affect cloud point [Van Gerpen 1997].

The limits for free and bound glycerin in EN 14214 are very similar to those for ASTM D 6751 at 0.02% mass and 0.25% mass respectively. In addition to the glycerin limits, EN 14214 has limits on mono-, di- and triglycerides of 0.80%, 0.20% and 0.20% mass respectively.

Phosphorus

Biodiesel specifications include limits on phosphorus content. Phosphorus is a known catalyst poison, which can produce a glaze over the washcoat surface. The exhaust gases can no longer contact the catalyst sites and the conversion efficiency of the catalyst decreases. Phosphorus specifications have been introduced to protect diesel emission control catalysts from exposure to excessive phosphorus levels. The biodiesel specifications ASTM D 6751 and EN 14214 require that the phosphorus level be less than 10 ppm by mass.

Some crude vegetable oils, soybean oil for example, can contain 600-900 ppm of phosphorus. During the biodiesel production process, the phosphorus is either transferred to the glycerin fraction or removed by water washing. According to some sources, the initial phosphorus content of the feedstock appears to have no effect on the final phosphorus content of the biodiesel [Van Gerpen 2004]. Biodiesels made from soybeans or rapeseed have both low phosphorus content—typically below 1 ppm in SME made in the USA [DOE 2004]. On the other hand, high phosphorus content in biodiesel has been reported with certain feedstocks, such as jatropha oils [Foidl 1996]. It is not clear if high phosphorus in the final product was caused by the use of high phosphorus feedstock, or else by inadequate production process.

The test method used to quantify phosphorus in ASTM D 6751 biodiesel is ASTM D 4951 and uses inductively coupled plasma atomic emission spectrometry. The sample to be tested is weighed and diluted with a solvent. A known amount of internal standard, an element not present in the original sample, is also added. Calibration standards are also prepared in a similar fashion. The diluted sample and calibration standards are analyzed with the instrument and by comparing the emission intensities of elements (in this case phosphorus) in the sample with emission intensities measured with the calibration standards and applying the appropriate internal standard correction, the concentration in the sample can be determined.

EN 14214 also has limits on other known catalyst poisons, sodium, potassium, calcium and magnesium. The limit for the sum of sodium plus potassium is 5 mg/kg as is the limit for the sum of calcium plus magnesium.

Distillation Temperature

Petroleum fuels exhibit a range of boiling points. For example, the lightest fractions of diesel fuel will start to boil at temperatures around 180°C at atmospheric pressure and the heaviest fractions will typically boil at temperatures around 340°C or higher. A curve drawn through a plot of temperature versus volume evaporated defines the distillation curve for a fuel. For purposes of fuel standards, rather than define the whole distillation curve, distillation temperature requirements are most often specified by one or two points on the curve. Diesel fuel defined by ASTM D 975 for example requires that for No. 2 diesel fuel, when heated at atmospheric pressure, 90% of the fuel must have evaporated when the temperature of the vapor has risen to a temperature between 282 to 338°C. This temperature is often referred to as T90. Distillation characteristics of diesel fuel are also closely tied to other fuel properties such flash point, viscosity, and low temperature operability. It is not usually possible to significantly vary any one of these properties without impacting the others.

With petroleum fuels, one of the important functions served by the specified distillation characteristics is to define the composition and properties of hydrocarbons that make up a given fuel. This ensures that the final fuel meets the safety and performance requirements for a given application. The following table outlines some of the major petroleum products and the range of boiling points of the compounds from which they are comprised [Schmidt 1986].

Table 3
Boiling Range of Petroleum Products

Product	**Boiling range, °C**
LPG	-40 - 0
Gasoline	30 - 200
Kerosene, No. 1 Diesel, jet fuel	170 - 270
No. 2 Diesel fuel, Furnace oil	180 - 340
Lube oils	340 - 540
Residual oils	340 - 650
Asphalt	> 540
Petroleum coke	Solid

Biodiesel has a very narrow distillation temperature range. The atmospheric pressure boiling temperature range of methyl esters in biodiesel generally falls in the range of 330 to 357°C. The maximum 90% distillation temperature for ASTM D 6751 biodiesel is set just above this range at 360°C. Including the distillation characteristics in the biodiesel specification serves a different function than that for petroleum fuels. Rather than defining the compounds that make up the fuel, the maximum distillation specification for biodiesel serves to ensure that the fuel has not been adulterated with high boiling point contaminants.

For petroleum fuels, ASTM D 86 is the test method used to determine the distillation characteristics. A 100 ml sample is distilled under prescribed conditions and at atmospheric pressure. Observations are made of the temperature of the saturated vapor and the volume of condensate collected. After corrections are made for barometric pressure, the data is expressed as percent evaporated versus temperature.

This test method is not appropriate for biodiesel. As biodiesel is heated in air, it can react with oxygen in air and form oxidation products that can alter the distillation characteristics. In order to minimize the exposure to oxygen as the biodiesel is heated, distillation is carried out at a reduced pressure. The test method that defines this procedure for the B100 component is ASTM D 1160. Since distillation is carried out at a reduced pressure, the recorded vapor temperatures need to be converted to atmospheric equivalent temperatures (AET) using an equation outlined in the test method.

An alternative test method for determining the distillation characteristics for diesel fuel is referenced in ASTM D 975, Standard Test Method for Boiling Range Distribution of Petroleum Fractions by Gas Chromatography ASTM D 2887. This method would not be recommended for biodiesel because its applicability to methyl esters has not been determined. It is intended for control of refinery operations as opposed to distillation characterization.

When blending biodiesel with diesel fuel, T90 of the final blend can be significantly altered because of the high boiling point range of biodiesel.

EN 14214 does not have a distillation requirement. Where the distillation requirement in ASTM biodiesel was added as an extra precaution to ensure the fuel has not been adulterated with high boiling point compounds, EN 14214 uses other parameters such as the minimum ester content specification of 96.5%.

Fuel Stability

Biodiesel stability can be broadly categorized as oxidative stability and thermal stability. The olefinic unsaturated structure of the fatty acid chains that make up the mono-alkyl ester molecules of biodiesel is the primary source of biodiesel instability. A survey prepared for the Coordinating Research Council deals with this topic in more detail [Waynick 2005].

Thermal polymerization of molecules with fatty acid chains is important above temperatures of 250 - 300°C. It may be of some importance in engine fuel systems that allow fuel to be heated by the engine and then recycled to the fuel tank. Biodiesel made from used cooking oils may also contain some products resulting from thermal instability.

Oxidative instability is the more important source of biodiesel instability concerns. Methylene carbon atoms located between double bonded carbon atoms on the fatty acid chains are where oxygen attack is initiated. The greater the number of unsaturated carbon bonds in the fatty acid chains, the more prone they will be to oxygen attack. Eventually, as the fuel continues its degradation process, insolubles form that can collect on critical fuel system components such as fuel injectors, pumps and filters.

One important consequence of using a fuel that is unstable is the potential for it to form deposits on critical parts of the fuel injection system. While a number of test methods exist to quantify the oxidation stability of biodiesel, there is still no laboratory test to measure the tendency of biodiesel to form deposits on these critical fuel system components. Tests methods are available to quantify the tendency of biodiesel to oxidize and also to quantify its tendency to form insolubles but there is still a significant lack of understanding on how these parameters are related and how they relate to potential problems with engine fuel systems.

The European biodiesel standard does include a number of parameters that relate to oxidation stability, the most significant being the oxidation stability requirement. This parameter is determined using the Rancimat test (also known as the Oxidation Stability Index test, OSI). Air is bubbled first through a small sample of the biodiesel maintained at 110°C and then through a tube into a small sample of water. The conductivity of this water is monitored. When the biodiesel starts to oxidize, it releases volatile acids that escape with the air and are collected in the water. A rapid rise in the conductivity of the water indicates the onset of biodiesel oxidation. The time it takes from the start of the test to the sharp rise in conductivity is known as the induction time. EN 14214 specifies a minimum induction time of 6 hours.

ASTM D 2274, Oxidation Stability of Distillate Fuel Oil (Accelerated Method), is one test method that can be adapted to measure the tendency of biodiesel to form insolubles. The formation of insolubles by B100 or by low sulfur petroleum diesel fuel by such tests is usually low. When the two fuels are blended however, much higher levels of insolubles are possible than with either the B100 or the petroleum diesel fuel. Biodiesel is more polar in nature than diesel fuel and increases in polarity as it oxidizes. Therefore B100 has a tendency to hold in solution compounds that would not dissolve in diesel fuel such as some of its oxidation products. When biodiesel that has oxidized is blended with diesel fuel, some of these oxidation products are no longer able to remain in solution and they can precipitate out of the fuel blend and can result in high levels of filterable solids.

How test methods that quantify the onset of oxidation (such as Rancimat) and the tendency to form insolubles (such as ASTM D 2274) relate to each other and to actual equipment performance is still not fully understood. In the small amount of work that has been done to date, fuels that perform poorly on either of these types of tests have not necessarily resulted in poor equipment performance. Yet problems related to increased deposits on fuel system components have been noted with fuels containing biodiesel that do not occur when only diesel fuel was used. This lack of understanding on how laboratory test results relate to equipment performance needs to be addressed before an appropriate specification can be set on biodiesel stability.

The current version of ASTM D6751 does not include an oxidative stability requirement. It is interesting to note that samples of US soy-based biodiesel have a significantly shorter induction time on the Rancimat test and have trouble meeting the European limit of 6 hours [Clark 2005]. The most common biodiesel used in Europe, rapeseed oil methyl ester, can meet the 6 hour induction time specification. While this would indicate that soy based biodiesel will start to oxidize sooner under the conditions of the Rancimat test, because of the current lack of understanding on how these results translate into performance on real fuel injection equipment, the practical implications of this are not clear.

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Appendix A: Other Countries

Following the adoption of US and European specifications, biodiesel standards are being developed in other countries. While many requirements are typically based on those in the USA and EU, the standards may also introduce country specific provisions that are different. The list of countries that adopted biodiesel and/or biodiesel blends specifications includes Canada and Australia.

In Canada, CAN/CGSB-3.520 establishes specifications for blends of automotive diesel fuel containing low levels of Biodiesel Esters (blends from B1 to B5), Table A-1. Most of the requirements mirror those of the automotive diesel fuel specification, CAN/CGSB-3.517. The B1-B5 standard requires that the biodiesel component blended into the fuel meets either ASTM D 6751 or EN 14214. A specification for blends with B6 to B20 is being developed.

Table A-1
CAN/CGSB-3.517 & CAN/CGSB-3.520 Biodiesel Blend (B1-B5) Specifications

Property	Value	Test Method
Flash point, min	> 40°C	D 93 or D 3828
Water and sediment, max	0.05% vol	D 1796 (mod.) or D 2709
Distillation T90, max	Type A: 290.0°C Type B: 360.0°C	D 86
Kinematic viscosity	Type A: 1.30 - 3.60 mm^2/s Type B: 1.70-4.10 mm^2/s	D 445
Ash, max	0.010% wt	D 482
Sulfur, max	0.05% wt	D2622 or D5453 or CAN/CGSB-3.0 No. 16.0
Cooper strip corrosion, max	No. 1	D 130

Property	Value	Test Method
Cetane number, min	40.0	D 613
Electrical conductivity, min	25 pS/m	D 2624
Low-temperature flow, one of: - cloud point - wax appearance point - LTFT	Location & season dependant	D 2500 or D 5773 D 3117 CAN/CGSB-3.0 No. 140.1
Carbon residue, max	Type A: 0.10% wt Type B: 0.16% wt	D 4530
Acid number, max	0.10 mg KOH/g	D 974
Lubricity	When operability temp. < -20°C min. lubricity requirement must be met. Several options are available to measure lubricity.	SAE952370 or SAE981363 or SAE961944 or D6079 or D6078

Australia has published a fuel standard for biodiesel under their *Fuel Quality Standards Act 2000*. It is referred to as *Fuel Standard (Biodiesel) Determination 2003*, Table A-2. While the technical requirements of this standard include limits that are found in both ASTM D 6751 and EN 14214, it is identical to neither of these. The Australian biodiesel standard could therefore be viewed as being substantially different from both ASTM D 6751 and EN 14214.

Table A-2
Australian Biodiesel Specifications

Parameter	Value	Test Method	Date
Sulfur, max	50 mg/kg 10 mg/kg	ASTM D5453	18 Sep 2003 1 Feb 2006
Density	860-890 kg/m^3	ASTM D1298 or EN ISO 3675	18 Sep 2003
Distillation T90, max	360°C	ASTM D1160	18 Sep 2003
Sulfated ash, max	0.020% mass	ASTM D874	18 Sep 2003
Viscosity	3.5-5.0 mm^2/s @ 40°C	ASTM D445	18 Sep 2003
Flashpoint, min	120°C	ASTM D93	18 Sep 2003
Carbon residue, max - 10% distillation residue, or - 100% distillation sample	0.30 % mass 0.050 % mass	EN ISO 10370 ASTM D4530	18 Sep 2003
Water and sediment, max	0.050% vol	ASTM D2709	18 Sep 2003
Ester content, min	96.5% mass	prEN 14103	18 Sep 2003
Phosphorus, max	10 mg/kg	ASTM D4951	18 Sep 2003
Acid value, max	0.80 mg KOH/g	ASTM D664	18 Sep 2003
Total contamination, max	24 mg/kg	EN 12662 ASTM D5452	18 Sep 2004
Free glycerol, max	0.020% mass	ASTM D6584	18 Sep 2004
Total glycerol, max	0.250% mass	ASTM D6584	18 Sep 2004
Oxidation stability, min	6 hours @ 110°C	prEN 14112 or ASTM D2274 (as relevant for biodiesel)	18 Sep 2004
Metals	≤ 5 mg/kg Group I (Na, K) ≤ 5 mg/kg Group II (Ca, Mg)	prEN 14108 prEN 14109 (Group I)	18 Sep 2004

Parameter	Value	Test Method	Date
		prEN 14538 (Group II)	
Methanol	< 0.20% mass	prEN 14110	18 Dec 2004
Copper strip corrosion (3 hrs @50°C), max	If the biodiesel contains no more than 10 mg/kg of sulfur: Class 1	EN ISO 2160 ASTM D130	18 Dec 2004
	If the biodiesel contains more than 10 mg/kg of sulfur: No. 3	ASTM D130	
Cetane number, min	51.0	EN ISO 5165 ASTM D613 ASTM D6890 IP 498/03	18 Sep 2005

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CHARACTERIZATION OF BIODIESEL OXIDATION AND OXIDATION PRODUCTS

CRC Project No. AVFL-2b

TASK 1 RESULTS

Technical Literature Review

SwRI® Project No. 08-10721

Prepared for:

The Coordinating Research Council
3650 Mansell Road, Suite 140
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August 2005

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EXECUTIVE SUMMARY

Stability Chemistry Fundamentals

Chemical reactivity of fatty oils and esters can be divided into oxidative and thermal instability. Both of these types of instability are determined by the amount and configuration of the olefinic unsaturation on the fatty acid chains. Many of the plant-derived fatty oils, including soy and rapeseed, contain polyunsaturated fatty acid chains that are methylene-interrupted rather than conjugated. This structural fact is key to understanding both oxidative and thermal instability.

In oxidative instability, the methylene carbons between the olefinic carbons are the sites of first attack. After hydrogen is removed from such carbons oxygen rapidly attacks and a hydroperoxide is ultimately formed where the polyunsaturation has been isomerized to include a conjugated diene. This reaction is a chain mechanism that can proceed rapidly once an initial induction period has occurred. The greater the level of unsaturation in a fatty oil or ester, the more susceptible it will be to oxidation. Once the hydroperoxides have formed, they decompose and inter-react to form numerous secondary oxidation products including aldehydes, alcohols, shorter chain carboxylic acids, and higher molecular weight oligomers often called polymers. Another polymerization mechanism, vinyl polymerization, has been proposed as being part of the degradation process of fatty oils and esters. However, conventional understanding of oxidation chemistry would imply that such processes would not be significant when oxygen was abundant, so its precise level of importance has not been determined.

Metals, free fatty acids, acidic fuel additives, the size of the alcohol group (for mono-esters), and the presence of natural antioxidants can all impact the oxidative stability of fatty oils and/or esters. Oxidation can also be catalyzed by light, but such photo-oxidation should not be a significant factor for the manufacture and transportation of biodiesel fuel.

Thermal polymerization of fatty oils and esters does not become important until temperatures of 250-300°C are reached. This is because the methylene-interrupted polyunsaturated structure cannot participate in such reactions until it isomerizes into a conjugated configuration, and such isomerization will not occur until that temperature range is reached. Thermal polymerization occurs by the Diels Alder reaction, and two fatty acid chains are linked by a cyclohexene ring. Higher order oligomers are also possible, although the exact mechanism is still not established. Certain thermal polymerization products in used cooking oils may carry over to non-distilled biodiesel. The verification of such compounds and their impact on fuel quality has not been determined. Thermal polymerization may be of limited importance in biodiesel fuel that is repeatedly heated by the engine and recycled to the fuel tank before actual combustion. However, thermal polymerization will not impact storage stability.

The understanding of the chemistry of fatty oils and esters is reasonably mature. While additional understanding of details is always possible, such new information will not for the most part improve the ability to understand any real world problems that exist with biodiesel or the ways to solve them.

Test Methodology Relating to Stability

Numerous test procedures have been either developed or adapted to measure the various factors associated with oxidative and thermal instability. Such test methods can be categorized as to whether they measure initial fatty oil composition, primary oxidation products, secondary oxidation products, physical properties, or stability test methods.

Compositional parameters pertaining to the initial fatty oil or ester include the ester content, fatty acid chain distribution within the fatty oil or ester, and the type and extent of olefinic unsaturation. Special indices designed to consider the amount of allylic or Bis-allylic carbons have been developed. Several methods to directly measure tocopherols or to indirectly measure the impact of natural antioxidants have also been proposed.

Primary oxidation products are hydroperoxides and conjugated dienes, and procedures to measure both are established for fatty oils and esters. Secondary oxidation products have been measured by many procedures depending on the type of compound of interest. Total Acid Number, Anisidine Value (aldehyde content), and an HPLC method for polymers are among the most important. An index designed to take into account both primary and secondary oxidation, TOTOX, has also been proposed, based on a weighted linear sum of peroxide value and anisidine value.

Physical properties that are sensitive to the effects of fatty oil oxidation include viscosity, refractive index, and di-electric constant.

Numerous accelerated stability test methods have been used. All involve stressing the fatty oil or ester by a combination of elevated temperature, time, and enhanced oxygen exposure while measuring one or more oxidation-sensitive properties such as peroxide value, insolubles, evolution of volatile short chain acids, or heat of reaction. Some of these methods include the Active Oxygen Method, ASTM D2274, ASTM D4625, Oxidation Stability Index (OSI), or pressurized differential scanning calorimetry. The OSI test has gained acceptance in Europe where it is part of the biodiesel specification. Within the U.S. it is a common research tool. The Metrohm Rancimat apparatus is frequently used to measure OSI, and the terms “Rancimat” and “OSI” are often used interchangeably in the open literature when referring to the test method. However, no one stability test or one measured stability-related parameter appears to be adequate to define all the stability characteristics of biodiesel fuel. It is highly unlikely that any one new test will be able to completely define biodiesel stability either.

Stability-Related Behavior

Fatty oil oxidation is a multi-step reaction process where primary products (conjugated diene hydroperoxides) decompose and chemically interact with each other to form numerous secondary oxidation products. Nonetheless, the evolution of primary and secondary oxidation products are related by several interdependencies. First, there appears to be some interdependency between some stability test methods that measure different parts of the total oxidation process. The OSI (Rancimat) induction period (IP), a measure of some acidic secondary products, appears to correlate well with tests that measure the evolution of ROOH by peroxide value (PV), a measure of primary products. Also, OSI IP values appear to correlate well with Active Oxygen Method (AOM) and ASTM D525 results. OSI IP values have also been shown to correlate with isothermal PDSC results.

The second type of interdependencies that are indicated in the prior research literature are between stability test method results and other test properties such as PV, TAN, viscosity, ester content, and polymer content. When oxygen is limiting, PV will tend to increase to a peak level and then decrease. During the stage where PV is increasing TAN and viscosity increase; when PV peaks and then decreases, TAN and viscosity continue to increase, but at a lower rate. When oxygen is not limiting, PV will tend to increase and approach a steady state value while OSI IP will decrease. Under these circumstances, TAN and viscosity will increase until the OSI IP approaches zero. At that point TAN and viscosity will continue to increase, but at a higher rate. In all reported studies, TAN and viscosity correlate well with each other. This implies that the polymeric material responsible for increased viscosity is formed in a way that is directly related to the formation of acidic compounds.

Storage temperature also has an effect on the interrelationships between OSI IP and other properties. When oxygen is available and storage temperatures are moderately elevated (43°C), OSI decreases while PV, TAN, viscosity, polymer levels increase. Ester content typically decreases. When storage is done at ambient or colder temperatures with or without oxygen availability, OSI IP decreases more slowly, and TAN, viscosity, and polymer content either do not change or increase only modestly. However, if the same biodiesel fuel is regularly agitated so as to greatly increase exposure to oxygen, OSI IP dramatically decreases over time. Other variables however change only slightly. At very high temperatures (180°C), PV remains low due to rapid ROOH decomposition. However, secondary products greatly increase as indicated by TAN and viscosity.

Neat biodiesels often do not give significant total insolubles when tested by storage stability tests such as ASTM D2274 and D4625. However, a significant number of studies have measured high insoluble levels. Furthermore, the amount of such total insolubles that are formed do not appear to correlate to OSI IP or any of the other test parameters that correlate to OSI IP. The high polarity of the methyl esters keeps the oxidation products in solution. However, if biodiesel is oxidized while blended with petroleum diesel fuel, greatly increased insolubles may result.

Likewise if oxidized biodiesel is blended with petroleum diesel fuel, similar increased insolubles may result. This antagonistic effect, driven by the low solvency of petroleum fuels, is likely to become more pronounced as the new ultra-low sulfur fuels are used for biodiesel blending. Very little work has been reported concerned with the deposit forming tendencies of biodiesel fuels. The very scant data that is available is based on the Jet Fuel Thermal Oxidative Stability Tester (JFTOT). While this method may hold promise if correctly used, the data currently available provides no real insight into the factors affecting biodiesel deposition characteristics. Thermal stability of biodiesel fuels is typically very good.

The apparent lack of correlation between insolubles formation and other stability-related parameters represents the one major disconnect in the biodiesel stability literature. That one area notwithstanding, additional work to fine tune the understanding of the chemical interdependencies will not likely improve the knowledge base concerning the level of problems existing with the transportation and use of biodiesel and possible remedies to such problems.

Antioxidants Used In Fatty Oils and Esters

For over 80 years antioxidants have either been used or proposed for use to control fatty oil oxidation. Two types of antioxidants are known: chain breakers and hydroperoxide decomposers. The phenolic compounds that have been used in fatty oils and esters are examples of chain breaking antioxidants. Crude fatty oils contain naturally occurring phenolic antioxidants, tocopherols. Tocopherols occur in four isomers: α, β, γ, and δ. The amount and distribution of these four tocopherols are a distinct characteristic of each fatty oil. Intentional use of additional amounts of tocopherols in fatty oils often provides no further benefit and sometimes decreases stability. When present in fatty oils, the γ and δ isomers appear to be the most effective antioxidants. Also, γ-tocopherol appears to be more oxidatively stable than α-tocopherol. However, when used in fatty oils and esters, tocopherols have consistently been shown to be much less effective antioxidants than synthetic antioxidants.

Many synthetic antioxidants have been investigated and used in fatty oils and esters. The most effective ones include tertiary butylhydroquinone (TBHQ), pyrogallol (PY), and propyl gallate (PG). Effective concentrations appear to be usually within the range of 200 ppm to 1,000 ppm, depending on the substrate and the type of stability test used to evaluate additive performance. Interestingly, 2,6-di-t-butyl-4-methylphenol (BHT) is usually one of the less effective synthetic antioxidants in fatty oils and esters, despite the fact that it is one of the most effective in hydrocarbon fuels and lubricants. In the same way tocopherol is generally very effective in hydrocarbon fuels and lubricants despite its relatively poor performance in fatty oils and esters. Apparently, the greatly different chemical structure of esters compared to non-polar hydrocarbons has a significant effect on antioxidant performance of phenolic compounds.

Minimal work has been done with other types of antioxidants in fatty oils and esters. There may be potential in some of them, but caution is advised since adverse effects including greatly decreased stability have been frequently shown to exist.

Impact On Diesel Engine Equipment

Work done in the early 1980's proved that vegetable oils do not make good alternative diesel fuels, either as a neat fuel or as a fuel extender. However, the methyl esters of vegetable oils appear not to have the catastrophic problems associated with triacylglycerides. However, this conclusion can be based only on the lack of overwhelming complaints among fleet users of biodiesel-based fuels. Very little actual controlled diesel equipment test work has been reported in the open literature. In the few pump tests, fuel injector tests, and vehicle fleet tests that have been documented, there is a consistent pattern of sub-catastrophic problems associated with biodiesel-based fuels. These problems are characterized by increased deposits on injectors and pump parts, increased pressure drops across filters, and a few failed injectors and pumps. The interesting thing is that these problems only occur in the fuels that contain biodiesel. The comparison petroleum diesel fuels that have been used in these limited programs never exhibited any of these problems.

To insure that biodiesel fuel is and remains a trouble-free alternative fuel does not require more laboratory stability test programs or the development of yet more stability test procedures. Although the exact details of how the chemistry of biodiesel fuel impacts its stability properties has not been determined, a reasonably clear level of understanding does now exist, as outlined earlier in this report. Except for the relationship between insolubles formation and other stability parameters, a more detailed understanding of the stability chemistry will not assist in making biodiesel safer for the end users. Linking the current understanding of biodiesel fuel stability with equipment performance characteristics is the one area of work that now needs to be accomplished in order to meaningfully advance biodiesel usage technology.

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1.0 ABSTRACT

Technical information pertaining to fatty oil and fatty ester stability chemistry is reviewed. Over 130 references within the open scientific literature are discussed in detail. This review is divided into five major technical sections, followed by conclusions, and a list of the cited references. Two appendices with additional information are also included. The five major technical sections are as follows:

STABILITY CHEMISTRY FUNDAMENTALS
TEST METHODOLOGY RELATING TO STABILITY
STABILITY-RELATED BEHAVIOR
ANTIOXIDANTS USED IN FATTY OILS AND ESTERS
IMPACT ON DIESEL ENGINE EQUIPMENT

Each of these five technical sections is further divided into sub-sections according to topic.

The conclusions are not a condensed re-iteration of the most salient technical points. Instead, they are specifically written to address where the state of the art of biodiesel science and technology is, where the gaps are, and the general approach that is needed to fill those gaps.

2.0 STABILITY CHEMISTRY FUNDAMENTALS

2.1 Fatty Oils (Triacylglycerides) vs. Alkyl Esters (Biodiesel)

Over the last two decades, alternative fuels research has increasingly focused on the potential use of alkyl esters (especially methyl esters) of renewable fatty oils, materials for which much chemical research has already been reported [1-133]. The degradation reaction pathways for methyl esters derived from naturally occurring fatty oils are determined by the olefinic unsaturation on the fatty acid chain[42]. The fatty acid chain is not changed during the chemical process whereby fatty oils are transesterified into alkyl esters[62]. Therefore, the chemistry of biodiesel degradation will be the same as that of the fatty oils from which they were derived. Although the chemical stability properties of biodiesel have been investigated for only about 20 years[50], the chemical stability properties of fatty oils have been the subject of research for 80 years[73]. This added perspective is valuable in understanding the chemical stability of biodiesel. The chemical reactivity of the olefinic unsaturation of fatty acid side chains (whether part of a triacylglyceride or a mono-alkyl ester such as a methyl ester) can be widely categorized into oxidative instability and thermal instability[41, 42]. This section deals with the former; a subsequent section deals with the latter. For purposes of convenience, the remainder of this report uses the term “fatty oils” to mean triacylglycerides such as animal and vegetable fats, whether crude or refined.

Likewise, the term “methyl ester” and “biodiesel” will be used interchangeably with the understanding that other alkyl monoesters of fatty oils such as ethyl esters can also be used as biodiesel-type fuels. When such other monoesters are discussed, they will be specifically identified.

2.2 Chemical Structure of Fatty Oils and Biodiesel

In order to understand the oxidation chemistry of unsaturated fatty acid groups occurring in fatty oils and biodiesel fuels, the structure of the unsaturation must be first understood. In most of the naturally occurring fatty oils, including linseed (flax), safflower, sunflower, corn, cottonseed, canola, rapeseed and soy, multiple olefinic unsaturation occurs in a methylene-interrupted configuration[41, 42]. This structure is depicted in Figure 1 for linolenic acid and contrasted with an isomer having a conjugated arrangement of unsaturation.

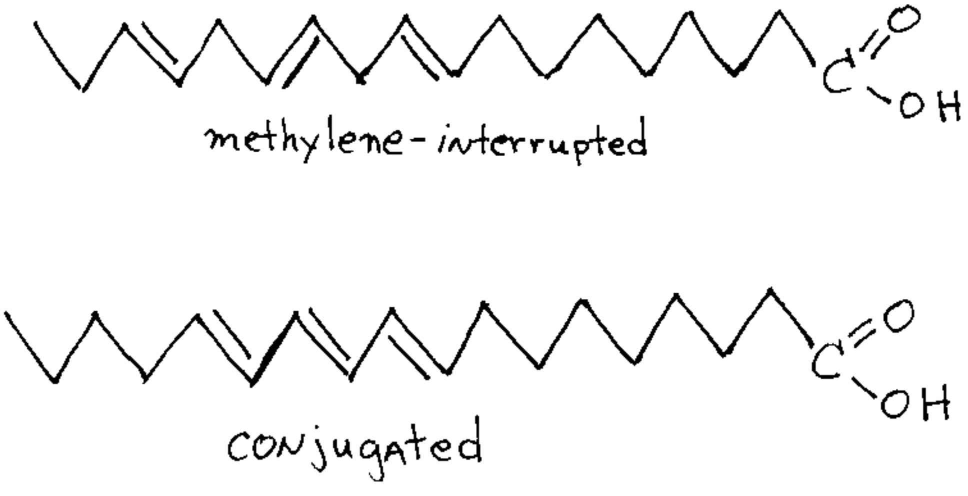

Figure 1. Structure

It should be noted that a conjugated arrangement of multiple olefinic unsaturation is the most thermodynamically stable arrangement, due to the partial stabilization imparted by delocalization of the pi electrons[56]. However, spontaneous rearrangement of a methylene-interupted configuration to a conjugated arrangement does not occur at ordinary temperatures due to the high activation energy associated with the breaking and reforming of pi bonds[15].

2.3 Oxidation Chemistry – Primary Oxidation

The earliest work on fatty oil oxidation chemistry postulated a direct attack of oxygen on the unsaturated carbon[42, 73]. However, this approach failed to explain certain observations in later work[73]. By the mid-1950's, the current theory of peroxidation chain reaction was firmly established. Peroxidation occurs by a set of reactions categorized as initiation, propagation, and termination[42]. General examples of these are given in Figure 2:

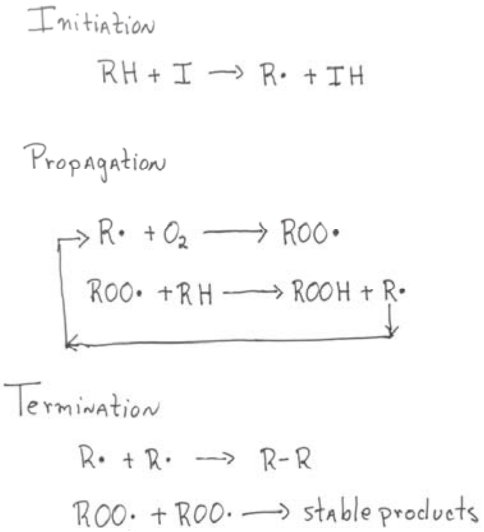

Figure 2. Examples of Reactions

As shown in Figure 2, the first set involves the removal of a hydrogen from a carbon atom to produce a carbon-based free radical. If diatomic oxygen is present, the subsequent reaction to form a peroxy radical is extremely fast, so fast as to not allow significant alternatives for the carbon-based free radical[41, 54]. The peroxy free radical is not as reactive as the carbon free radical, but nonetheless is sufficiently reactive to quickly abstract another hydrogen from a carbon to form another carbon radical and a hydroperoxide (ROOH). The new carbon free radical can then react with diatomic oxygen to continue the propagation cycle. This chain reaction ends when two free radicals react with each other in a termination step.

During the initial period of oxidation the ROOH concentration remains very low until an interval of time has elapsed. This period of time is called the induction period and is determined by the oxidation stability of the fatty oil or biodiesel fuel and the conditions under which it is stressed. Once the induction period is reached, the ROOH level increases rapidly, signaling the onset of the overall oxidation process. Other properties of fatty oils and biodiesel fuels can also change in a way directly or indirectly related to ROOH induction period. These trends will be discussed in a subsequent section of this report.

In the above peroxidation chain mechanism, the most easily abstracted hydrogens are generally the ones that are involved. Hydrogen bonded to carbons allylic to olefinic unsaturation are more easily removed than hydrogen bonded to non-allylic carbons or to the carbons involved in the olefinic unsaturation[42]. This is because of the resonance stability imparted by the pi electron system in the adjacent olefin group. Carbons that are simultaneously allylic to two olefinic groups will be extremely susceptible to hydrogen abstraction. The methylene groups that interrupt the multiple olefinic unsaturation in polyunsaturated fatty acids in many vegetable oils are examples of carbons that are bis-allylic, hence very susceptible to the initiation of peroxidation [54, 107].

The reaction scheme in Figure 3 shows the two carbons most susceptible to reaction, the free radicals formed, and the resulting hydroperoxides, using a portion of a linolenic (18:3) fatty acid chain as the substrate.

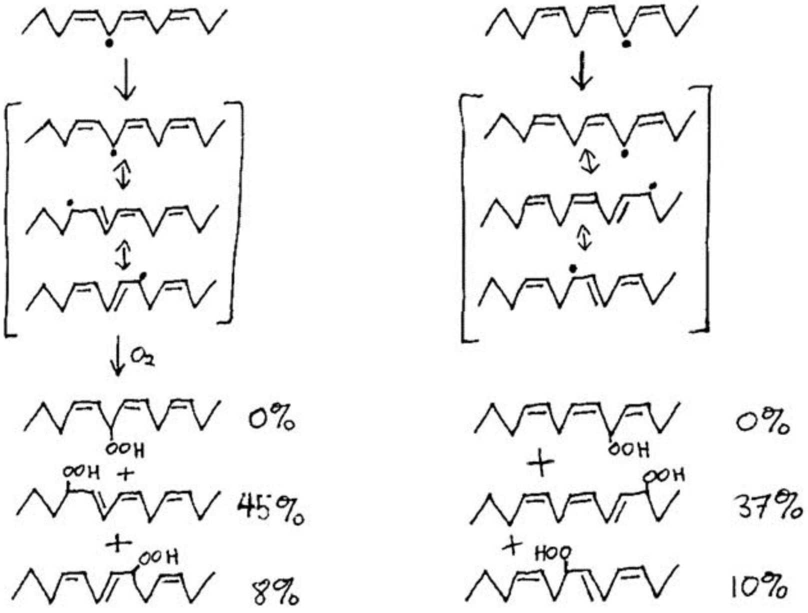

Figure 3. Reaction Scheme

As can be seen, the resulting hydroperoxides retain the same level of olefinic unsaturation as the parent fatty acid chains with one important difference: two-thirds of the total possible hydroperoxides have polyunsaturation that is no longer entirely methylene-interrupted but now contains a conjugated diene[48]. The reader can satisfy himself that the same scenario will result when a linoleic (18:2) acid chain is oxidized. In fact, studies have shown that in the case of linolenic acid oxidation, the two hydroperoxides formed by direct attack of oxygen on the methylene carbons contribute an insignificant percentage to the total distribution of the six theoretical structures[48]. This important distinction is often glossed over in research papers that discuss chemical trends that occur as fatty oils oxidize.

As expected, fatty oils that contain more polyunsaturation are more prone to oxidation. An early study[6] measured the relative rate of oxidation for the methyl esters of oleic (18:1), linoleic (18:2), and linolenic (18:3) acids to be 1:12:25. More recent work has shown that the rate of oxidation of pure unsaturated fatty acids as measured by oxygen consumption in closed systems is proportional to the number of bis-allylic carbons present[54]. As linoleic (18:2) and linolenic (18:3) acid content in fatty oils or esters increases, the oxidation stability decreases[64]. Two tables taken from Internet sites that provide typical fatty acid compositions for various vegetable oils are given in Appendix A. Not surprisingly, when methyl esters of fatty acids are chemically modified to dramatically reduce the polyunsaturation by methods such as fractional crystallization or hydrogenation, oxidation stability is greatly increased[123].

As fatty oils or the alkyl monoesters of fatty oils oxidize, the hydroperoxide ROOH levels increase. Studies have shown that the development of ROOH over time exhibits one of two behaviors. First, ROOH levels can increase, achieve a plateau, and then hold that level in a steady state[4, 50, 87, 95, 100, 101, 106]. Alternatively, ROOH levels can increase, achieve a peak level, and then decrease[4, 50, 70, 96, 106, 117]. The reasons why two such behaviors exist are not clearly resolved in prior work. However, factors such as oxygen availability[95, 96], temperature [4. 70], extent of pre-existing oxidation[106], and the presence of metals that catalyze the decomposition of hydroperoxides[70] are likely involved. If oxygen is not available in sufficient abundance, the formation of ROOH can slow or even stop while ROOH decomposition continues. This will tend to cause a peak in the ROOH concentration followed by a decrease. Similarly, at higher temperatures or in the presence of hydroperoxide decomposing metals such as copper or iron, ROOH decomposition rate will be greatly increased, also supporting a peak in ROOH followed by a decrease. Regardless of the profile of ROOH formation with time, the maximum ROOH levels formed are typically reported to be 300-400 meqO_2/kg[4, 50, 95, 96, 100, 106]. In one study much higher ROOH levels (1100 – 1300 meqO_2/kg) were observed for two of nine methyl esters[117]. No reason for this unusually high hydroperoxide level was given.

2.4 Secondary Products of Oxidation

Once fatty oil hydroperoxides are formed, they decompose to ultimately form aldehydes such as hexenals[86], heptenals, and propanal[64, 65]. Hexanal, pentane, and 2,4-heptadienal have also been detected[65]. One study detected about 25 aldehydes during the oxidation of vegetable oils[112]. Aliphatic alcohols, formic acid, and formate esters have also been detected[32, 55]. Increased acidity is always a result of oxidation of fatty oils and biodiesel[50, 87, 100, 101, 106], due to the formation of shorter chain fatty acids[32, 101].

As hydroperoxides decompose, oxidative linking of fatty acid chains can occur so as to form species with higher molecular weights, i.e. oxidative polymerization. Such polymeric species rarely become larger than trimers or tetramers[12, 23, 42], although an explicitly stated reason for this cannot be found in the open literature. One of the obvious results of polymer formation is an increase in the oil viscosity[18, 43]. Under conditions where oxygen is available, fatty acid moieties are joined by both C-O-C linkages [3, 23, 42] and C-C linkages[42]. When ROOH decomposition occurs under an inert atmosphere, C-C linkages in resulting polymers are observed[23]. The fact that oxygen is incorporated in the oxidative polymerization has been demonstrated by the oxidation of soybean oil and the isolation and analysis of the resulting polymeric compounds. The polymers contained 21.4% O compared to 11.8 for the non-oxidized soybean oil[14]. Not surprisingly, increased levels of polyunsaturated fatty acid chains enhance oxidative polymerization in fatty oils. During air oxidation at 250°C, safflower oil high in linoleic (18:2) acid was found to increase in viscosity much more than safflower oil high in oleic acid (18:1)[43]. The increase in viscosity is an obvious result of the formation of significant levels of higher molecular weight materials.

Vinyl polymerization has also been proposed as a mechanism whereby higher molecular weight oligomers of fatty oils or esters can be formed[42]. In this mechanism, as depicted in Figure 4, a carbon-based free radical adds directly to an olefinic carbon to create a C-C bond and another free radical. This dimer can either abstract a hydrogen from another molecule or continue the process by adding to an olefinic carbon on yet another fatty oil or ester. In fatty oils and esters this process is not believed to go beyond a tetramer[43]. However, the cited source[42] does not explain how carbon-based free radicals can significantly participate in such reactions when oxygen is available.

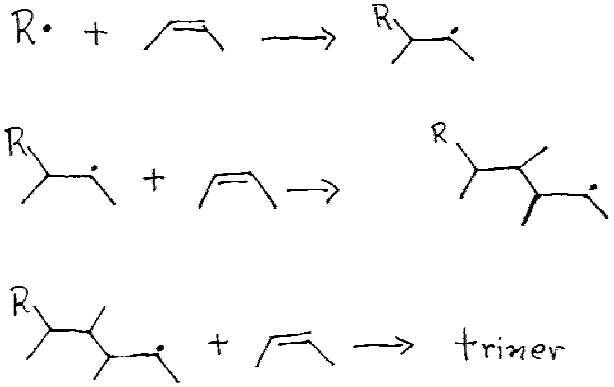

Figure 4. Vinyl Polymerization Mechanism

2.5 Other Factors Affecting Fatty Oil Oxidation

For more than 70 years it has been known that the presence of certain metals such as Cu, Fe, Ni, Sn, and brass (a copper rich alloy) can increase the oxidizability of fatty oils[1]. Even from the earliest work, copper has been known to generally be the worst offender. More recent work has verified that even 70 ppm Cu in rapeseed oil greatly increased oxidation as measured by headspace oxygen consumption[107]. Hexanal and 2-hexenal levels were increased by factors of 70 and 200, respectively, relative to rapeseed oil without copper. Copper has also been shown to reduce the Oxidation Stability Index (OSI) of methyl oleate more than either Fe or Ni[107]. (OSI is a test to measure oxidation stability of fatty oils and esters and is described in a later section of this report.) However, iron has been shown to be a potent hydroperoxide decomposer, and its effect in rapeseed oil methyl esters was more pronounced at 40°C than at 20°C[70]. In another study using soy methyl esters, iron promoted increases in Total Acid Number (TAN) more than copper[82].

Fatty oils and fatty acid esters will invariably have some free fatty acids present, and such acids have been shown to have a significant effect on the oxidizability of the oil. In one study that compared the oxidation of oleic (18:1), linoleic (18:2) and linolenic (18:3) acids with their corresponding methyl esters, the free acids were each found to be far more oxidatively unstable than their corresponding ester[51]. Also, as expected for both acids and esters, the trend of increasing stability was linolenic < linoleic < oleic. Moreover, when stearic (18:0) acid was added at levels up to about 5% to methyl linolenate, ROOH decomposition was accelerated compared to control samples. Likewise, decreases in conjugated diene levels were observed relative to methyl linolenate samples without stearic acid. A commonly used fuel dimer acid corrosion inhibitor has been shown to greatly increase formation of secondary oxidation products such as polymeric gums when present at only 20 ppm in a 50/50 blend of soy biodiesel and LS No. 2 diesel fuel[83]. Since such additives are present in all No. 2 diesel fuels and will likely continue to be present at current or higher levels in the future, this result is very significant for fuel blends that contain significant levels of biodiesel. Although additional research in this area is clearly warranted, no follow up work to this original 1997 work can be found in the open literature.

The size of the alcohol group used to make the biodiesel fuel from given fatty oil can affect the oxidation stability of the resulting monoesters. When air-oxidized at 95°C, soy ethyl esters gave lower TAN values (less secondary oxidation products) than soy methyl esters[90]. Also, the ethyl esters had longer oxidation induction periods than then the methyl esters when measured by ASTM D525, a pressurized bomb test procedure commonly used for gasoline oxidation stability evaluation. Increasing the alcohol group size from methyl to butyl increased oxidation stability (as measured by OSI), but this may simply have been due to the increasing molecular weight and the resulting decrease in double bonds present in a constant weight sample procedure. In a storage study done at 50°C with open exposure to air, ethyl esters of sunflower oil gave more rapid increase in TAN compared to the corresponding methyl esters[50]. Likewise, the maximum level of ROOH developed in the ethyl esters was greater than maximum ROOH level in methyl ester. However, this may have been due to the ethyl ester having a higher initial TAN (0.22 mg KOH/g vs. 0.11 mg KOH/g) and lower initial ester content (92.0% Vs 95.5%) compared to the methyl ester.

Crude fatty oils derived from plant sources contain naturally occurring antioxidants. The best understood of these compounds are the tocopherols[78]. Depending on the refining processes used during manufacture of the fatty oil, tocopherols may[33] or may not[29] carry over into the final oil. Under some circumstances, fatty oils can still retain 500-1,000 ppm of tocopherols after refining[37]. When methyl esters are produced from fatty oils, the resulting biodiesel fuel, if distilled, will typically have reduced or no tocopherols. There is indirect evidence that other naturally occurring compounds in fatty oils not yet identified may improve or inhibit the antioxidant capability of tocopherols[58, 106]. A more complete discussion of tocopherols and other antioxidants is provided later in this report.

Oxidation of fatty oils and esters can be accelerated by exposure to light. This process is called photo-oxidation and its initial steps have been shown to proceed by a different mechanism whereby oxygen directly attacks the olefinic carbons[42, 48]. Photo-oxidation should not be a significant factor in the manufacture and transportation of biodiesel fuels, and no further discussion of this topic is included in this report.

2.6 Thermal Polymerization

At sufficiently high temperatures, the methylene-interrupted polyunsaturated olefin structure will begin to isomerize to the more stable conjugated structure[2]. Once this isomerization has begun, a conjugated diene group from one fatty acid chain can react with a single olefin group from another fatty acid chain to form a cyclohexene ring[2, 42]. This reaction between a conjugated di-olefin and a mono-olefin group is called the Diels Alder reaction, and it becomes important at temperatures of 250-300°C or more[8, 18, 23]. The products formed are called dimers. The Diels Alder reaction is shown below in Figure 5.

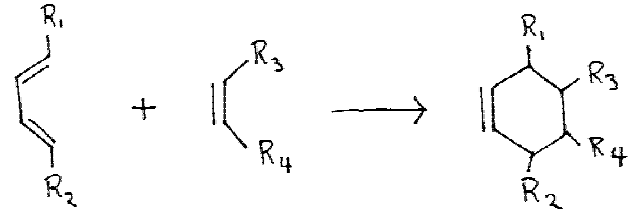

Figure 5. Diels Alder Reaction

Thermal polymerization can also form trimers, but there is disagreement as to how they form. One study concluded that trimers are formed by reaction of an isolated double bond in a dimer side chain with a conjugated diene from another fatty oil or ester molecule (a Diels Alder reaction)[23]. However, an earlier study provided evidence that may support the non-Diels Alder coupling of two side chain olefin groups from a dimer and a fatty oil molecule[8]. Thermal polymerization is characterized by rapid reduction in total unsaturation[23] as three olefin groups become one. When linseed oil was thermally polymerized at 300°C, initial polymerization resulted in dramatic lowering of total unsaturation as measured by Iodine Value (IV). However, no increase in molecular weight was observed. This was found to be due to an intra-molecular Diels Alder reaction between two fatty acid chains in the same triacylglyceride molecule[17]. This may have ramifications for biodiesel made from used cooking oils. Such oils may be subjected to temperatures in excess of 300°C when used in high pressure cookers. If such intra-molecular dimers were to form during such thermal stressing, they would retain their linking when transesterified to methyl esters for use as biodiesel. The resulting species would be a di-ester with a molecular weight about twice that of a normal biodiesel ester molecule. If such biodiesels (i.e. yellow greases) were not distilled, these dimers would be present in the final fuel. No work can be found that investigates if such dimers are indeed present in used cooking oils, and if so, what their effect on fuel properties would be in the corresponding non-distilled biodiesel fuels. Certainly, the potential existence of these dimeric species in non-distilled yellow grease biodiesel is not addressed within the published literature of the U.S. biodiesel manufacturing/marketing industry. To the extent that sufficiently high temperature conditions are achieved, thermal polymerization may be of limited importance in biodiesel fuel that is repeatedly heated by the engine and recycled to the fuel tank before actual combustion[43]. However, thermal polymerization will not impact storage stability.

3.0 TEST METHODOLOGY RELATING TO STABILITY

3.1 Initial Fatty Oil Composition

The ester content of a biodiesel fuel is a basic property that should be known. An early method using gas-liquid chromatography (GLC) has been used[51], but the standard method usually used now is a gas chromatographic procedure (Pr EN 14103 or AOCS Ce 1-62)[111] commonly called FAME (fatty acid methyl ester) analysis[106]. This procedure gives not only the percent ester in the fluid, but also the percentage of the individual esters according to their fatty acid structure.

One of the oldest and most common methods of determining the level of unsaturation in a fatty oil or ester is the iodine value (IV)[91, 92, 107]. Two ASTM methods exist for measuring this parameter, D1541 and D1959. D1959 will determine total olefinic unsaturation only in systems that contain no conjugated polyunsaturation. D1541 will accurately determine total olefinic unsaturation regardless of the isomeric configuration, but is a very tedious procedure involving a photographer's darkroom for part of the laborious sample work up. Accordingly, this procedure is seldom used in the fatty oils industry. Also, IV has been shown to be a poor predictor of relative oxidation stability of fatty oils and esters as well as the relative tendency of a biodiesel fuel to form engine deposits[105]. More specifically, IV has been shown to not correlate with OSI IP in a series of mixtures of pure methyl ester compounds[107].

Several more useful indices have been developed using FAME analysis results[105, 107]. The allylic position equivalent (APE) is a theoretical measure of the number of singly allylic carbons present in the fatty oil or ester, assuming that all poly-olefinic unsaturation is methylene-interrupted. The Bis-allylic position equivalent (BAPE) is a similar theoretical measure of the number of doubly allylic carbons present in the fatty oil or ester. Both of these indices correlate with OSI IP[107]. The BAPE, in particular, has been shown to correlate with the OSI IP with an R^2 value of 0.983. Of course, these two indices can be correctly calculated from FAME analysis results only for fatty oils or esters that derive from methylene-interrupted sources such as rapeseed or soy. For oils that do not have methylene-interrupted poly-olefinic unsaturation (such as jojoba oil and meadowfoam oil) the standard APE and BAPE formulae are not valid. The APE and BAPE values of such oils must be calculated individually depending on the exact known isomeric structure of the poly-olefinic unsaturation[105].

Another index, the oxidizability (OX) of a fatty oil or ester has been defined as follows[61]:

$$OX = [0.02(\%O) + (\%L) + 2(\%Ln)]/100$$

In this equation, O refers to oleic acid (18:1), L refers to linoleic acid (18:2) and Ln refers to linolenic acid (18:3). The linear coefficients derive from kinetic studies[54] previously discussed in this report. For oils that have a methylene-interrupted polyunsaturation, the above formula is similar to APE and BAPE since it recognizes the importance of allylic and bis-allylic carbons in the oxidative process.

Over the last 25 years, several high performance liquid chromatography (HPLC) methods have been developed to measure one or more of the four isomers of tocopherol[40, 46, 59, 86]. The HPLC method that has been used most recently in the biodiesel industry is ISO 9936[84, 106].

Several methods have been developed to attempt to measure the "antioxidant power" of fatty oils and esters. One method uses an amperiometric procedure to determine the oxidation potential of a fatty oil or ester[93]. The authors claim that the most effective fatty oil antioxidants gave oxidation potentials between +0.4V and +0.6V relative to an Ag/AgCl reference electrode. Two methods have been reported that use a stable colored radical that acts as a hydrogen scavenger for active hydrogen available in antioxidants. As the radical captures the hydrogen, the color is reduced, and the progress of this reaction can be measured by appropriate measurements in the UV/Visible spectra. One method uses a neutral radical 2,2-diphenyl-1-picrylhydrazyl (DPPH)[75]. A later method uses a radical cation 2,2'-azinobis (3-ethylbenzothiozoline-6-sulfonic acid) (ABTS)[94]. The main difference between these two methods is that the earlier method requires up to 6 hours reaction time for the color reduction reaction to come to equilibrium. The later method has a reaction time of about 2.5 minutes.

3.2 Primary Oxidation Products

As already discussed, primary oxidation products are characterized as conjugated diene hydroperoxides. Hydroperoxides are measured by ASTM D3703 or by similar procedures[34, 50, 51, 96, 100, 108]. Conjugated dienes are measured by UV adsorption at 232 nm as per ISO 3656[50, 74, 108].

3.3 Secondary Oxidation Products

A very sensitive wet method to detect carbonyl compounds[11] and a UV adsorption method used to determine unsaturated carbonyls compounds[18] have been reported. The thiobarituric acid (TBA) test was an early test to measure the levels of aldehydes produced during the oxidation of fatty oils[26]. However, the chemical reaction critical to this procedure has more recently been shown to produce significantly erroneous amounts of the final measured product during sample workup[49]. The anisidine value (AV) test (EN ISO 6885 or AOCS Cd 18-90)[98] is a more reliable method now used to determine aldehyde levels in oxidized fatty oils and esters. A similar method using benzidine instead of anisidine has been reported[20] but does not appear to be used to any significant extent. Several methods to measure volatile aldehydes in closed system headspace have been reported[61, 65, 71].

Since oxidation is a multi-step reaction sequence involving both primary and secondary species, an index has been proposed to better track the oxidation process. This index, the TOTOX value, is defined as follows[34, 37]:

$$\text{TOTOX} = 2{*}\text{PV} + \text{AV}$$

Development of acidic materials during oxidation is typically measured by simple titration such as Total Acid Number, ASTM D664 (TAN)[50, 70, 96, 100, 106].

Early methods to measure polymer levels in fatty oils and esters have been proposed[35, 52]. The procedure most often used in the biodiesel industry is BS EN ISO 16931, a size exclusion HPLC procedure using a refractive index detector[106]. A similar procedure is AOCS Cd 22-91.

3.4 Physical Properties

The most obvious physical property that can be used to measure oxidation is viscosity, since polymerization will necessarily increase that property. Kinematic viscosity appears to be the most often used procedure [18, 50, 96, 100], although absolute viscosity could also be used. Several studies have used refractive index as a way to show the formation of polymers[13, 14, 16, 18]. The fact that fatty oil or ester polymers have higher refractive indices is undoubtedly the reason why a refractive index detector is used in the BS EN ISO 16931 procedure. Di-electric constant has also been used as a means to measure the development of oxidation products more polar than the original fatty oil or ester[52].

3.5 Stability Test Methods

Various procedures designed to accelerate the oxidative and/or thermal instability of fatty oils have been developed or adapted from similar procedures used in other industries (most notably the fuels and lubricants industries). One of the oldest methods is the Schaal oven test[2, 29]. In this procedure, a convection oven is held at a specified temperature and open samples of fatty oils are stored within. The endpoint of the test was originally detected by organoleptic analysis (smell and taste). Later modifications of this procedure used other chemical parameters such as a rapid increase in PV to determine the endpoint[88]. Another heated oven storage test used weight gain of a pre-weighed sample as the determining parameter[24,33]. The onset of a rapid weight gain was interpreted as the incorporation of oxygen into the oil.

Methods involving heating a sample of fatty oil or ester in a closed vessel while measuring the oxygen content of the headspace have been used[5, 54, 92] and are commonly referred to as an oxygen adsorption or oxygen uptake test. In each of these tests a sudden increase in the rate of oxygen consumption is considered to be an indication of the onset of rapid oxidation.

The Active Oxygen Method, AOM (AOCS Method Cd 12-57)[80] has been used for sixty years[5] in various modifications[9,27, 29, 53, 69]. This test procedure involves heating an oil sample at a predetermined temperature while bubbling dry air through at a set rate. The time (usually in hours) required for a specific peroxide value to be achieved is considered the measured parameter. Sometimes the rapid increase in PV is used as the endpoint determination. A similar method developed in the petroleum fuels industry, ASTM D2274, uses a filtration and gravimetric determination to measure the insolubles produced during a heated oxidation period in which O_2 is bubbled through the sample (typically 16 hours at 95°C)[90]. A less oxidatively severe test is ASTM D4625. In this test, a sample in a vented bottle is stored at 43°C for 13 or more weeks[90,101]. The resulting fuel is filtered to measure total insolubles as an indication of the instability of the fuel. ASTM D525, a pressurized bomb test was developed to measure oxidation stability of gasoline and has been used for biodiesel fuels[90].

The Oxidation Stability Index (OSI) test has become commonly used in Europe where biodiesel fuels are required to meet an induction period (IP) of at least 6 hours when tested at 110°C[108]. The Metrohm Rancimat apparatus is frequently used to measure OSI, and the terms "Rancimat" and "OSI" are often used interchangeably in the open literature when referring to the test method. OSI has been commonly used in experimental programs[69, 70, 100] and involves passing air through a heated sample of the fatty oil or ester. The air then passes out of the sample and into a tube of water where conductivity is monitored. A sharp rise in conductivity is interpreted as indicative of the formation of short chain, water-soluble carboxylic acids, i.e. secondary oxidation products. Studies have been done that show that the primary acidic species formed in the Rancimat OSI test is formic acid[55]. A chemical mechanism to explain how hydroperoxides decompose to form formic acid has been proposed[55]. An alternative approach has been reported where chemiluminescence is used to monitor the oxidation during the OSI test[77]. Several studies have been done showing that if the Rancimat test is run at different temperatures, the logarithm of the induction period (IP) will be a linear function of test temperature, i.e. plots of log (OSI IP) Vs T give straight lines [60, 63, 92].

The Rancimat apparatus has also been adapted to measure thermal stability by not using an airflow and measuring polymer content in an 8 gram sample after 6 hours at 200°C[108]. A more traditional test for thermal stability, ASTM D6468, heats a sample at 150°C for either 90 or 180 minutes. The resulting sample is then cooled and either filtered to determine filterables via a total reflectance meter or gravimetrically in a manner similar to ASTM D2274[90].

Pressurized differential scanning calorimetry (PDSC) has been used in several studies to measure the oxidation stability of fatty oils and esters with and without added antioxidants[97, 102, 109]. When run using an isothermal procedure, the time required to detect an exothermic reaction is considered the induction time. When run using a non-isothermal procedure, the temperature where an exothermic peak is detected is called the oxidation temperature (OT).

4.0 STABILITY-RELATED BEHAVIOR

4.1 Interdependence of Stability Test Methods

Recent proponents of the OSI (Rancimat) procedure have claimed that it is superior to PV-based stability tests[63]. The rationale for this claim is that the Rancimat procedure measures volatile acidic products formed during secondary oxidation reactions, whereas methods using peroxide values are limited to only the primary oxidation products. Since oxidation is a multi-step process, measurements pertaining more to the end of the oxidation process should be a better indication of oxidation than measurements limited to the very beginning of the oxidation process. However, data provided by numerous studies show that the OSI IP correlates well with other stability test results, including PV-based tests.

In one study[68], six vegetable oils were evaluated by the Rancimat test at 100°C. The oils were also stored in the dark at 20°C under loosely covered conditions. The times required to achieve peroxide values of 5, 10, and 20 meq O_2/Kg were determined. The OSI IP data for the six oils correlated well with each of the three times required for attainment of the target peroxide values. Specifically, the R^2 for the linear correlation increased from 0.796 to 0.933 as the PV target value used went from 5 meq O_2/Kg to 20 meq O_2/Kg. In another study[53], the Active Oxygen Method test (AOM) and the Rancimat test were run on six fatty oils at 100°C, 110°C, and 120°C. The IP values of both tests were plotted for each test temperature and a linear correlation was determined. The R^2 values for the 100°C, 110°C, 120°C, and pooled data were respectively 0.974, 0.953, 0.819, and 0.974. An early study showed that results of the AOM and an oxygen uptake procedure gave corresponding rankings for several lard oils[5]. OSI IP and ASTM D525 IP have also been shown to tightly correlate with each other[117]. In this same study, peroxide values typically peaked, then decreased. Finally, one study cites work that showed that isothermal PDSC gives IP values that correlate well with OSI IP[102].

This data appears to indicate that although primary and secondary oxidation reactions are sequentially linked, there is nonetheless some interdependencies between them. Studies that have further demonstrated these interdependencies are discussed in the next section.

4.2 Interdependence of Primary and Secondary Oxidation Products - Initial

Numerous studies have been done to investigate how the stability-related properties of biodiesel fuel and fatty oils change when stressed under various storage conditions. An examination of these studies and their results reveals some consistent interdependencies of test results. Perhaps the most important of these studies is the recently reported BIOSTAB project results[108]. In part of this study, distilled and un-distilled methyl esters from four fatty oil sources (eight methyl esters total) were evaluated by the Rancimat procedure at 110°C. These tests were run on the esters as received without first stressing them in any stability test. During each test, portions of the sample were also evaluated for PV, TAN, AV, conjugated dienes, polymer content, ester content, and methyl linolenate (18:3) content. The induction period for each of these properties was determined in the same way that the OSI IP was determined. For the eight esters evaluated the OSI IP correlated well with the IP values of each of the other test properties. In addition, the OSI IP correlated well with the mean of the IP values for the entire set of other test properties. This shows that during the stress conditions of the Rancimat procedure the evolution of primary oxidation products (ROOH and conjugated dienes) not only correlate with each other (as expected), but they also correlate with the evolution of the secondary oxidation products as indicated by TAN, AV, and polymer content. In addition, the OSI IP correlates with decreases in the overall reactant as measured by ester content and methyl linolenate (one of the most reactive of the ester components).

4.3 Interdependence of Primary and Secondary Oxidation Products – After Stressing

Other studies have shown that interdependencies in various test parameters are found when fatty oils and esters are first stored or in some other way stressed and then evaluated. In one study, methyl and ethyl esters of sunflower oil were stored for 90 days at 20°C, 30°C, and 50°C. Samples were stored both with and without access to air. Samples stored without available oxygen did not produce significant ROOH or conjugated dienes, and the TAN remained low. When the samples were stored open to air, ROOH and conjugated dienes both increased. TAN and viscosity increased more in samples exposed to air than for samples not exposed to air.

The linking between TAN and viscosity increase has been noted in several other studies[85, 95, 96, 100, 101, 106, 117]. This strong interdependency suggests that the formation of polymers is chemically linked to the formation of acidic secondary oxidation products[96].

The linking of TAN with respect to PV is more interesting. In one study[96], B20 and B50 blends (using LS No. 2 diesel fuel) were cyclically pumped at 60°C. Peroxide value reached a definite peak for all tests and then decreased, presumably due to limited oxygen supply that eventually caused ROOH decomposition to outpace ROOH formation. TAN and viscosity increased as PV increased, but once PV began to decline, TAN and viscosity continued to increase, but at significantly reduced rates.

In another study involving un-distilled and distilled methyl esters of rape, soy, tallow, and used frying oils, the esters were stored as per ASTM D4626 (43°C) for 24 weeks[101]. During that time the PV of all samples continued to rise. However, OSI IP decreased over time so that by 8 weeks duration all but one sample had reached an OSI IP value of zero. During the entire 24 weeks TAN dramatically increased for all samples with relative increases between 700% and 1,800%. However, the rate of increase markedly increased for each sample after the OSI IP had become zero. Polymer levels behaved in the same manner. This continues to underscore the importance of oxygen availability in determining the interdependency trends between test properties. When oxygen availability is limiting, then the secondary oxidative processes that form acidic products are slowed. This in turn also reduces the formation of polymeric materials that are the cause of increased viscosity. Not surprisingly, ester content of these eight samples also decreased during the 24-week storage. The authors concluded that ester reduction was caused by two factors: ROOH formation and polymer formation. Technically this is not quite correct. As already seen, when hydroperoxides are initially formed, the only change that occurs is an isomerization of the polyunsaturation to form a conjugated diene. The ester linkage is not broken at the time that the hydroperoxide is formed. However, as ROOH decomposition reactions occur, ester linkages are obviously broken as part of the complex set of secondary oxidation reactions. Since these secondary oxidation reactions are responsible for polymer formation, it may be correct that polymer formation is directly or indirectly linked to the breaking of ester linkages in biodiesel molecules.

The effect of storage temperature and oxygen availability is further demonstrated by contrasting the results of the previously described study[101] with one done by the same researchers using a similar set of biodiesel fuels. In this case, ten methyl esters were stored in sealed drums outside for one year. Ambient temperatures ranged from –1.2°C to 30.1°C[106]. One of the ten esters was also stored in an open drum with occasional shaking to increase contact with air. The ten samples in sealed drums experienced no significant change in TAN, ester content, methyl linolenate content, polymer content, and only a minor decrease in OSI IP. This behavior is in marked contrast to the 43°C, 24 month study[101] where those same properties changed very significantly. The one methyl ester stored in an open drum with occasional shaking experienced a dramatic decrease in OSI IP over the 12 months, but only minor increases in TAN and polymer level. This data seems to suggest that while ample oxygen availability can, with time, cause the OSI IP to dramatically decrease, secondary oxidation products such as acidic and polymeric compounds may not necessarily increase unless the fuel temperature is sufficiently elevated.

This conclusion is further supported by two other studies done by different groups or researchers. In one study[100] un-distilled rapeseed methyl ester and both un-distilled and distilled used frying oil methyl esters were stored at 20°C to 22°C for 170 to 200 days. Samples were stored in both open and sealed polyethylene bottles so as to determine the effect of oxygen availability. As expected OSI IP decreased rapidly in the air-exposed samples, with the OSI IP reaching zero for one sample in about 150 days. Although significant increases in peroxides occurred for the air-exposed samples, the increases in TAN and viscosity were minimal, averaging about 0.3 mg KOH/ g and 0.3 mm^2/s, respectively.

In the other study[85]six rape methyl esters were stored at 4°C and at ambient temperature. The authors did not discuss availability of air. Stability as measured by OSI IP decreased more for the ambient-stored samples than the lower temperature samples, as expected. For the ambient samples, TAN and viscosity increased only by small amounts. The notable exception was an ambient temperature sample exposed to daylight. This sample increased in TAN and viscosity by about 250% and 14%, respectively. This anomalous data is most likely due to photo-oxidation.

However, a similar two year, ambient temperature study[87]with both methyl and ethyl esters showed more increases in TAN and viscosity than the one year study, but less then the 43°C, 24 month study. Even though the fuels for this study are different from the ones used in the previously described work, the overall data indicates that time is a factor that must also be considered. Given sufficient time, the secondary oxidative processes that increase TAN and polymeric compounds (viscosity) will eventually begin to accelerate, even when the fuel is stored at non-elevated temperatures.

The other extreme in storage temperature is illustrated in an earlier study where cottonseed oil was heated to 180°C while open to the air[35]. Peroxide values remained low due to the high temperature and rapid ROOH decomposition rate. However, conjugated dienes levels, TAN, and viscosity all increased significantly, indicating that oxidation was indeed taking place. Also, linoleic (18:2) fatty acid chains decreased while oleic (18:1) fatty acid chains increased which is another indication that oxidation was occurring.

4.4 Insolubles Formation

The formation of insolubles by neat biodiesel as measured by tests such as ASTM D2274 and D4625 are often low (i.e. < 0.5 mg/100 ml)[83, 89, 108]. However, some studies have reported very high levels (2.5 – 72.0 mg/100 ml) of total insolubles[90, 132, 125, 127]. The authors of these studies did not take note of nor comment on these inconsistencies. There are a number of possible reasons for the great difference that exists in total insoluble levels within these studies. The presence or absence of synthetic antioxidants or other additives in the initial B100 (which can both increase or decrease total insolubles), the presence of natural antioxidants, sample storage/handling conditions prior to testing, and variables in the test procedure itself are some of the factors that can greatly influence the total insolubles level in tests such as ASTM D2274. Unfortunately, such factors are usually not discussed in such reports. Based on the information provided within these previous works, it is not possible to arrive at a cogent reason for why B100 D2274 total insolubles are sometimes very low and sometimes very high.

When biodiesel is blended with low sulfur No. 2 diesel fuel, high levels of insolubles (13 mg/100 ml) have been measured[83, 115, 125, 133]. In these studies, blends of biodiesel with petroleum No. 2 diesel fuel generate more total insolubles during the stability tests then either the neat biodiesel or neat petroleum fuel. In one study, this antagonistic effect was shown to be roughly four times as great when the biodiesel fuel blends were made using No. 1 diesel fuel compared to blends made using No. 2 diesel fuel[115]. The authors of this study concluded that the biodiesel fuel was acting as an oxidant to cause the petroleum fuel to produce the large levels of insolubles. However, this explanation is almost certainly wrong. Other work has concluded that the higher molecular weight products formed in biodiesel fuel tend to stay in solution due to the high polarity of the biodiesel fuel[83, 108, 132]. In fact, as the biodiesel fuel oxidizes, the polarity tends to increase[52] and further promote solubilization. However, when such oxidized species are mixed with a very non-polar material such as No. 2 diesel fuel, they can be expected to precipitate out of solution. Since No. 1 diesel fuel has even less solvency than No. 2 diesel fuel, the effect will be even more pronounced in the No. 1 fuel. Indeed, another study showed that ASTM D4625 total insolubles were more than ten times as great when biodiesel fuel blends were made using

JP-8 (a military-grade No. 1 distillate fuel) compared to blends made using No. 2 diesel fuel[133].

This solvency effect in biodiesel blends has been further demonstrated in one study[132] where several B100's were tested according to D2274. After the fuel was filtered and total insolubles had been measured, the filtered fuel was diluted with iso-octane, allowed to set, and then filtered again. In all cases, the additional amount of insolubles formed after adding the non-polar iso-octane was significant. In some cases, the additional amount of iso-octane insolubles after D2274 was greater than the original total insolubles generated before the iso-octane was added.

In one study[125], seven biodiesel fuels were custom manufactured from seven different fatty oil feedstocks including soy, canola (rapeseed), lard, two tallows, and two used cooking oils. Three of the biodiesels when blended with a low sulfur diesel fuel gave extremely increased D2274 total insoluble levels (as high as 133 mg/100 ml) compared with either the neat biodiesel or diesel fuel. However, the seven neat biodiesel fuels all gave unusually high D2274 total insoluble levels (6.2 – 72.0 mg/100 ml) relative to values observed in other studies. Also, the low sulfur (300 ppm) No. 2 diesel fuel used in this work had a D2274 total insolubles level of 2.34 mg/100ml. Such a value is extremely high and virtually never observed for such petroleum fuels[134, 135]. The author of this study did not make note of or comment on these unusual values. Therefore, the entire body of D2274 data in this study is questionable.

The tendency of unstable biodiesel fuels to form increased levels of insolubles when blended with low sulfur petroleum distillate fuel has serious implications for the future when the diesel fuel used for blending with biodiesel will conform to the upcoming 15 ppm sulfur specification. Such ultra-low sulfur diesel fuel will have significantly reduced solvency characteristics. Thus far, no work can be found exploring the behavior of blends of biodiesel fuel with ultra-low sulfur No. 2 diesel fuel.

Interestingly, in the previously mentioned 60°C cyclic pumping test[96], the B20 and B50 biodiesel blends did not produce any evidence of insolubles formation based on constant pressure drop across filters. Therefore, the link between the high insolubles in accelerated tests such as ASTM D4625 and actual equipment performance may not be straightforward.

It has also been shown that total insolubles as measured by ASTM D2274 does not correlate with OSI IP for various biodiesel fuels[117]. Since OSI IP has been shown to correlate with other test parameters such as PV, TAN, AV, and polymer content, there appears to be a major disconnect between biodiesel stability as measured by the most common methods and the amount of insolubles formed. Since fuel filter plugging and engine deposit formation may be related to total insolubles formation, this illustrates the most significant gap in understanding between stability-related test data and actual performance data. A subsequent section of this report will discuss the seriousness of this gap in more detail.

4.5 Deposit Forming Tendencies

One of the potential problems associated with using an unstable fuel is the increased tendency to form deposits on engine parts such as injectors and critical fuel pump components[81, 96, 100, 103]. No laboratory testing can be found in the open literature that was specifically and explicitly designed to measures the tendency of a biodiesel fuel to form deposits on a hot metal surface under dynamic conditions. Therefore, it is not surprising that the relationship between biodiesel oxidation and deposit forming tendency has also not been established. However, a few studies have been reported where the Jet Fuel Thermal Oxidation Tester (JFTOT), ASTM D3241, has been used to evaluate the stability of biodiesel fuels. These JFTOT studies do provide at least some evidence of biodiesel deposit forming tendencies.

The JFTOT involves passing 600 ml of fuel across the exterior surface of an annular heated metal tube and determining the deposits on the tube after the conclusion of the test. Unless otherwise specified, the heater tube temperature is usually 260°C. Usually, the heater tubes are evaluated visually and given a numerical rating from 1 (best rating) to 4 (worst rating), with allowances for abnormal or peacock appearing deposits. Other more quantitative methods of measuring the heater tube deposits have also been used. In a previously cited study[125], a series of biodiesel fuels custom manufactured from seven different fatty oil feedstocks including soy, canola (rapeseed), lard, two tallows, and two used cooking oils were evaluated by the D3241 procedure. All fuels except one gave numerical tube ratings of 1, despite their very high levels of ASTM D2274 total insolubles. The previously described suspect nature of the D2274 data combined with the relatively non-discriminating visual tube rating method makes it impossible to gain much insight from these results.

In another report a soy-based biodiesel was evaluated by ASTM D3241 initially and after 8, 12, and 18 weeks of storage at 43°C under ASTM D4625 conditions[133]. For comparison purposes a low sulfur (0.04%) No. 2 diesel fuel, a high sulfur (0.37%) No. 2 diesel fuel, and a JP-8 were also evaluated. The JFTOT heater tube deposits were quantified using a device that measures the di-electric constant. Initially, the biodiesel fuel gave more deposits than the JP-8, but less than either of the No. 2 diesel fuels. As the fuels were stored at 43°C, the JFTOT tube deposits for the biodiesel and two No. 2 diesel fuels decreased; only the JP-8 fuel gave increasing JFTOT tube deposits with storage time. However, during these JFTOT tests the pre-filter that is upstream from the heater tube was not removed. This extremely fine filter may remove polymeric deposit precursors from the aged fuel. Also, the authors of this work reported that gummy deposits formed in the lines and fuel pump when biodiesel fuel was tested. These factors make any comparison of biodiesel with the petroleum fuels uncertain.

A third paper reported JFTOT testing of a soy-based biodiesel and a yellow grease biodiesel[132]. JFTOT tests were run at temperatures ranging from 225°C to 245°C. Heater tube deposits were quantified using an ellipsometer, a device that provides an accurate measure of deposit thickness and volume. For the soy-based biodiesel, tube deposits increased as the tube temperature increased from 225°C to 245°C. The yellow grease biodiesel had tube deposits that decreased as tube temperature increased from 225°C to 235°C. Overall, tube deposits were significantly higher for the soy-based biodiesel compared to the yellow grease biodiesel. The author suggested that the temperature dependent behavior may have resulted from competing factors of polymer formation (leading to increased tube deposits) and increased oxidation and resulting polarity of the bulk fuel (leading to decreased tube deposits). Obviously, more work is needed to verify this hypothesis.

The two biodiesel fuels of this study[132] were also evaluated for ASTM D2274 total insolubles. The D2274 total insolubles for the soy-base biodiesel was greater than that for the yellow grease biodiesel, directionally similar to the comparison of the overall JFTOT tube deposit levels. However, when the iso-octane insolubles for the two fuels were measured and added to the ASTM D2274 total insolubles, the new total insoluble value for the yellow grease biodiesel was much greater than the corresponding soy-based biodiesel value. Obviously, the relationship between insolubles formation and deposit formation tendency is not clear, based on the very limited experimental data currently available.

4.6 Thermal Stability

Thermal stability of biodiesel as typically measured by ASTM D6468 has been shown to be excellent in several studies[83, 90, 124, 132]. In one study, D6468 was modified to measure the filterable insolubles formed during the 90°C, 180-minute thermal stressing[90]. All neat biodiesels and blends of biodiesel with No. 2 diesel fuel were found to be very stable. The BIOSTAB project results also showed excellent thermal stability by D6468[108]. However, when the thermal stability test procedure was increased in severity by using the Rancimat apparatus at 200°C without airflow, significant evidence of instability was observed. Specifically, TAN and viscosity significantly increased in all eight methyl esters. Polymer levels also greatly increased, with final values ranging from 5.5% to 18.2%. It should not be surprising that biodiesel fuels would have good thermal stability since they derive from vegetable oils that are known to be well-suited in high temperature cooking applications such as deep-fat frying and pressure cooking.

5.0 ANTIOXIDANTS USED IN FATTY OILS AND ESTERS

5.1 General Chemistry Considerations

Antioxidants are chemicals that inhibit the oxidation process. Two types of antioxidants are generally known[116]: chain breakers and hydroperoxide decomposers. To date, work in fatty oils has been almost exclusively limited to chain breaking antioxidants. Openly reported work with biodiesel fuel has been entirely limited to them. The two most common types of chain breaking antioxidants are phenolic-types and amine-types. Almost all work in fatty oil and ester applications has been limited to the phenolic type of antioxidant. The general mechanism by which all chain breaking antioxidants work is depicted below in Figure 6:

$$ROO\cdot + AH \rightarrow ROOH + A\cdot$$

$$A\cdot \longrightarrow \text{stable products}$$

Figure 6. General Mechanism by which all Chair Breaking Antioxidants Work

As can be seen, the antioxidant contains a highly labile hydrogen that is more easily abstracted by a peroxy radical than a fatty oil or ester hydrogen. The resulting antioxidant free radical is either stable or further reacts to form a stable molecule that does not contribute to the chain oxidation process. In this way chain breaking antioxidants interrupt the oxidation chain reaction.

Hydroperoxide decomposer antioxidants work by chemically reacting with hydroperoxides and converting them to alcohols while the antioxidant changes to an innocuous oxidized form. Zinc dithiophosphate additives, organic phosphites, and certain organothio derivatives used in motor oils and industrial lubricants are examples of hydroperoxide decomposing antioxidants.

In fatty oils and esters, antioxidants can come from two sources: natural antioxidants (tocopherols) and added synthetic antioxidants.

Antioxidant effectiveness is generally measured by stressing a fatty oil or ester both with and without the antioxidant and comparing the results of the two oils. Virtually all of the previously mentioned stability tests have been used in this way.

5.2 Occurrence and Use of Tocopherols

Tocopherol is a phenolic compound that exists in four isomers (α, β, γ, δ), all of which occur naturally in vegetable oils[78]. Tocopherols do not occur in animal-derived fats except at trace levels[116]. The concentration of the various tocopherol isomers are characteristic of each vegetable oil[77]. Various studies indicate that the natural occurring levels of tocopherols are optimized with respect to antioxidant capability. Further addition of tocopherols generally has either no further benefit or may even be deleterious[7, 37]. Depending on fatty oil processing conditions, tocopherols may be retained, partially lost, or completely lost[29, 33]. Likewise, post-transesterification processing of biodiesel such as distillation can remove any tocopherols that were originally present in the vegetable oil feed.

5.3 Relative Effectiveness of Tocopherols

Many studies have been done to determine the relative effectiveness of the four tocopherol isomers. Although *in vivo* (within living systems) studies have usually ranked tocopherol effectiveness as $\alpha > \beta > \gamma > \delta$, most studies done *in vitro* (outside of living systems) in fatty oils have ranked them as $\delta > \gamma \sim \beta > \alpha$[78]. However, this ranking is not always exactly observed. In lard samples evaluated using both the AOM and an O_2 adsorption test, tocopherols when used at 100 ppm gave a relative performance of $\gamma > \beta >> \alpha$[5]. A destabilized sunflower oil methyl ester was subjected to a 65°C open-air storage test with oxidation determined by PV. Tocopherol isomers were added to this oil at 0 to 2,000 ppm. Relative effectiveness was $\gamma > \delta > \alpha$[108]. In another study purified soybean oil (containing essentially no tocopherols or hydroperoxides) was additized with 0 to 1,000 ppm of various tocopherol isomers. Results showed relative effectiveness to be $\delta > \gamma > \alpha$[58]. Notice that α-tocopherol, the one most commonly added to fatty oils, is also the one that is least effective.

One study looked at α and γ tocopherol and compared their performance in linoleic acid and methyl linoleate[57]. The γ isomer was the more effective at suppressing ROOH formation at 500 ppm and its performance at 50,000 ppm (5%) was unchanged. The α isomer gave dramatic reduction in performance at 50,000 ppm compared to 500 ppm. It was noted that the reaction product formed by γ-tocopherol when it reacts with a peroxy radical is still an antioxidant[33, 57]. However, α-tocopherol reaction product does not have this property. In the same study it was also determined that γ-tocopherol is more oxidatively stable than α-tocopherol. In another study, when a sample of rapeseed methyl ester was stored at ambient temperatures for one year in an open drum with periodic shaking, total tocopherols decreased by 50%. However, α-tocopherol was completely depleted in nine months, whereas γ-tocopherol decreased by only 51% during the entire one-year period[106]. This is consistent with γ-tocopherol being more stable than α-tocopherol.

When looking at the entire body of work concerning the effectiveness of tocopherols in fatty oils and esters, the most striking observation is how poor their performance is compared to synthetic antioxidants. Various methods including AOM, PDSC, and Rancimat OSI have been used with substrates including various vegetable oils and methyl esters, and results consistently show that the most common synthetic antioxidants are superior to tocopherols[5, 7, 19, 66, 97, 106, 108]. In some studies, tocopherols were shown to actually decrease the oxidative stability of a rapeseed oil[68], rapeseed oil methyl ester[108], and used frying oil methyl ester[108].

5.4 Relative Effectiveness of Synthetic Antioxidants

The first paper to discuss the use of phenolic compounds to arrest fatty oil oxidation was published in 1922[9]. Nordihydroguaiaretic acid (NDGA) was the first phenolic antioxidant approved for food use[9]. Over the years numerous other phenolic antioxidants have been proposed and used in fatty oils and esters. The names and abbreviations of some of the more important ones are given below. The structures of these antioxidants are provided in Appendix B. Please note that for the remainder of this report the antioxidants will be referred to by their abbreviations as they appear below:

Pyrogallol	PY
Gallic Acid	GA
Propyl Gallate	PG
Catechol	C
Nordihydroguaiaretic acid	NDGA
2-t-butyl-4-methoxyphenol	BHA
2,6-di-t-butyl-4-methoxyphenol	di-BHA
2,6-di-t-butyl-4-methylphenol	BHT
t-butyl hydroquinone	TBHQ

Numerous studies have been reported where various synthetic antioxidants have been evaluated in fatty oils and esters. One group of researchers developed a relative index by determining the performance of a given antioxidant in a fatty oil compared to the performance of a 1 micromole/g solution of Catechol in the same fatty oil. The ratio of PV based induction periods obtained was called the Catechol index[19]. A set of 28 phenolic antioxidants were evaluated with results ranging from 0 to 3.91. (Higher values imply better performance.) PY was the best, but GA, PG, and BHT also did well.

One study reported the evaluation of BHT, BHA, TBHQ, and PG in lard, various vegetable oils, and poultry fat[27]. The additives were added at 50, 100, and 200 ppm and evaluated by the AOM. In the vegetable oils and poultry fat, TBHQ was the best performer. In lard, TBHQ was equivalent to BHA and superior to the other two antioxidants. In another study, BHA, PG, and TBHQ were each added at 200 ppm to crude safflower oil, sunflower oil, soybean oil, and cottonseed oil[29]. The resulting oils and corresponding control samples were evaluated by the AOM at 210°F. and by a four-month open-air storage at temperatures ranging from 76°F to 110°F. In all four oils and in all tests TBHQ gave the best performance. Using crude whale oil as the substrate, TBHQ, PG, BHA, and di-BHA were each added at 200 ppm[33]. The resulting oils and the corresponding control samples were stored at 40°C to 60°C with oxygen replenishment occurring partially through the storage. The samples were also exposed to light for part of the 146-day storage period. Stability was determined by sample weight gain, PV, and AV. TBHQ was much more effective than the other three additives as measured by all three tests, demonstrating that both primary and secondary oxidation processes were being inhibited under the conditions of this test. The authors claimed that one reason for TBHQ's superior performance was the fact that its immediate oxidation products still possessed antioxidant properties, unlike other commonly used synthetic antioxidants[33]. Another study has also shown TBHQ to have reduced the amount of polymers formed during 180°C heating of olein[52].

An interesting common theme in these previous studies is the relatively poor performance of BHA and especially BHT compared to other antioxidants. It has been well established that BHT is among the best phenolic antioxidants for petroleum hydrocarbon materials such as fuels and lubricants. However, BHT has often been found to be one of the least effective synthetic phenolic antioxidants in fatty oils and esters [25, 35, 68, 108 114]. The reason for this may be two-fold. First, the greatly different structure of fatty oils compared to non-polar hydrocarbons (fuels and mineral oil or polyalphaolefin lubricants) may interact with the highly hindered polar phenol group of BHT to reduce its antioxidant capability. Second, BHT is relatively volatile, and under the conditions of many of the procedures used much of the additive may be lost during the early parts of the tests[35, 38, 68]. The volatility of BHT, BHA, and TBHQ is ranked as follows: BHT > BHA > TBHQ[38].

In more recent antioxidant evaluations involving biodiesel methyl esters, TBHQ was frequently found to be the best overall performer. When methyl ester of sunflower oil was stored at 20°C, 30°C, and 50°C, TBHQ at 400 ppm was found to control ROOH, conjugated dienes, and viscosity at 20°C and 30°C, but not at 50°C[50]. Soy methyl ester was heated for 6 to 48 hours at 60°C with air bubbling through it[95]. TBHQ was added at 40, 400, and 4,000 ppm and compared against a control sample. At 400 ppm, TBHQ arrested the production of ROOH (measured by PV), TAN, and polymers (measured by viscosity). Additive performance was unchanged at 4,000 ppm and was inadequate at 40 ppm. In a recent work, non-isothermal PDSC was used to evaluate TBHQ, BHT, BHA, PG, and α-tocopherol. Additives were evaluated in soy methyl ester at 500 to 5,000 ppms. All additives increased the oxidation temperature (OT). However, the four synthetic antioxidants were all more effective than α-tocopherol. Most of the total additive benefit was apparent when the concentration had reached 1,000 ppm. TBHQ and PG were the overall best performers.

The BIOSTAB project evaluated 20 phenolic antioxidants at 1,000 ppm, and none of the tocopherol additives provided any benefit[108]. The two best performing additives were PY and PG, although TBHQ did well.

Very little work has been done with antioxidants other than phenolic antioxidants [25, 79]. One study evaluated a series of antioxidants including non-phenolics in sunflower and cottonseed oil using the AOM[25]. A hydroperoxide decomposer additive, 3, 3'-dithioproprionic acid, was the most effective candidate tested, even more effective than TBHQ or PG. Another study showed some good beneficial synergism between phenolic antioxidants, zinc and bismuth dithiocarbamates, and a common amine antioxidant. However, caution should be used when evaluating new additives. Metal-containing additives cannot be used in fuels to any significant concentration. This will also be true of sulfur-containing antioxidants once the ultra-low (<15 ppm) sulfur diesel fuels are required. Since most biodiesel fuel will be blended with No. 2 diesel fuel, the effect of the additives in such blends must be considered. One study has shown that an amine-type chain breaking antioxidant actually increased total insolubles in blends of soy methyl ester and No. 2 diesel fuel even though it apparently was significantly reducing the oxidation processes[116]. Numerous studies have demonstrated that antioxidants are not always effective[22, 25, 43, 108, 132] and are, in fact, sometimes detrimental[29, 66, 68, 79, 108, 117, 132] to the stability of fatty oils and esters. This underscores the importance of having experience as both a fuels chemist and formulator when working with such additives[36].

6.0 IMPACT ON DIESEL ENGINE EQUIPMENT

6.1 Early Work

The most remarkable aspect of the work done evaluating the impact of biodiesel fuels on actual engine equipment is the virtual lack of such information. During the early 1980's, there was significant engine test work done to evaluate vegetable oils as either diesel fuels or diesel fuel extenders. However, all such work showed very serious problems[96]. One study used linseed oil due to its extremely high linolenic (18:3) acid content (>50%)[44]. Not surprisingly, extremely severe injector fouling and ring sticking occurred in less than 10 hours during the engine testing. Data indicated that the linseed oil viscosity was not the cause of the problem. However, a similar engine test was performed using methyl esters of the linseed oil. Interestingly, this fuel gave much improved performance. The authors concluded that fatty oil methyl esters may show promise as an alternative diesel fuel. Another paper cited similar studies where serious injector fouling and crankcase oil thickening problems had occurred when vegetable oils were used as diesel fuels[45].

6.2 Pump Tests

A 1997 study reported a series of six diesel fuel pump tests using two B20 fuels[81]. One B20 was made from a soy-based methyl ester that complied with the U.S. B100 specification. The other B20 was made from a B100 that was described as "high acid" due to its TAN value being above the maximum allowed specification value. Both B20 fuels used an on-specification No. 2 diesel fuel. No problems were observed during the pump tests that used the "on-spec" B20. However, when the high acid B20 was tested, increased pressure drops across filters were observed, indicating increased filter deposits. Also, increased deposits/varnish on pump parts after disassembly were observed. No elastomer-related problems were observed. The authors concluded that the high TAN of the off-specification B20 was the cause of the problems. However, the only TAN of the high acid fuel that was explicitly reported was only 0.85 mg KOH/g, while the specification maximum allowed value was 0.80 mg KOH/g. The on-specification B100 had a TAN of 0.72/mg KOH/g. Although the authors claimed that the high acid fuel was "drastically off-specification", clearly the 0.05 mgKOH/g was not a drastic violation of the specification. If such a small amount above the specification limit can by itself cause significant equipment problems, then the specification limit is much too high. Furthermore, both B100 fuels were "high acid" if compared to the European biodiesel specification[108], so the distinction of the two-biodiesel fuels from a 0.05 mg KOH/g difference is even less significant. The authors entirely failed to note that the high acid B100 had a total glycerin level that was nearly six times the value of the on-specification B100 (0.180% vs. 0.029%). The glycerin and partial glycerol species that contribute to total glycerin levels are well known to cause severe engine deposits[121, 126]. Although the total glycerin values of both fuels were within the 0.240% maximum allowed specification limit, the much greater difference of that compositional parameter is a more plausible explanation than the small difference in TAN values, based on the data that was explicitly provided, notated, and discussed within the actual text of the paper.

6.3 Fuel Injector Tests

One study ran a short –term engine test to measure injector-coking tendency on eight biodiesel fuels[129]. The fuels were methyl and ethyl esters of soy, canola, rapeseed, and tallow fatty oils. A low sulfur No. 2 diesel fuel was also run for comparison. Results showed that the eight biodiesel fuels has injector coking indices ranging from 2.1 to 3.1, whereas the No. 2 diesel fuel has a value of 1. The methyl and ethyl esters of rapeseed oil gave the highest injector coking index values. It was not clear from the report whether such injector coking index values represent any real problem.

The BIOSTAB project concluded with some diesel fuel injector tests and a very limited vehicle fleet test[108]. Three rapeseed methyl esters were used for these tests: a low stability fuel, a standard stability fuel, and a high stability fuel. OSI IP was used to evaluate fuel stability. The low stability fuel had OSI IP values below 4 hours. Standard stability fuels had OSI IP of between 5 and 7 hours. High stability fuels had OSI IP values of more than 16 hours. The high stability fuel was obtained by adding 250 ppm pyrogallol to the standard stability fuel. The low stability fuel was obtained by stressing with air and elevated temperature (exact conditions not reported). No problems were observed in any of the tests using the high or standard stability fuels. With the low stability fuels the injector tests had some failures and some increased "fat similar deposits" compared to injector tests involving the higher stability fuels. In some passenger car common rail injector tests no difference was observed between low and high stability fuels except for some increased abrasion at the injector nozzle seats in the low stability fuel test runs.

6.4 Vehicle Fleet Tests and Engine Tests

A single heavy-duty truck was evaluated on a 202,160-mile on-road test using a blend of 20% hydrogenated soy ethyl ester and 80% low sulfur No. 2 diesel fuel[128]. The purpose of the test was to determine the effect of the biodiesel blend on emissions, power output, and fuel economy of the truck engine. However, engine inspection and analysis after the test showed no significant wear in the valve train, piston, and ring areas.

The BIOSTAB fleet test consisted of only four vehicles[108]. The only unusual observations were some increased deposits on the distributor pump and corrosion in some parts of the fuel injector when the low stability fuel was used. However, the authors could not make any conclusions due to the extremely small number of vehicles involved.

Two 1,000 hour durability tests were reported during 1995[130, 131]. Both studies used a 20% soy methyl ester blend in low sulfur No. 2 diesel fuel. The first study used a Detroit Diesel 6V-92TA DDEC II engine[130]. The performance of all fuel injectors deteriorated significantly during the test. By the end of the 1,000-hour test there was almost no atomization of the fuel. Serious ring damage was also noted. The researchers noted that the viscosity, heat output, specific gravity, and vapor pressure of the 20% biodiesel fuel blend was similar to that of a typical low sulfur No. 2 diesel fuel. From this fact the authors of the paper concluded that the B20 fuel was not a likely cause of the engine problems. No mention was made concerning the actual chemistry and stability of the fuel and its potential impact on engine performance.

The other 1,000-hour durability test was performed using a Cummins N14 diesel engine and a 20% soy methyl ester blend in low sulfur No. 2 diesel fuel[131]. The test experienced an early pump failure, and at 650 hours the test was terminated due to fuel pump deposits and filter plugging. Analysis of the deposits showed the presence of fatty acid esters and carboxylic acids as well as carboxylic acid salts.

Finally, a series of Cummins L-10 injector cleanliness tests were run on a series of three B20's made from a B100 and three diesel fuels (Cat 1K reference fuel, No. 1 diesel fuel, No. 2 diesel fuel)[89]. Test runs were also performed on the B100 and the three neat petroleum fuels. Test results showed that while the average flow loss was never a problem on any fuel, the visual deposit rating of the injectors showed that each B20 fuel was significantly worse than either the B100 or the petroleum fuel from which it was blended. Although the Cummins L-10 test was never fully understood, and its relevance to today's diesel engine technology is questionable, these results are very interesting. The trend in the visual injector deposit ratings exactly corresponds to the total insolubles trends observed by several previous studies of blends of biodiesel and petroleum fuels[83, 115].

7.0 CONCLUSIONS

The information from the open literature that has been reviewed in the previous sections of this report support the following conclusions:

1. The level of technical understanding of the stability chemistry of biodiesel fuel has reached a reasonable level of maturity. The one major gap that exists is the apparent lack of correlation between insolubles formation tendency and typical oxidation parameters such as PV, TAN, AV, and polymer content.

2. The number and types of test methods already known and documented are sufficient to either adequately characterize the stability properties of biodiesel, or can be made sufficiently adequate without significant additional development.

3. Other than the major gap discussed above in item 1, additional research to further define the interrelationships between the important stability properties will not answer the questions concerning biodiesel's overall impact on diesel engine equipment.

4. The lack of any significant body of adequately controlled engine equipment test results makes it impossible to tie the existing understanding of biodiesel chemistry to the real world. If such adequate controlled engine equipment test results did become available, the needed ties between it and the chemistry aspects could probably be made without further chemistry research except in the area pertaining to the relationship between insolubles formation and other stability-related parameters.

5. In the absence of actual (and extremely costly) diesel engine equipment testing, specialized test rig programs designed to reasonably simulate engine equipment dynamics may provide valuable information to assist in defining the potential real world problems associated with using biodiesel and the solutions to those problems.

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Appendix A. Tables from the Internet

Fat content and fatty acid composition of seed oils(1)

Note that content and composition can vary widely with variety and growing conditions. Where sources vary, average values are given.

Seed	Fatty acids (% total oil)						Notes
	18:3w3 linolenic	18:2w6 linoleic	of which GLA	18:1w9 oleic	18:0'	16:0'	
Almond		17		78	5		
avocado (seed?)		10		70	20		
avocado (flesh)							
Beech		32		54	8		
Brazil		24		48	24		
calendula (marigold)							
Cashew		6		70	18		
Chia	30	40					
coconut		3		6		91	
corn		59		24	17		
cottonseed		50		21	25		toxin risk
evening primrose		81	9	11	2	6	
fig							oil not available
filbert		16		54	5		
flax (linseed)	58	14		19	4	5	
grape		71		17	12		
hemp	20	60	23	12	2	6	drug traces
hickory		17		68	9		
kukui (candlenut)	29	40					
macadamia		10		71	12		
neem	1	20		41	20		bitter
olive		8		76	16		
palm kernel		2		13		85	
peanut (groundnut)		29		47	18		fungus risk
pecan		20		63	7		
perilla	55						
pistachio		19		65	9		
pumpkin	8	50		34	'0	9	
rape (canola)	7	30		54	7		10% erucic acid
rice bran	1	35		48	17		
safflower	3	75		13	12		
sesame		45		42	13		
soybean	7	50		26	6	9	
starflower (borage)			22				
sunflower		65		23	12		
walnut	6	51		28	5	11	
wheatgerm	5	50		25	18		

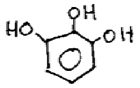
(1) Taken from http://www.queenhill.demon.co.uk/seedoils/oilcomp.htm

Fatty Acid Composition of Various Oils(1)

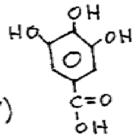
Oil	Saturated fat %	Mono-unsat. fatty acid % (MUFA)	Poly-unsat. fatty acid % (PUFA)	linolenic fatty acid %	linoleic fatty acid %	EPA (timnodonic) 20:5n-3 %	DHA 22:6n-3 %
Almond	8.2%	69.9%	17.4%	0.0%	17.4%		
Brazilnut	24.4%	34.8%	36.4%	0.0%	36.0%		
Canola	7.1%	58.9%	29.6%	9.3%	20.3%		
Cashew	19.8%	58.9%	16.9%	0.0%	16.5%		
Cocoa Butter	59.7%	32.9%	3.0%	0.1%	2.8%		
Coconut	86.5%	5.8%	1.8%	0.0%	1.8%		
Corn	12.7%	24.2%	58.7%	0.7%	58.0%		
Flaxseed	4%	22%	74%	57%	17%		
Hazelnut	7.4%	78.0%	10.2%	0.0%	10.1%		
Macadamia	15.0%	78.9%	1.7%	0.0%	1.7%		
Olive	13.5%	73.7%	8.4%	0.6%	7.9%		
Palm	49.3%	37.0%	9.3%	0.2%	9.1%		
Palm kernel	81.5%	11.4%	1.6%	0.0%	1.6%		
Peanut	16.9%	46.2%	32.0%	0.0%	32.0%		
Pecan	8.0%	62.3%	24.8%	1.0%	23.6%		
Safflower	9.6%	12.6%	73.4%	0.2%	73.0%		
Sesame	14.2%	39.7%	41.7%	0.3%	41.3%		
Soybean	14.4%	23.3%	57.9%	6.8%	51.0%		
Walnut	9.1%	22.8%	63.3%	10.4%	52.9%		
Wheat germ	18.8%	16.6%	61.7%	6.9%	54.8%		
Salmon	19.9%	29.0%	40.3%	1.1%	1.5%	13.0%	18.2%

(1) Taken from http://animalscience.tamu.edu/nutr/202s/LectureOutlines/oils.html

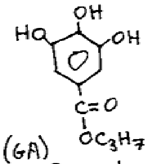
Appendix B. Structure of Antioxidants



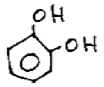
Pyrogallol (PY)



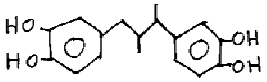
gallic acid (GA)



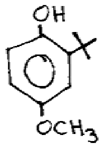
propyl gallate (PG)



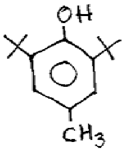
catechol (c)



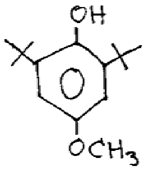
nordihydroguaiaretic acid
(NDGA)



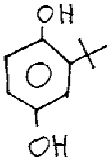
2-t-butyl-4-methoxyphenol
(BHA)



2,6-di-t-butyl-4-methylphenol
(BHT)



2,6-di-t-butyl-4-methoxyphenol
(di-BHA)



t-butyl hydroquinone

From: Richardson, Charles (C.E.)
Sent: Monday, March 21, 2005 9:40 AM
To: Fulton, Brien (B.L.); Soper, Todd (R.); Smetana, Stephen (S.)
Cc: Tiernan, Hunter (H.G.); Wright, Robin (R.A.); Misangyi, Pete (P.W.); Baker, Dick (Richard E.); Harrison, Mike (M.J.); Koszewnik, John (J.J.)
Subject: CRC Diesel Fuel Study

Attachments: Light Duty Diesel - Low Temperature Operability Test Proposal - r11092004.doc

Please review the attached program that will be conducted by CRC (Coordinating Research Council) and let us know if a particular 6.0L diesel vehicle should be recommended for this program. Your response by **Friday April 1** would be appreciated.

CRC will conduct a diesel fuel study to evaluate fuel effects on low temperature operability of light-duty diesel (LDD) vehicles. CRC is a joint auto/oil consortium that conducts vehicle programs to determine the effects of fuel properties on vehicle performance. The objective of this program is to evaluate existing low temperature operability prediction test methods, CFPP (Cold Filter Plugging Point) and LTFT (Low Temperature Flow Test), and determine their applicability to LDD engines using data developed from the LDD vehicle tests. The scope of the project will be extended in order to develop new test methods or modify existing test methods if currently employed methods fail to adequately correlate with the vehicle test data. The deliverable will be a practical laboratory test method that adequately predicts low temperature operability limits for light-duty diesel vehicles.

The CFPP method has been used for low temperature operability in Europe for many years. The LTFT method is the test method of choice in the U.S. With the introduction of more European-like LDD vehicles in the U.S., the program will be timely and very useful to determine if the CFPP method can be used. An existing CEC testing protocol, CEC M-11-T-91, will be used as a guideline. The CRC diesel group is also looking for recommendations from OEMs on testing protocol to be used to conduct the low temperature operability program. The test program will be conducted in an all-weather chassis dynamometer, most likely, the Imperial Oil facility in Sarnia. The test program will include three ultra-low sulfur fuels provided by BP (No. 1 and No. 2 fuel) and ChevronTexaco (No. 2 fuel), two additives, and six vehicles.

Funding for CRC programs come from a pooled fund budgeted by the Alliance (auto co.) and API (oil co.) with engineers and tech support donated from each of the auto and oil company members. Incremental costs to participate include an engineer's time and travel costs, and possibly the loan of a vehicle if not available from a rental fleet.

If you require further information regarding this program, please let us know.

Light Duty Diesel -
Low Temper...

Regards
Chuck Richardson
Ford Motor Company

Fuels and Lubricant Engineering
313.322.7136
Fax: 313.845.3169
cricha12@ford.com

Proposal for the

EVALUATION of LOW TEMPERATURE OPERABILITY PREDICTION TESTS for LIGHT DUTY DIESEL VEHICLES for NORTH AMERICA.

Project: CRC Project No. DP-2-04

CRC Diesel Performance Group May 2004
Submitted by the Low Temperature Operability Subgroup

This document contains the LTO group proposal followed by the initial comments and responses on the proposal.

LTO Group members
Chandler, John - Infineum
Daniels, David – Octel-Starreon (Leader)
Davidson, Rob – Afton Chemical Corp.
Martin, Harold – Cummins/Fleetguard
Mitchell, Ken – Shell Canada
Nikanjam, Manuch – Chevron Products Co.
Pistillo, W. Rocco – Lubrizol
Wong, Chung-Lai - ExxonMobil

CRC Diesel Performance Group

Title: EVALUATION of LOW TEMPERATURE OPERABILITY PREDICTION TESTS for LIGHT DUTY DIESEL VEHICLES for NORTH AMERICA.

Project: CRC Project No. DP-2-04

Rational for the project:

Low temperature operability has always been an issue with middle distillate fuels because they contain straight and branched chain hydrocarbons (paraffin waxes). These waxes precipitate as crystals at ambient wintertime temperatures in colder geographic areas. When this happens, the wax may plug the fuel filter, reduce pumpability or it may completely gel the fuel, making it impossible for the fuel system to deliver sufficient fuel to the engine. The end result can be stumbling or in severe cases of wax formation, the vehicle may not start.

Previous work conducted by the CRC and by others has shown that both vehicle fuel system design and fuel properties are important in determining the susceptibility of a particular diesel vehicle operating on a particular fuel to filter plugging and other low-temperature operational problems. Some of these investigations have also shown substantial benefits in low-temperature operation when middle distillate flow improvers are included in the fuel.

The successful introduction of an extensive passenger fleet of light duty diesel (LDD) vehicles in North America will require consumer satisfaction. This satisfaction will be impeded if extensive winter operability problems plague the end user. The first step in precluding this problem is to have a practical bench test that adequately predicts the low temperature operability of diesel fuel relative to light duty diesels in North America. As yet, however, no laboratory test has been identified which adequately predicts the behavior of North American fuels both with and without flow improvers in a wide range of LDD fuel system designs.

The purpose of this project is to obtain data on the low-temperature performance of a wide variety of light duty diesel fuel systems operating on a representative sampling of on road diesel fuels under real-world temperature conditions. It is intended that these data be used to evaluate laboratory techniques that may characterize the low-temperature performance of diesel fuels in light-duty equipment more realistically than existing test methods.

Objective:

Evaluate existing low temperature operability prediction test methods and determine their applicability to LDD engines using data developed from LDD vehicle tests.

The scope of the project` will be extended in order to develop new test methods or modify existing test methods if currently employed methods fail to adequately correlate with the vehicle test data.

Deliverable:

A practical laboratory test method that adequately predicts low temperature operability limits for light duty diesel vehicles

Test Program Outline

Options:

The test program can have a variety of options. Several example recommendations are listed towards the end of the document.

Protocol Options:

Method

- Recommend using a modified version of the existing CEC testing protocol, CEC M-11-T-91, as a guide (Cold weather performance test procedure for diesel vehicles)
- Test program to be run in an All Weather Chassis Dynamometer
  - Permits better control of test environment
  - Doesn't rely on 'Mother Nature' to provide the desired temperatures
  - Allows year-round testing
  - Broader range of test temperatures can be accomplished (-10°C to -40°C)
- The test program can consist of a varying number of vehicles and fuels.

Vehicles:

- The work group recommends a minimum of four LDD vehicles, if available. Additional vehicles are preferred if there is an adequate difference in fuel system design.
- Vehicles tested on the same day must have similar wheel base to avoid having to move the dynamometer rollers.
- Vehicles will be selected from domestic manufacturers and import vehicles that are presently available or are proposed for introduction into the North American market in the near future, if they can be made available.

Fuels:

- One to six base test fuels
- Recommended Minimum: three well defined No. 2 low sulfur diesel fuels meeting appropriate specifications.
  - An ultra low sulfur diesel fuel is recommended if a truly representative fuel can becomes available.
  - Fuels will be acquired during winter production periods to ensure representative winter quality.
  - The fuels* will represent an unadditized cloud point range of -10°C to -35°C for testing in the -10°C to -40°C range.
- Complete analysis of each test fuel plus retain vehicle tank samples and drum quantities of each blend for future test development if needed.
- Base fuels treated with Cold Flow Additives at 1 or 2 treat levels.

- Recommended Minimum of two different dose levels of cold flow improving additives *(or 2 additives at 1(same or different) dose level)*.

Protocol Options

- The test program can consist of a varying number of vehicles and fuels. The work group recommends a minimum of four vehicles, three well defined fuels and two different dose levels of cold flow improving additives *[or 2 additives at 1(same or different) dose level]*. A wider range of vehicles, additional fuels and additive dose levels would allow for a greater database and increased confidence level. The test program as outlined is based on the above minimum requirements of three fuels, two additive dose levels per fuel and six vehicles.
- Fuels will be analyzed <u>prior</u> to acceptance and vehicle testing, using existing test methods to ensure they are suitable for the test program. The analysis will consist of base physical properties and additive response curves.
- Test Facility: An all weather chassis dynamometer facility.
    - Location: To be determined.
    - Personnel: Driver, mechanics, dynamometer operators, fuel blender (6 to 7 people)
- Timing: Fuel collection should occur between 12/01/04 and 2/01/05. Testing can occur at any time, but it is recommended that analysis occur as soon as possible after fuel collection and re-analyzed just before or during the vehicle testing.

Program Cost Estimate

- Estimated Program Costs. Test costs will depend on the extent of the trial. Estimated Costs range from $ 86,000 to $ 250,000 based on the two example options presented.
- Funds requested $ 250,000.
- Case 1 – Single Fuel with Two Additive Levels/Six Vehicle Program

Dynamometer Facility - 9 days	$ 56,000
Labor, Parts, Lubes, Filters Driver	$ 10,000
One Fuel, & Additives	$ 5,500
Six LDD Vehicle Rentals (1 month)	$ 15,000
Miscellaneous, drumming, shipping samples,	<u>$ 5,000</u>
Estimated Total	$ 91,500

- Case 2 – Three Fuel with Two Additive Levels/Six Vehicle Program

Dynamometer Facility - 27 days	$ 170,000
Labor, Parts, Lubes, Filters Driver	$ 25,000
Three Fuels, & Additives	$ 15,000
Six LDD Vehicle Rentals (2 month)	$ 30,000
Miscellaneous, drumming, shipping samples,	<u>$ 6,000</u>
Estimated Total	$ 246,000

Other Options

- For additional Fuels and days of operation assume approximately 9 days of testing.
    - Add ~**$80,000.00** per Fuel. (Includes two additive treated fuels and one without additive)

    - For an additional additive or treat rate add ~**$27,000.00**. (Three days testing.)
- Donation of fuels and vehicles by participants would reduce the Estimated Total Cost for Case 1 to ~**$72,300.00** and Case 2 to ~**$203,000.00**. Additional savings can be had if we are able to determine low temperature limits in fewer tests thereby reducing the number of days charged.

Summary

The CRC Diesel Performance Group has determined that Low Temperature Operability was the second most critical physical property for satisfactory introduction and operations of LDD in North America. Time constraints require a budget decision if the program is to commence in the 2004-2005 winter season. The available budget will determine feasibility and extent of the study. A final proposal based on approved funding levels will determine the optimum matrix of fuels and vehicles.

Other notes

Fuel analysis and cold flow improving additive response curves will incorporate the following standardized test methods prior to acceptance for the test program.

- Fuel analysis and cold flow improving additive response curves will incorporate the following standardized test methods prior to acceptance for the test program.
    - Cloud Point** – D2500, or D5773 / D5772 / D5771
    - Pour Point** – D97 or D5949
    - CFPP – D6371
    - SFPP – IP 496
    - LTFT – D4539
    - Distillation – D86
    - Density – D1298 or D287
    - Flash Point – D56 or D93
    - Viscosity @ 40^{o}C - D445
    - Viscosity @ -20^{o}C - D445
    - Sulfur ppm wt. – D2622
    - Sediment and Water - D2709
    - Water, ppm wt. - D1744
    - Ramsbottom carbon residue on 10 %distillation residue, – D524
    - Ash % wt. – D482
    - Copper Strip Corrosion - D130
    - Cetane Number - D613

Cetane number has an impact on cold start ups. Careful selection of fuels with adequate cetane number will have to made when selecting fuels for the project.

*Fuels will be obtained and blended to meet criteria, if needed, from commercially supplied fuels.

** Each method is slightly different but should yield acceptable results. It is suggested that multiple methods be used for these two tests only.

Comments on the initial ballot and LTO group response

The following comments were received and the LTO group responses are attached

LTO Group members
Chandler, John - Infineum
Daniels, David – Octel-Starreon (Leader)
Davidson, Rob – Afton Chemical Corp.
Martin, Harold – Cummins/Fleetguard
Mitchell, Ken – Shell Canada
Nikanjam, Manuch – Chevron Products Co.
Pistillo, W. Rocco – Lubrizol
Wong, Chung-Lai - ExxonMobil

Ballot comments

Comment l. Jim Simnick, BP
BP supports the multi-fuel program over the single-fuel option. BP recommends that multiple laboratories perform the fuel inspections. CRC member labs should be encouraged to perform these tests gratis. Depending upon the detailed specification targets for the test fuels, BP may supply one or more of the needed fuels if needed.

<u>Response summary;</u> Five laboratories to date have offered to perform most or all of the suggested laboratory analysis as outlined in the proposal at no cost. Alphabetically they are ExxonMobil, Infineum, Lubrizol, Octel-Starreon, and Shell Canada.

Comment 2. Tom Livingston, BOSCH
I would recommend Biodiesel be included as a test fuel. Perhaps a B20 and/or B5 blend level should be considered.

<u>Response summary;</u> The group feels that the limited resources can accomplish the basic goal of the proposal if performed as it stands now. The addition of alternative fuels would potentially dilute the ability to accomplish the primary task.
The project could expand beyond the three petroleum fuels with additional funding. We suggest that any additional effort be supported by an appropriate biodiesel organization or OEM if they so choose and only if it does not dilute the efforts or alter the goal of the original proposal. The additional all weather chassis dynamometer testing could be “piggy backed” and the bench correlations follow <u>only</u> after our primary goal is accomplished.
➲An initial inquiry has been sent to NBB & USDA by Daniels. They have responded indicating an interest but no additional word as of 11/09/04.

Comment 3. Ralph Cherrillo, Shell
The proposal appears sound. Am sure that there will be some tweaking when the RFP gets developed, and interested laboratories work toward a delivery plan.

<u>Response summary;</u> The initial draft method has had a brief review and comment. “Tweaking” the method to be appropriate to the goals will be a natural evolution.

4. Cherie Rainforth, CARB
I am abstaining on this because I don't feel that I know enough about low temperature operability to vote on it. Maybe I am just unclear on the concept, but I felt that it would have been useful to include some discussion of the candidate laboratory techniques that will be evaluated.

Response summary;
The concern listed above will be addressed by individual discuss with Cherie. The actual methodology development is addressed above in section 3. A presentation on cold flow issues, additives function and test procedures can be developed for the CRC if they so desire.
➲A call has been placed to Cherie Rainforth by Daniels. Awaiting a return call.
➲Daniels had a brief discussion with Cherie Rainforth. Cherie appears satisfied with the general goals of the program at this time.

5. Ken Rose and Lai Wong, ExxonMobil Research and Engineering
We think we should include running the LTFT tests at different cooling rates.

Response summary;
The group consensus is that the project focus is to determine if current test methods adequately predict low temperature operability for light duty diesel applications in North America. The participants would then develop new test methods to more accurately predict failures as noted in paragraph two of the “Objective”.

Running modified LTFTs would fit into the second part of the program. It should be noted that the group also feels that participating laboratories should not be dramatically impaired on running additional testing, such as the suggestion above, as long as the efforts are coordinated through out all of the participating laboratories. A large quantity of fuel will need to be held for vehicle testing, bench testing and anticipated development work.

6. Rock Pistillo, Lubrizol
I missed the ballot deadline but agree with the contents of the program. The only question is about the additive. I understand that this is meant to correlate bench test prediction to actual vehicle operability and not an additive assessment program. However, would it be useful to include a top performing flow improver along with a mediocre one to see if the correlation holds for different performance polymers? Not everyone will be using the best, state-of-the-art EVA in the field.

Response summary;
This idea will be discussed as the test method is developed. See item 3.

1) Identify diesel products (last 3 yrs)

The following is an overview…however, there could be some complications since vehicle model year and engine model year may not align. Fyi…vehicle model years typically occur summer of the previous year being quoted while engine model year typically aligns with calendar year of that engine build.

7.3L Navistar

last sold as a 2003MY vehicle (F- & E- Series)

6.0L Navistar

2004-2005MY Excursion
2003-2007MY F-Series Super Duty (for example: F250-550)
2004-2010MY E-Series (for example: E350-450)

6.4L Navistar

2007-2010MY F-Series Super Duty

6.7L Ford Motor Company

2011MY F-Series Super Duty (F250-550)

6.7L Cummins & other engines are supplied by other Engine Manufacturers for Heavy Duty vehicles

For example: 2011MY F-Series (F650-750)

2) Identify diesel technologies used (and short review of changes over last 5-10 years)

Broad range of CR systems, both HP and intensifier designs.

Cat HEUI – A: Used on 7.3L Powerstroke application
Navistar / Sturman G2: Used on 6.0L Powerstroke application
Continental (Siemens): Application on P356 Powerstroke
Bosch (Piezo): 6.7L Scorpion fuel system

7.3L HEUIA – Hydraulic Electronic Unit Injection; return fuel from injectors
The injection system is driven by high pressure oil where the injection pressure is made internal to the injector.
6.0L G2 – Hydraulic Electronic Unit Injection; return fuel from injectors;
The injection system is driven by high pressure oil where the injection pressure is made internal to the injector.
6.4L Siemens 2.3+; (Piezo CR w/Return) injector fuel return diverted back to FIE system (recirculation)
6.7L Bosch CR 4.2; (Piezo CR w/Return)
2007 D-max Bosch CR 3.NH (ITP); older Bosch pump
2007 Cummins Bosch
2010 GM Duramax uses same pump as 6.7L Ford

A high-pressure CR fuel system uses a high-pressure pump, high-pressure rail and fuel injectors. The pump and the rail maintain fuel pressure of the system independent of the fuel injection quantity and the fuel injector to the cylinders delivers timing, fuel injection quantity and timing. This system allows each aspect of fuel delivery (quantity, timing and pressure) to be independently controlled. There are two major types of CR systems that are used today, piezo stack injectors and solenoid type injectors. Solenoids and piezo are used to actuate the injector to control fuel quantity and timing.
HPCR systems are also capable of multiple shots (6 or more) in single engine cycles (e.g., early pilot, close-coupled pilot, main, split main, close-coupled post and late post). This ability to have multiple shots with accurate fuel quantity and timing makes high-pressure CR fuel systems a required enabler to meet all vehicle attributes including performance, fuel economy, emissions and NVH requirements.

a. Operating systems/pressures

1980-1994MY Indirect Injection Diesel used low pressure maximum of 3,000psi
Prior to 2008MY used maximum of 26,000psi
2010MY+ uses 30,000 psi

Fuel pressure sensor detects when fuel pressure is low; High Pressure Fuel Rail can illuminate an indicator light on IP (Instrument Panel) to protect FIE equipment. Second pressure switch on the low pressure side detects low pressure and derates the engine to protect the FIE.

i. Vehicles using common rail

Pressure is maintained in the rail by the high pressure fuel pump which results in not having to generate during the fuel-injection cycle.

b. Suppliers

There are a large number of suppliers of this equipment here are three main: (Siemens (Continental), Bosch, Delphi), each offering unique features; but seemingly headed in the same direction: common rail piezo based system. *"Solenoids are still being used."*

i. High-pressure fuel pumps

The high-pressure pump is the pressure generation aspect of the fuel system and the actual link between the low-pressure fuel system and the high-pressure fuel system. The pump requirement is to provide sufficient fuel under pressure for all engine-operating modes for the life of the vehicle. By using this type of pump, pressure is maintained in the rail and does not have to be generated during the fuel-injection cycle.

Hydraulic Electronic Unit Injector, fuel pressure is generated internally to the injector. (up to the end of 6.0L Engines E-Series 2010MY).

Pump design is dictated fuel delivery rate and pressure required to achieve engine attributes, mounting requirements and pump drive requirements.

High-pressure pumps are driven a number of ways on an engine including, but not limited to, direct drive (e.g., from the camshaft), coupling gear, chain, and toothed belt, all of which make pump speed directly proportional to engine speed.

This means that power required to drive the pump is proportional to the fuel rail pressure and pump speed. To help improve pump efficiency, high-pressure pumps have the capability to disable one or more pumping elements to reduce total fuel delivery thereby limiting excess fuel delivered to the rail.

c. Sensitivity to fuel lubricity

Diesel fuel systems using high pressure pumps can "scar" due to the loss of clearances supported by fluid hydrodynamics provided by the lubricity of diesel fuel. Clearances (3-6 microns) are far smaller than the diameter of a human hair (~60 microns), gasoline in diesel fuel can allow metal to come into contact with metal leading to debris "little pieces of metal" and then catastrophic failure of the high pressure pump.

U.S. ASTM standard is 520 microns maximum (lower is better) as measured by HFRR (High Frequency Reciprocating Rig). The request made previously was for a maximum of 400 microns HFRR via WWFC.

Biodiesel >= High Sulfur Diesel >> Ultra-Low Sulfur Diesel >>>> Gasoline

Biodiesel has very good lubricity (2% biodiesel can produce <400 micron HFRR) while gasoline can't get a measured result on HFRR "very poor no lubricity"

Market fuel surveys (SGS) are suggesting that U.S. diesel fuel quality is not so high quality and especially from the perspective of lubricity, there are samples that are >520 micron HFRR limit (as high as 662 microns) we need to have a 460 microns HFRR maximum and it to be enforceable.

It is possible that if a vehicle would consistently operate with a fuel containing let's say 600 micron lubricity, there is a high confidence that the high pressure pump would experience excessive wear enough to cause fuel pump seizure and possibly contamination throughout the FIE system.

To accommodate the poor lubricity found in the U.S. Ford had incorporated an enhanced high pressure pump package.

In a development program, there is some indication that operating with a poor lubricity fuel (such as 600 microns HFRR) could result in fuel pump functional concerns when using a fuel pump designed for a good lubricity market.

3) Discuss experience with fuel quality concerns (and details – vehicles/region/equipment/mode/etc)

a. Gasoline contamination

Ford has released a SSM(Special Service Message) #21820 in 1Q2011…this has led into a Diesel Fuel System Contamination Diagnosis and Service Procedure Job Aid.

The evolutionary steps involved in engine reaction to gasoline exposure include:

- Crank No Start
- Long Crank/Hard Start
- Runs Rough
- Low Power
- Engine Knocking
- Exhaust Smoke
- Fuel Rail Pressure (FRP) slow to build

If gasoline is used instead of diesel, the engine will run EXTREMELY rough. If the customer continues to drive in the presence of all of these evolutionary steps then the engine may eventually stall.

b. Ultra-low sulfur diesel

If ULSD does not contain the proper additives, it will have poor lubricity.

c. Bio-diesel

Good quality biodiesel is comparable to diesel fuel; however, biodiesel has the ability to decompose. When biodiesel decomposes it can lead to the formation of insolubles (particulates) that can plug filters.

Higher fuel freezing temperature (higher cloud point, pour point, filter plug point)…in cold regions, there is a possibility that high biodiesel concentration can lead to fuel filter plugging.

Water Content

Biodiesel has the ability to contain more water than petroleum diesel
Biodiesel is hygroscopic which then affects the ability of water-fuel separator to separate the water.
Water in biodiesel can accelerate fuel degradation (also microbial growth can increase).

d. Other

Particles

Particle filter is included in the fuel system to remove particles. Recall tolerances are very tight.

4) Field experience

a. High pressure fuel pump durability/wear related failures

Driveability symptoms…

5) Discussion of test methods for component/pump durability

a. How durability testing is done

Much individual component bench testing is done through suppliers. There is a structured testing approach where suppliers do component bench testing on worst case lubricity fuel as measured by HFRR…then Ford runs worst case lubricity for engine dynamometer and vehicle durability testing.

b. Reference fuels used

In-house test fuel include worst case lubricity. Some durability testing includes biodiesel and other characteristics to evaluate different portions of the engine/FIE systems.

c. Publicly available studies (pump durability, effects of fuel quality issues – lubricity, gas contamination, other?)

Investigation required…check SAE/CRC etc...
Studies on ULSD…

d. Any open/ongoing work by ASTM or others related to pump durability vs fuel lubricity

SAE J1681 - Including biodiesel from the aspect of materials compatibility but not related to pump durability. Nothing specific, there was some work done via CRC Performance committee, but results were not so clear – unsure if final report has been released.

DieselNet Technology Guide

What is Diesel Fuel

Abstract: Diesel fuel is a mixture of hydrocarbons obtained by distillation of crude oil. The important properties which are used to characterize diesel fuel include cetane number (or cetane index), fuel volatility, density, viscosity, cold behavior, and sulfur content. Fuel properties are often improved through the use of additives. Diesel fuel specifications differ for various fuel grades and in different countries.

Crude Oil Refining

The beginnings of the petrochemical industry date back to 1859, when crude oil was discovered in Pennsylvania. The first product refined from crude was kerosene, which was used as lamp oil [Chevron 1998]. Since only a fraction of the crude could be refined into kerosene, the early refiners were left with quantities of petroleum by-products. These petroleum by-products attracted the attention of Rudolf Diesel, the inventor of compression ignition reciprocating engine. Diesel—whose first engine concept was designed to use coal dust as the fuel—recognized that liquid petroleum products might be better fuels than coal. The engine was re-designed for operation with liquid fuels, resulting in a successful prototype in 1895. Both the engine and the fuel still bear the name of Diesel.

Diesel fuel is a mixture of hydrocarbons—with boiling points in the range of 150 to 380°C—which are obtained from petroleum. Petroleum crude oils are composed of hydrocarbons of three major classes: (1) paraffinic, (2) naphthenic (or cycloparaffinic), and (3) aromatic hydrocarbons. Unsaturated hydrocarbons (olefins) rarely occur in the crude. The composition of the crude can vary from thin light-colored brownish or greenish crude oils of low density, to thick and black oils resembling melted tar. The thin, low density oils are called “high-gravity” crude oils, and the thick high density ones, “low-gravity” crude oils. This convention, rather confusing to those outside the petroleum industry, is explained by the use of “API gravity” which is a fuel property inversely proportional to its density, Equation (3).

In the refining process, the crude oil is converted into transportation fuels—gasoline, jet fuel, and diesel fuel—and other petroleum products, such as liquefied petroleum gas (LPG), heating fuel, lubricating oil, wax, and asphalt. High-gravity crude oils contain more of the lighter products needed for the production of transportation fuels, and generally have lower sulfur content. Modern refining processes can also convert low-gravity crude oils into lighter products, at an added expense of more complex processing equipment, more processing steps, and more energy.

Modern refining processes can be classified into three basic categories:

- *Separation:* The crude is separated into components based on some physical property. The most common separation process is distillation, where the components of the crude are separated into several streams based on their boiling temperature. Separation processes do not change the chemical structure of feedstock components.
- *Conversion:* These processes change the molecular structure of feedstock components. The most common conversion processes are catalytic cracking and hydrocracking, which—as suggested by the names—involve "cracking" of large molecules into smaller ones.
- *Upgrading:* Commonly used in *reformulated fuels* to remove compounds present in trace amounts that give the material some undesired qualities. The most commonly used upgrading process for diesel fuel is hydrotreating, which involves chemical reactions with hydrogen.

A schematic of modern refinery with diesel streams highlighted is shown in Figure 1 [Chevron 1998]. In the primary distillation column, operating under atmospheric pressure, the crude oil feedstock is separated into a number of streams of increasingly higher boiling point, which are called *straight-run* products (e.g., *straight-run diesel*). The material that is too heavy to vaporize in atmospheric distillation is removed from the bottom of the column (so called "atmospheric bottoms"). In most refineries, the atmospheric bottoms are further fractionated by a second distillation carried out under vacuum.

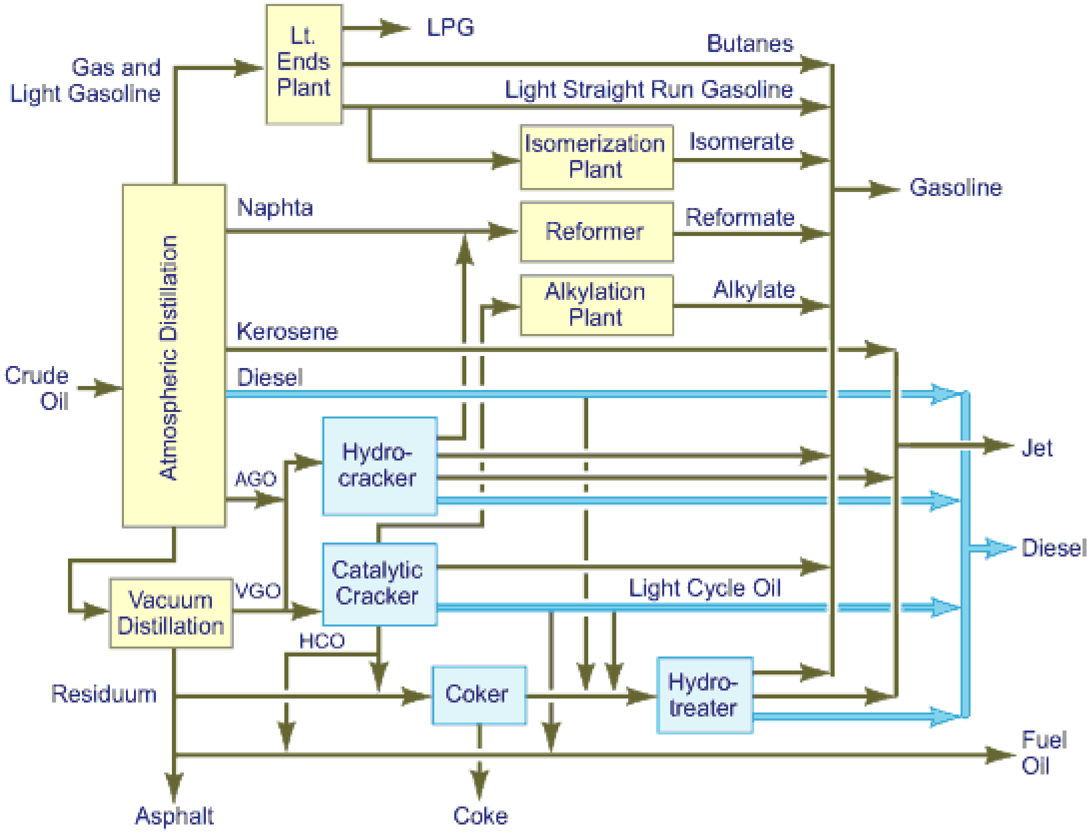


Figure 1. Diesel Streams in Modern Refinery

AGO - atmospheric gas oil; VGO - vacuum gas oil; HCO - heavy cycle oil

(Courtesy of Chevron)

The quantity and quality of the streams drawn off from distillation depends on the chemical composition of the crude oil. Crude oils also yield proportions of gasoline, diesel, residual fuel oil, and other products which are usually different from the product demand patterns in particular markets. The only way to balance the refinery production pattern with market demands is through downstream conversion processes. In these conversion processes large hydrocarbon molecules are broken into smaller ones by application of heat, pressure, or catalysts. Refineries use thermal cracking (visbreaking and coking), catalytic cracking, and hydrocracking (also utilizing catalyst, but carried out under a high pressure of hydrogen) to increase the yield of desired products by cracking unwanted heavy fractions. The final products are obtained by *blending* conversion products (crack components) with the primary distillation streams.

Both blended and straight-run products may require a varying degree of upgrading, to reduce the content of sulfur, nitrogen, and other compounds. A range of processes called *hydroprocessing* use hydrogen with an appropriate catalyst to upgrade refinery streams. Hydroprocessing can vary from mild condition *hydrofinishing* that removes reactive compounds like olefins and some sulfur and nitrogen compounds, to more severe condition *hydrotreating* that saturates aromatic rings and removes almost all sulfur and nitrogen compounds.

As apparent from Figure 1, diesel fuels used in road transportation are *distillate fuels*, i.e., they do not contain (uncracked) residuum fractions. Petroleum residuum materials are contained in heating oils, as well as in marine fuels (also known as bunker fuels). Those products usually have largely different properties from distillate diesel fuels.

Components of Diesel Fuel

Diesel fuel is a mixture of thousands of hydrocarbon compounds, most of which have carbon numbers between 10 and 22. A typical carbon number distribution in diesel fuel is shown in Figure 2 [Chevron 1998]. Most of the compounds in diesel fuel are hydrocarbons of the paraffinic, naphthenic, or aromatic class. Diesel fuel also contains small quantities of organic compounds of sulfur (e.g., dibenzothiophene), nitrogen (e.g., carbazole), and oxygen.

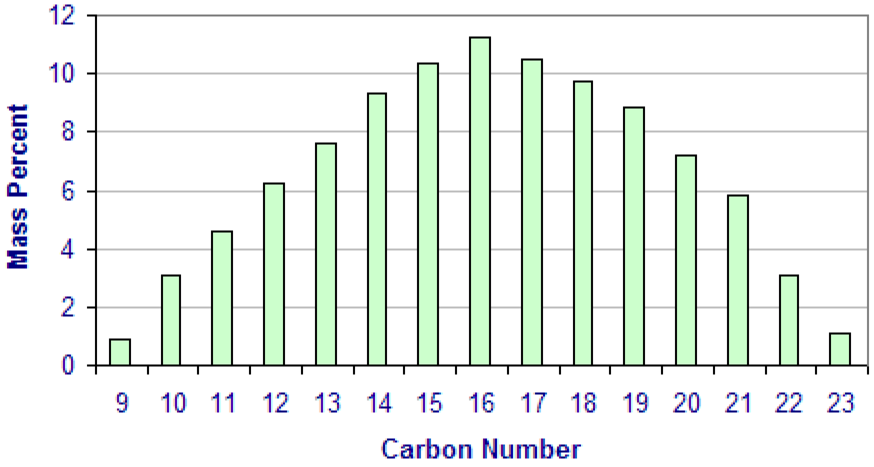


Figure 2. Typical Carbon Number Distribution

US No. 2 Diesel Fuel

The properties of a given diesel fuel depend on its exact formulation. An important factor which makes one fuel different from another is the relative proportion of paraffinic, naphthenic, and aromatic hydrocarbons. For instance, high content of paraffinic hydrocarbons yields good ignition quality of fuel, but it may pose problems in meeting low-temperature specifications, especially with high wax content crude oils. Lower wax content occurs in blend components from cracking processes, but oils from catalytic and thermal cracking have also lower ignition quality. The final blend has to be a careful choice of particular components to meet the fuel specifications.

Cetane number—a measure of the ignition quality of fuel—for selected hydrocarbon components of diesel fuel are listed in Table 1. The cetane number depends on the hydrocarbon class, as follows:

- Normal paraffins have high cetane numbers, which increase with carbon number.
- Cetane numbers of isoparaffins can range from about 10 to 80. Molecules with many short side chains have low cetane numbers, while compounds with one side chain of four or more carbons have high cetane numbers.
- Naphthenes tend to have cetane numbers from 40 to 70. Higher molecular weight molecules with one long side chain have high cetane numbers, while lower molecular weight compounds with short side chains have low cetane numbers.
- Aromatics have cetane numbers from 0 to 60. Molecules with a single aromatic ring with a long side chain are in the upper part of the range. Molecules with a single ring with several short side chains are in the lower part of the range. Molecules with two or three aromatic rings fused together have low cetane numbers of below 20.

Table 1
Cetane Number of Representative Diesel Fuel Hydrocarbons

Compound	Hydrocarbon Class	Formula	Cetane Number
n-Decane	n-Paraffin	$C_{10}H_{22}$	76
n-Pentadecane	n-Paraffin	$C_{15}H_{32}$	95
n-Hexadecane*	n-Paraffin	$C_{16}H_{34}$	100
n-Eicosane	n-Paraffin	$C_{20}H_{42}$	110
3-Ethyldecane	Isoparaffin	$C_{12}H_{26}$	48
4,5-Diethyloctane	Isoparaffin	$C_{12}H_{26}$	20
Heptamethylnonane*	Isoparaffin	$C_{16}H_{34}$	15
8-Propylpentadecane	Isoparaffin	$C_{18}H_{38}$	48
7,8-Diethyltetradecane	Isoparaffin	$C_{18}H_{38}$	67
9,10-Dimethyloctane	Isoparaffin	$C_{20}H_{42}$	59
Decalin	Naphthene	$C_{10}H_{18}$	48
3-Cyclohexylhexane	Naphthene	$C_{12}H_{24}$	36
2-Methyl-3-cyclohexylnonane	Naphthene	$C_{16}H_{32}$	70
2-Cyclohexyltetradecane	Naphthene	$C_{20}H_{40}$	57
1-Methylnaphthalene*	Aromatic	$C_{11}H_{10}$	0
n-Pentylbenzene	Aromatic	$C_{11}H_{16}$	8
Biphenyl	Aromatic	$C_{12}H_{10}$	21
1-Butylnaphthalene	Aromatic	$C_{14}H_{16}$	6

n-Nonylbenzene	Aromatic	$C_{15}H_{24}$	50
2-Octylnaphthalene	Aromatic	$C_{18}H_{24}$	18
n-Tetradecylbenzene	Aromatic	$C_{20}H_{34}$	72
* Primary reference material for cetane number scale			

Boiling and freezing temperatures of selected compounds of diesel fuel are listed in Table 2. For compounds of the same class, the boiling temperature increases with carbon number. For compounds with the same carbon number, the order of increasing boiling point by class is isoparaffin, n-paraffin, naphthene, and aromatic. Melting (freezing) temperatures also increase with molecular weight, but they are strongly influenced by the molecular shape.

Table 2
Boiling and Melting Points of Representative Diesel Fuel Hydrocarbons

Compound	Hydrocarbon Class	Formula	Boiling Point	Melting Point
			°C	°C
Naphthalene	Aromatic	$C_{10}H_8$	217.8	80.0
Tetralin	Aromatic	$C_{10}H_{12}$	207.8	-35.0
cis-Decalin	Naphthene	$C_{10}H_{18}$	196.1	-42.8
1,3-Diethylbenzene	Aromatic	$C_{10}H_{14}$	181.1	-83.9
n-Butylcyclohexane	Naphthene	$C_{10}H_{20}$	181.1	-75.0
n-Pentylcyclopentane	Naphthene	$C_{10}H_{20}$	181.1	-82.8
Decane	n-Paraffin	$C_{10}H_{22}$	173.9	-30.0
Anthracene	Aromatic	$C_{14}H_{10}$	341.1	215.0
1-Pentylnaphthalene	Aromatic	$C_{15}H_{18}$	306.1	-23.9
n-Nonylcyclohexane	Naphthene	$C_{15}H_{30}$	282.2	-10.0
n-Decylcyclopentane	Naphthene	$C_{15}H_{30}$	278.9	-22.2
n-Pentadecane	n-Paraffin	$C_{15}H_{32}$	271.1	10.0
2-Methyltetradecane	Isoparaffin	$C_{15}H_{32}$	265.0	-7.8
1-Decylnaphthalene	Aromatic	$C_{20}H_{28}$	378.9	15.0
n-Tetradecylbenzene	Aromatic	$C_{20}H_{34}$	353.9	16.1
n-Tetradecylcyclohexane	Naphthene	$C_{20}H_{40}$	353.9	25.0
n-Pentadecylcyclopentane	Naphthene	$C_{20}H_{40}$	352.8	17.2
Eicosane	n-Paraffin	$C_{20}H_{42}$	343.9	36.1
2-Methylnonadecane	Isoparaffin	$C_{20}H_{42}$	338.9	17.8

Density and heat of combustion for selected representative diesel fuel hydrocarbons are listed in Table 3. Within the same hydrocarbon class, density increases with carbon number. For compounds of the same carbon number, the order of increasing density is paraffin, naphthene, and aromatic.

For compounds with the same carbon number, the order of increasing heat of combustion (heating value) on a weight basis is aromatic, naphthene, and paraffin. However, the order is reversed if the heat of combustion is expressed on a volume basis, with aromatic highest and paraffin lowest.

Table 3
Density and Heat of Combustion for Representative Diesel Fuel Hydrocarbons

Compound	Hydrocarbon Class	Carbon Number	Density	Heat of Combustion	
			g/cm^3, 20°C	MJ/kg, 25°C	MJ/m^3, 25°C

Naphthalene	Aromatic	10	1.175	38.855	45,656
Tetralin	Aromatic	10	0.9695	40.525	39,290
1,3-Diethylbenzene	Aromatic	10	0.8639	41.386	35,753
n-Butylcyclohexane	Naphthene	10	0.7992	43.419	34,702
n-Pentylcyclopentane	Naphthene	10	0.7912	43.587	34,484
Decane	n-Paraffin	10	0.7301	44.238	32,299
2,2-Dimethyloctane	Isoparaffin	10	0.7245	44.147	31,984
Anthracene	Aromatic	14	1.251	38.413	48,056
n-Nonylbenzene	Aromatic	15	0.8558	42.149	36,070
n-Nonylcyclohexane	Naphthene	15	0.816	43.433	35,441
n-Decylcyclopentane	Naphthene	15	0.811	43.547	35,318
n-Pentadecane	n-Paraffin	15	0.7684	43.982	33,796
n-Tetradecylbenzene	Aromatic	20	0.8549	42.484	36,321
n-Tetradecylcyclohexane	Naphthene	20	0.825	43.447	35,842
n-Pentadecylcyclopentane	Naphthene	20	0.8213	43.526	35,750
Eicosane	n-Paraffin	20	0.7843	43.854	34,395

The impact of the hydrocarbon class on fuel properties is summarized in Table 4 [Chevron 1998]. Normal paraffins have high cetane numbers, but very poor cold flow properties and low volumetric heating values. Aromatics have very good cold flow properties and high volumetric heating values (due to their high density), but very low cetane numbers. Isoparaffins and naphthenes occupy an intermediate position, with values of these properties between those of n-paraffins and aromatics.

Table 4
Relationship of Hydrocarbon Class Properties to Fuel Properties

Fuel Property	n-Paraffin	Isoparaffin	Naphthene	Aromatic
Cetane number	++	0/+	0/+	0/-
Low temperature operability	-	0/+	+	+
Volumetric heating value	-	-	0	+

\+ positive or beneficial effect on the fuel property
0 neutral or minor effect
\- negative or detrimental effect

Diesel Fuel Properties

Overview

Diesel fuel properties can affect many important diesel engine performance characteristics. Therefore, a number of properties are subject to various specifications. The most important quality requirements placed on diesel fuels are specified in national industrial standards, such as the ASTM D975 in the USA, EN 590 in the European Union, and JIS K2204 in Japan. Certain properties (e.g., sulfur content, aromatics) may be subject to environmental regulations. Some companies that transport diesel fuel through pipelines have limits for certain properties, such as density or pour point. Still other properties may be specified by engine manufacturers [DDC 2004][Caterpillar 2003] and/or by some fuel purchasers. Fuel refiners themselves have internal specifications to ensure the suitability of fuels for their intended use.

The most important diesel fuel properties—most of which being subject to standards—include:

- Ignition quality: cetane number and cetane index
- Density (and gravity)
- Heating value
- Volatility
- Viscosity
- Cold behavior properties, such as cloud point, pour point, cold filter plugging point (CFPP), and low temperature flow test (LTFT)
- Flash point
- Engine/components wear properties: lubricity, cleanliness, acidity
- Fuel Stability
- Sulfur

Fuel properties can be divided into those that are physical properties of the liquid (e.g., density, viscosity, volatility, heating value, or sulfur), and those that are not (e.g., cetane number, flash point, or lubricity). While physical properties can be in principle determined using a number of measurement techniques, the latter category are properties that are defined and measured through interaction of the fuel with a standardized measurement apparatus, for example a standard test engine for cetane number measurement.

Diesel fuel properties are also categorized into (1) bulk and (2) minor properties. A bulk property is determined by the composition of the fuel as a whole. Example bulk properties are cetane number, density, or volatility. A minor property is determined by the presence or absence of small amounts of particular compounds. Examples are sulfur, cloud point, or flash point.

Finally, fuel properties can be divided into those that have (1) an immediate effect or (2) a long-term effect on the engine performance. Example properties with an immediate effect are cetane number, heating value, or density. On the other hand, properties affecting engine wear or fuel stability have typically long-term effect.

Some fuel properties can influence diesel emissions. The impact of fuel was generally more significant in older, mechanical engines. Emissions from advanced, electronic engines often show very little sensitivity to fuel quality. The most important fuel parameters linked to emission effects are:

- Cetane number—Increasing the cetane number improves fuel combustion and tends to reduce NO_x, and in some engines also PM emissions.
- Aromatics—Reducing the aromatics content reduces NO_x and PM in some engines. Emission effects from the reduction in polynucleararomatics are probably higher than those from the reduction of single-ring aromatics.
- Density—Studies in heavy-duty engines indicate that reduced fuel density can decrease NO_x emissions in older technology engines.
- Sulfur—Reduced sulfur content produces a reduction in sulfate particulates. This effect is rather limited, especially at lower sulfur levels (sulfates comprise no more than about 10% of total PM in a 0.1 g/bhp-hr PM engine operated with 300 ppm S fuel). Sulfur, however, plays a special role due

to its adverse effect on several catalytic emission control technologies. Emission aftertreatment is the main driver behind the worldwide push for reformulated fuels of ultra low sulfur content.

Ignition Quality

Diesel fuel ignition quality is characterized by the ignition delay time, the time between the start of injection and the start of combustion (see also paper on diesel combustion). The shorter the ignition delay time for a particular fuel, the higher the ignition quality. Fuels with a high ignition quality provide several advantages for diesel engine performance:

- Improved cold starting performance (although at temperatures below freezing starting aids are usually needed regardless of ignition quality).
- Reduced white smoke emission associated with cold start.
- Reduced combustion noise.
- Reduced NO_x and PM emissions.

It should be noted that the *autoignition temperature* is *not* a measure of fuel ignition quality. Autoignition temperatures—measured using such methods as ASTM E659—are often used to characterize safety properties of various flammable liquids. They are determined in a standardized apparatus (similar to that used for flash point measurement) where the air-fuel mixing, heating method, duration of experiment, and other test conditions are entirely different from those in the engine cylinder.

The ignition quality of a diesel fuel is increased by a high proportion of paraffins, while high proportion of aromatics of the types found in cracked fuel components impairs the ignition quality. Ignition quality can be also improved by using fuel additives, most commonly 2-ethylhexyl nitrate (EHN).

Cetane Number. The most common ignition quality test is that for cetane number. There is a similarity between cetane number for diesel fuel and octane number for gasoline, with both properties describing the autoignition tendency of the fuel. Both scales were designed to produce higher values for better quality fuels in their respective applications (easier to self-ignite for diesel, more difficult to self-ignite with less tendency to knock for gasoline). Therefore, fuels with high cetane number have low octane rating, and vice versa.

Cetane numbers are measured by running the fuel in a standard single cylinder variable compression ratio engine—known as the CFR (Cooperative Fuel Research) engine—and comparing it with reference fuels. The cetane number scale is defined by blends of two pure hydrocarbon fuels. Cetane (n-hexadecane, $C_{16}H_{34}$), a hydrocarbon with high ignition quality, represents the top of the scale with a cetane number of 100. An isocetane, heptamethylnonane (HMN), which has a very low ignition quality, represents the bottom of the scale with a cetane number of 15. Thus, cetane number (CN) is given by

$$CN = \%\ n\text{-}cetane + 0.15 \times (\%\ HMN) \qquad (1)$$

The minimum cetane number of diesel fuels is 40 in the USA and Canada, 45 in Japan, and 51 in the EU. Even for modern engines, cetane numbers well above 50 are desirable for optimum operation. Long term requirements will depend on the evolution of diesel combustion technologies. If homogeneous charge compression ignition (HCCI) is adopted for diesel engines, very high cetane numbers may no longer be advantageous [Duffy 2004].

Cetane Index. Determination of the cetane number is time consuming, expensive, and obviously requires that the CFR engine test stand is available. Cetane index—a calculated value, derived from fuel density and volatility properties—has been introduced as an estimate of the cetane number. It is now widely used to monitor and control diesel ignition quality. In addition to providing a means of quality control for diesel fuel cetane, the cetane index is also incorporated into diesel specifications as an additional parameter to control base fuel quality. It can be used to limit the amount of cetane improver additives blended into a base fuel or to limit the aromatics content. For example, the European specification for automotive diesel fuel, EN 590:2004, specifies the minimum cetane number of 51 and the minimum cetane index of 46 while ASTM D975-04 requires the No. 1 and No. 2 S15 and S500 diesel fuels maintain either a minimum calculated cetane index of 40 (based on the older ASTM D976 equation) or a maximum aromaticity of 35%.

It should be noted that when cetane index is intended to be a measure of the natural cetane number of diesel fuel, it is only applicable to those fuels with properties that are similar to the fuels used to develop the correlation and before the addition of any cetane improving additives. It may not be reliable for fuels with cetane improver additives or with fuels whose properties differ significantly from those used to develop the correlation. In cases where the cetane number of a fuel has been established, the cetane index is useful as a cetane number check on subsequent samples of that fuel, provided that its source and mode of manufacture remain unchanged. In the case cetane index is used to control aromatics, correlation with cetane number is less of an issue.

Density And Heating Value

Density (ρ) is the mass of a unit volume of material, typically expressed is such units as g/cm^3 or kg/m^3. *Relative density* (RD) is the ratio of the material density to the density of water, Equation (2). The relative density of petroleum products in the USA is determined at a reference temperature of 60°F (15.6°C).

$$RD = \rho_s/\rho_w \qquad (2)$$

where:

ρ_s, ρ_w - density of the sample and of water, respectively.

A common measure of the density of petroleum products in the USA is the *API gravity*, expressed in degrees API, Equation (3). API gravity is an arbitrary scale developed by the American Petroleum Institute. API gravity increases inversely to density, with lower density products having higher API gravities (these were the higher value products). The API gravity scale was constructed so that most values are between 10 and 70.

$$°API = (141.5/RD) - 131.5 \qquad (3)$$

where:

RD - relative density at 60°F.

The *heating value* (energy content) of diesel fuel is its heat of combustion—the amount of energy released when a unit quantity of fuel is burned. Two types of heating values, gross (higher) and net (lower), are distinguished, depending on the physical form of water from the combustion of fuel. For gross heating value, the water is condensed to liquid. For the net heating value, the water remains a vapor. Since engines exhaust water as gas, the net (lower) heating value is usually used to describe petroleum fuels. The heating value of fuel affects the fuel economy of the engine or vehicle.

Heating values can be expressed per unit of mass or volume of fuel (volumes typically at 60°F). As clients buy fuels by volume, the volumetric representation has been more common in the petroleum industry. The volumetric heating value is obtained by multiplying the per mass heating value by the density of fuel. Typical heating values and densities for common petroleum fuels are shown in Table 5 [Chevron 1998]. Lighter, less dense fuels (gasoline) have higher heating values on a mass basis. Heavier, more dense fuels (e.g., diesel) have higher heating values on a volume basis.

Table 5
Typical Density and Net Heating Value of Different Fuels

Fuel	Density	Net Heating Value	
	g/cm^3	MJ/kg (Btu/lb)	MJ/m^3 (Btu/gal)
Regular gasoline	0.735	43.335 (18,630)	31,831 (114,200)
Premium gasoline	0.755	42.893 (18,440)	32,388 (116,200)
Jet fuel	0.795	42.847 (18,420)	34,061 (122,200)
Diesel fuel	0.850	42.638 (18,330)	36,235 (130,000)

Volatility

The volatility characteristics of diesel fuel are expressed in terms of the temperature at which successive portions are distilled from a sample of the fuel under controlled heating in a standardized apparatus. One of the most widely used methods is the ASTM D86. The distillation or boiling range of the fuel depends on the fuel chemical composition and, therefore, influences other properties such as viscosity, flash point, autoignition temperature, cetane number and density.

The fuel sample is placed in the distillation apparatus and heated. The vapors, which form as the temperature increases, are condensed and collected in a cylinder graduated in percentage of the initial volume of the liquid. The information recorded during distillation includes:

- initial boiling point (IBP)
- end point (EP) or final boiling point (FBP)
- percent of condensate recovered
- percent of non-volatile residue

The temperatures corresponding to the amounts distilled as the test proceeds are plotted in a distillation graph, as illustrated in Figure 3.

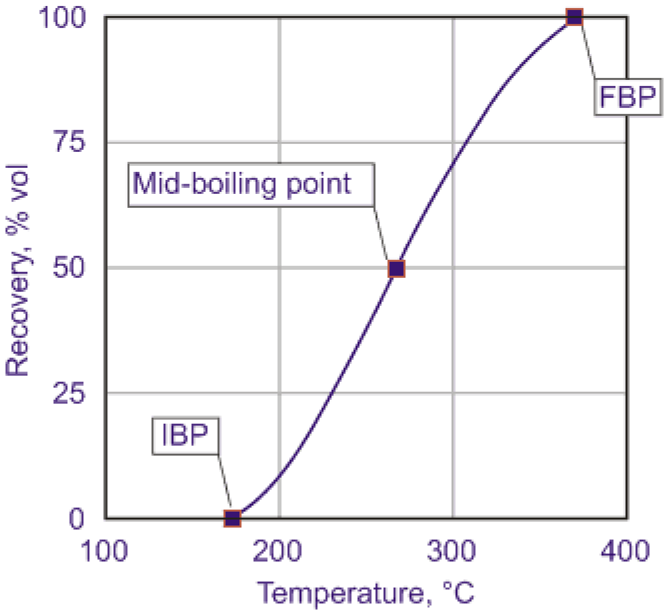


Figure 3. Typical distillation curve of diesel fuel

Viscosity

The viscosity of a fluid indicates its resistance to flow; the higher the viscosity, the greater the resistance to flow. A dynamic (or absolute) viscosity of a fluid (in Pa·s) is defined as the force (in N) required to move an area of 1 m^2 at a speed of 1 m/s past a parallel surface 1 m away and separated from it by the fluid. A kinematic viscosity is calculated by dividing the dynamic viscosity by the fluid density.

Viscosity of diesel fuel is important for the operation of fuel injection equipment which has to accurately measure the small quantities of fuel to be injected. As viscosity decreases with increasing temperature, the tolerance band between maximum and minimum viscosity values should be kept as small as possible.

A high viscosity at low temperature could reduce the flow of fuel and result in incomplete filling of the metering chamber. If the fuel is very viscous, there is a possibility of pump distortion due to the heat generated by the shearing action in the small clearances. A low viscosity fuel can significantly increase leakage from the pumping elements, particularly at low speeds. Such a situation can arise when attempting a hot restart after a brief engine shut down, following a period of operation at high load. The temperature of the already hot fuel injection equipment is further increased by heat soak-back from the engine, reducing the fuel viscosity to the point that leakage may make restarting impossible until the fuel system cools down.

Cold Behavior Properties

Most diesel fuels include a significant proportion of paraffinic components, which include waxes. At low temperatures, the precipitation of paraffin crystals (wax) can cause clogging of the fuel filter and an interruption in fuel supply. Depending on the fuel properties, the start of paraffin precipitation can be as early as 0°C. Consequently, winter diesel fuels must be specially selected, or treated, in order to ensure problem-free operation in cold weather.

The following is a list of some of the properties which have been defined to describe the cold behavior of diesel fuels:

- *Cloud point* (CP) is the temperature at which wax first becomes visible when the fuel is cooled (ASTM D2500)
- *Pour point* is the temperature at which the amount of wax out of solution is sufficient to gel the fuel (ASTM D97).
- *Cold filter plugging point* (CFPP) is the lowest temperature at which fuel will pass through a fine wire mesh screen. The CFPP is widely used in Europe (EN116:1981). The CFPP method is also described by ASTM standards (ASTM D6371), but it does not correlate well with the low-temperature performance of North American fuels in North American equipment.
- *Low temperature flow test* (LTFT) (ASTM D4539) is a US procedure similar to the CFPP. LTFT correlates better with low temperature operability field tests, but due to its slow cooling rates, the test requires 12 to 24 hours to complete, making it impractical for routine fuel testing.

Usually flow improvers are added to fuels at the refinery. Although the flow improvers do not prevent precipitation of paraffins, they limit their crystal growth. The crystals are so small that they can still pass through the filter pores. As a result, filterability can be extended to lower temperatures.

The resistance to cold can be improved even further by additives which prevent the precipitation of paraffin crystals. Winter diesel fuels which are available today guarantee cold resistance to at least -22°C. Additional measures are filter heating or addition of petroleum products to the diesel fuel. An addition of regular gasoline can also delay precipitation. However, due to the very low cetane number of gasoline, the ignition quality is impaired and the flash point considerably reduced.

The cloud point of a fuel is also affected by its distillation characteristics. The maximum 90% distillation point is, therefore, limited to 315°C in Canada, a country with extremely cold winters, while a 90% distillation point as high as 379°C is possible in tropical or sub-tropical areas.

Flash Point

The flash point is the temperature at which a combustible liquid gives off just enough vapor to produce a vapor/air mixture that will ignite when a flame is applied. The flash point is measured in a standardized apparatus using standard test methods, such as ASTM D93 or ISO 2719.

The importance of flash point is primarily related to safe handling of the product. If the flash point is too low, there could be a fire hazard. For this reason mandatory minimum limits on flash point have been set by government agencies and insurance companies. Typical minimum values for automotive diesel fuels range from 38°C in the USA to 56°C in some European countries.

The flash point of a diesel fuel is not significant for the engine performance. Variations in flash point do not influence autoignition temperature or other combustion characteristics.

Engine & Components Wear Properties

Lubricity. A number of factors are critical to ensure the long term durability and trouble free performance of diesel engines. All fuel injection equipment relies either wholly or partially on the fuel to provide adequate lubrication. Therefore the fuel injection equipment must be designed to ensure that clearances, surface finishes and material properties are chosen with this in mind. However, even the best designed equipment will fail if the fuel does not meet certain requirements. The fuel must be clean and have low levels of contaminants. This is often achieved through a combination of on-board filtration and water separation, and having the fuel meet requirements that minimize the amount of contaminants that can cause corrosive or abrasive wear. The fuel must also meet minimum and maximum viscosity requirements to ensure not only that hydrodynamic films will form where they are required but also to ensure that material stresses do not become too high. The fuel must also meet some minimum requirements to ensure that parts experiencing boundary lubrication do not fail unexpectedly.

Until the early 1990s, with the exception of aviation fuels and fuels intended for arctic conditions, the ability of diesel fuel to provide adequate lubricity was not a significant issue and there was little need to develop standards, specifications and test methods. Most fuel injection equipment was simply designed to perform well on the commercial fuels available at the time [Nikanjam 1999]. The importance of lubricity specifications was first recognized when California regulated low aromatics diesel fuel starting in 1993. While no major problems surfaced in California after the introduction of low aromatics diesel fuel, two years later when Sweden introduced fuels with almost no aromatics and sulfur (10 ppm S), the poor lubricity of the resulting fuel led to catastrophic injection equipment failures; sometimes after less than one tank of fuel.

The natural lubricity of fuels is to a large extent determined by polyaromatics and oxygen-containing polar impurities, while sulfur impurities can actually increase engine wear [Wei 1986]. However, high sulfur fuels do generally have sufficient levels of polyaromatics and polar impurities that do impart lubricity to diesel fuel to more than offset the deleterious effect of sulfur. The apparent correlation between sulfur and lubricity is explained by the fact that the processing (hydrotreating) required to remove sulfur from the fuel tends to destroy these compounds as well, resulting in poor lubricity of low sulfur fuels.

As fuel suppliers became more knowledgeable and treated their low sulfur fuels with lubricity additives, other regions in the world introducing low sulfur fuels were able to avoid the equipment failures experienced in Sweden. Fuel injection manufacturers also incorporated some design changes to help accommodate fuels with poorer lubricity. As fuels of lowered sulfur and aromatics content are introduced and fuel injection systems become more complex, the ability of the fuel to provide adequate lubricity is becoming more important. Reduced clearances between components that are needed to accommodate higher injection pressures are also putting increased demands on diesel fuels to provide adequate lubricity.

The possible wear and failure mechanisms in fuel injection equipment include improper hydrodynamic film formation, oxidation, adhesive wear, scuffing, abrasive wear, fatigue, corrosion, fretting and erosion. A *simple* test method that could test a fuel for all of these possibilities has not been developed. Many of these wear mechanisms can be addressed through proper equipment design, meeting minimum and maximum fuel viscosity limits and ensuring that only clean and contaminant free fuel enters the fuel injection equipment. Preventing wear mechanisms such as oxidation, adhesive wear, scuffing and fretting associated with boundary lubrication are more challenging to address.

The general approach to ensure that boundary lubrication problems do not arise is to ensure that fuel meets minimum lubricity requirements. Lubricity additives are commonly used in fuels of insufficient natural lubricity. In order to determine appropriate levels of lubricity additives, fuel suppliers and users rely on the results from tests methods that have been developed to measure fuel lubricity. The available test methods range from vehicle tests, through pump rig tests, to bench top tests that can be performed quickly. A number of bench tests that try to recreate boundary lubrication conditions similar to those found in fuel injection equipment have been developed to allow rapid and relatively inexpensive measurements of fuel lubricity. Some of these are outlined in Table 6.

Table 6
Selected Fuel Lubricity Test Methods

Method		Reference
BOCLE	Ball-on-Cylinder Lubricity Evaluator	ASTM D5001
SLBOCLE	Scuffing Load Ball-on-Cylinder Lubricity Evaluator	ASTM D6078
HFRR	High Frequency Reciprocating Rig	ASTM D6079
BOTD	Ball on Three Disks	[Voitik 1995]

Among these methods, the HFRR and the SLBOCLE are most commonly used. The HFRR test was adopted by the ASTM for its diesel lubricity specification which became effective from 2005.

Cleanliness. If diesel fuel is contaminated with abrasive inorganic particles, it can also cause abrasive wear of fuel system components and piston rings. Components with very close tolerances between moving parts, such as fuel injection pumps and injectors, are particularly susceptible for this type of wear. Most diesel fuel specifications include limit on ash, which includes contributions from suspended inorganic particles, as well as from soluble organometallic compounds. The ash limit in ASTM diesel fuel specification is 0.01% m/m (ASTM D482 analysis).

The ASTM standard does not address particle sizes. Engine manufacturers typically recommend fuel filters of a nominal pore size of 10 µm. According to a study by the Southwest Research Institute, the critical particle size for initiating significant abrasive wear in high-pressure fuel injection systems is 6-7 µm [Chevron 1998].

Acidity. Corrosive wear of the fuel system can be also caused by organic acids in diesel fuel. This wear mechanism is more important in high sulfur fuels. Hydrotreating processes employed to reduce sulfur also destroy organic acids.

Fuel Stability

Formation of gum and sediment (sometimes called the “diesel sludge”) may occur in some diesel fuels during storage, which can lead to injector deposits or particulates that can plug fuel filters or the fuel injection system. The precursors include certain sulfur and nitrogen compounds, olefins, and organic acids. The conversion process involves a complex chain of chemical reactions, leading to the formation of insoluble compounds of high molecular weight. The process is usually initiated by oxidation of certain fuel components (such as phenalenones), followed by reactions with acids [Pedley 1989]. Some dissolved metals—especially copper and iron—can destabilize the fuel by acting as oxidation catalysts.

Interestingly, two fuels of good stability may form a less stable blend when mixed together. Such effect is possible when each fuel contains some of the precursors needed for the formation of higher molecular weight species. In some cases fuel instability may be also increased by certain additives, e.g., by the cetane number improver EHN [Chevron 1998].

Fuel stability is improved by using antioxidants and other stability additives. The need for a stability additive varies from one fuel to another. For best effects, stability additives should be added immediately after the fuel is manufactured.

Storage and oxidation stability is assessed by several tests, some of them at elevated temperature, including:

- ASTM D2274—*Oxidation Stability of Distillate Fuel Oil*
- ASTM D4625—*Distillate Fuel Storage Stability at 110°F (43°C)*
- ASTM D5304—*Assessing Distillate Fuel Storage Stability by Oxygen Overpressure*
- Octel/Dupont F21 method—*150°C Accelerated Fuel Oil Stability Test*

Another source of fuel contamination during storage is growth of microorganisms—bacteria and fungi (yeasts and molds). Diesel fuel, sterilized at high temperatures during refinery processing, becomes contaminated with microorganisms which are present in air or water. Most microorganisms need free water to grow. Therefore, biogrowth is usually concentrated at the fuel-water interface, if one exists. Aerobic microorganisms need air to grow, while anaerobic microorganisms can only grow in the absence of air. Biogrowth is also favored by higher temperatures and by the presence of elemental nutrients.

With time, large colonies of organisms may form, which produce enough microbial slime to plug filters. They also produce acidic by-products that can accelerate tank corrosion. Biogrowth is promoted primarily by the presence of water, rather than by the properties of the fuel itself. To prevent growth of microorganisms, the amount of water in fuel storage tanks should be kept as low as possible.

Sulfur

Sulfur Effects on Diesel Engines

Diesel fuels contain chemically bound sulfur. The amount of sulfur depends on the crude oil quality and the components used in blending the fuel. In particular, some crack components have high sulfur content. Refineries can reduce the sulfur content of diesel fuel by treatment with hydrogen. As already mentioned, high sulfur fuels typically have sufficient natural lubricity. The hydrotreating used to remove sulfur also removes compounds that improve fuel lubricity, for instance polyaromatics. Therefore, fuels of low sulfur levels typically require lubricity additives to avoid potential damage to fuel injection equipment [Batt 1996].

There are a number of negative effects of sulfur in diesel fuel, which can be categorized as follows [Ruzicka 1999]:

- Emissions
    - Sulfur dioxide emissions—most of the sulfur is converted in the engine into sulfur dioxide, a substance of a negative environmental impact.
    - Sulfate particulate emissions—a fraction of the sulfur is oxidized to sulfur trioxide. The SO_3 binds with water, forms sulfuric acid, and contributes to the total PM emission.
- Corrosion and wear
    - Corrosion of exhaust system components by sulfur condensates—especially troublesome in exhaust gas recirculation coolers [McKinley 1997][Kreso 1998b].

  - Increasing wear of engine parts through the corrosion of internally formed acid.
- Exhaust aftertreatment
  - The SO_2/SO_3 shift is increased very significantly if oxidation catalysts are used in the emission control system, resulting in increased PM emissions.
  - Sulfate particulates are also generated in catalytic particulate filters, both the CRT and catalyzed traps. At certain conditions, the benefit of reducing the carbon fraction of diesel PM can be more than offset by the generated sulfates.
  - Deactivation of NO_x adsorbers by sulfur is one of the most important obstacles in implementing this technology.
  - Many catalysts are, reversibly or not, poisoned by sulfur. There may be interferences with future emission control systems that are currently not known.

Reduction of Sulfur in Diesel Fuels

In order to minimize these adverse effects, the sulfur content in diesel fuels has been gradually limited, as summarized in Table 7.

Table 7
Reduction of Sulfur Content in Highway Diesel Fuel

Fuel Type	Sulfur Level	Reason for Reducing Sulfur	Targeted Emission	Emission Standards
Standard diesel	≥0.5% (5000 ppm)	n/a	n/a	US before 1993 EU before 1996
Low sulfur diesel	500-350 ppm	• sulfate PM control • SO_2 control	PM, SO_2	• US1994: 0.1 g/bhp-hr PM • Euro II/III: 0.25/0.1 g/kWh PM
Ultra low sulfur diesel	50-10 ppm	• to enable catalytic DPFs • to enable NO_x aftertreatment • sulfate PM control	PM, NO_x	• US2007/10: 0.2 g/bhp-hr NO_x; 0.01 g/bhp-hr PM • Euro IV/V: 0.02 g/kWh PM
Sulfur-free diesel	≤10 ppm*			• Euro V/VI

* EU: phase-in from 2005-2009. Simultaneous introduction of sulfur-free gasoline would enable lean NO_x control from spark-ignited engines to reduce CO_2 emissions through increased fuel economy.

Until the early 1990s, sulfur level in diesel fuel was not subject to environmental regulations. The maximum sulfur level in good quality fuels, as listed by fuel specifications, was at about 0.5% (5000 ppm = 5000 mg/kg).

Environmental legislation limiting the maximum content of sulfur in diesel fuel has been driven first by the impact of sulfur on PM emissions (sulfate particulates). At the time when the typical sulfur specification amounted to 0.5%, sulfur dioxide emissions from the diesel engines still had a noticeable contribution to the global SO_2 emission inventory, thus creating additional pressure on lowering the sulfur level in diesel. In the 1990s, environmental regulations limited the maximum sulfur level to about 500 ppm; this type of diesel fuel was typically referred to as “low sulfur diesel”.

Further sulfur reductions were necessary to facilitate the introduction of emission control catalysts on diesel engines. Ultra low sulfur fuels of maximum sulfur content between 50 - 10 ppm have been introduced as a “technology enabler” for catalytic diesel particulate filters and other catalyst technologies. The associated SO_2 emission benefit is small and may be important only in some specific environments, such as in “street canyons” of high intensity of traffic and slow movement of air. Diesel fuels of typically

15 ppm S (but not more than 50 ppm) are commonly referred to as “ultra low sulfur diesel” (ULSD). In Europe, diesel (and gasoline) fuels of maximum sulfur content of 10 ppm are termed “sulfur-free” fuels.

All major steps in reducing the sulfur level in fuel have been synchronized (and in fact are an integral part of) diesel emission standards, both in the USA and in the EU. The first significant reduction of sulfur in diesel fuel took place in the USA in October 1993, when a 500 ppm S cap was implemented. That move was coordinated with the 1994 0.1 g/bhp-hr standard for diesel PM. Sulfate particulate emission levels in pre-1994 engines operated with fuels of about 0.3% S could be as high as 0.07 g/bhp-hr and more. Obviously, a total PM standard of 0.1 g was not feasible without lowering the sulfur content.

The next reduction in sulfur level in the USA became effective in mid-2006, just before the 2007 PM emission standard for heavy-duty highway engines of 0.01 g/bhp-hr. The sulfur has been lowered to 15 ppm to enable advanced PM control technologies in 2007 engines, as well as advanced NO_x aftertreatment for metting the 2010 standard of 0.2 g/bhp-hr. A similar evolution of fuel quality changes along with emission standards can be seen in the EU, as illustrated in Figure 4.

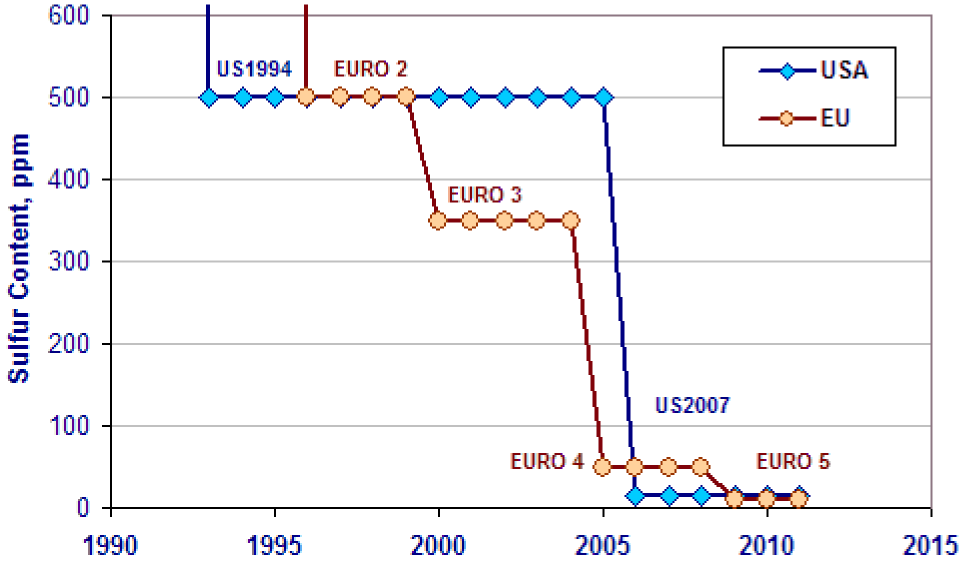


Figure 4. Diesel Fuel Sulfur Limits Driven by Emission Legislation

Corresponding emission standards marked in the chart area. Data refers to highway fuels.

Although ultra low sulfur fuel of 50 ppm S has been legislated in the EU since 2005, a number of European countries introduced fuels with sulfur levels between 10 and 50 ppm already in the late 1990s and early 2000s by means of tax incentive programs. Ultra low sulfur fuels were first available in such countries as Sweden, UK, Ireland, Denmark, the Netherlands, Germany, and Belgium.

In 1998, motor vehicle manufacturers established a World-Wide Fuels Charter—a document that lists specifications for diesel and gasoline automotive fuels that are desired to harmonize fuel quality worldwide in accordance with the needs of vehicle and emission control technologies [ACEA 2000][ACEA 2002][ACEA 2006]. Since its year 2000 revision, the Charter calls for the introduction of “sulfur-free” fuels, both diesel and gasoline. Governments have followed the Chapter recommendations with the EU legislation requiring the availability of sulfur-free fuels in 2005 and a complete switch to 10 ppm S diesel and gasoline in 2009.

Ultra Low Sulfur Diesel Issues

With the introduction of any planned changes in fuels, fuel producers, equipment manufacturers and other interested parties make every effort to ensure smooth transitions. In order to provide technical coordination to facilitate the transition to ULSD in the USA, the Clean Diesel Fuel Alliance was formed, including the US DOE, the US EPA, engine, vehicle and component manufacturers, all sectors of the petroleum industry, and fuel consumers, such as truckers. According to the Alliance, this transition should be relatively smooth [CDFA 2006]. There should be no noticeable impact on overall power; ULSD should be fully compatible with the existing fleet, including 2006 and earlier model year vehicles; and ULSD should contain the required additives to ensure lubricity and corrosion are not issues.

However, several issues have been also identified that users of ULSD should be aware of. Fuel economy may be reduced slightly and ULSD may affect fuel systems of older vehicles and result in fuel leaks and/or it may loosen deposits in fuel tanks and cause premature filter plugging.

Fuel Economy. The processing required to reduce sulfur levels in diesel fuels to less than 15 ppm can also reduce the aromatics in the fuel. On a volumetric basis, the energy density of aromatics is significantly higher than other components of diesel fuel. Reducing the concentration of aromatics in a fuel will result in less energy per unit volume. Furthermore, ULSD has a lower density. Due to the combined effect of lower aromatics and lower density, ULSD has a lower volumetric heating value, typically by about 1-2% compared to the low sulfur diesel of 500 ppm S.

Seal Compatibility. While newer engine designs would take seal compatibility into consideration there are at least two possible reasons why seal compatibility may be a concern with ULSD fuels for some older engines:

- Desulfurization can also remove naturally occurring antioxidants from middle distillate fuels. The antioxidants can prevent the build up of peroxides in the fuel. If these antioxidants are not replaced, peroxides could build up in the fuel if it is stored for long periods of time. Peroxides can cause the embrittlement of neoprene and nitrile elastomers and possibly lead to seal failure.
- Aromatic fuel components can cause some elastomer materials to swell. Fuel systems that have been designed to accommodate seal swelling may not create a tight seal between metal parts and prevent fuel leakage with fuel low in aromatics. Elastomers may even shrink and crack in some cases.

Deposits. Fuel chemical and physical property changes can affect the way fuels interact with deposits in pipelines, storage tanks and vehicle fuel systems. In some cases, relative changes in these fuel properties can lead to the loosening of deposits in the transition period from low sulfur diesel to ultra low sulfur diesel. This could necessitate the changing fuel filters ahead of their regularly scheduled intervals.

According to Lubrizol, loss of antioxidants and the subsequent increase in peroxides can eventually lead to the formation of insoluble polymers in the fuel [Cummins 2006]. These polymers could potentially could build up on sensitive fuel system components such as injectors and affect their performance.

Static Dissipation. Fuel processing to remove sulfur also removes polar compounds that give diesel fuel electrical conductivity and prevent the build up of static electrical charge. Discharge of static electricity can occur during bulk fuel handling if fuel conductivity is not sufficient. This can cause serious damage if a flammable mixture is also present. This type of accident is most likely to occur in tanks being switch-loaded from gasoline to diesel fuel. The previous gasoline load leaves a combustible mixture of fuel vapour and air in the tank. If a load of diesel with poor conductivity is then loaded and a static discharge occurs, an explosion can result. ULSD will likely require the use of static dissipater additives.

Low temperatures can reduce the conductivity of diesel fuels that may have sufficient naturally occurring conductivity at higher temperatures (this is one reason the Canadian diesel fuel standard has a minimum conductivity specification).

Diesel Fuel Additives

Overview

Quality improvement by the addition of additives, which has been a common practice with gasoline fuels for many years, has also become popular for diesel fuels. Depending on their purpose, diesel fuel additives can be grouped into four major categories:

i. Engine performance
ii. Fuel handling
iii. Fuel stability
iv. Contaminant control

The effects of different additives may be seen in different time frames. Some additives have an immediate effect (e.g., cetane improvers), others may bring an effect after a long period of operation (e.g., detergent additives). The overall concentration of additives is generally below 0.1%, so that the physical properties of the fuel, such as density, viscosity, and volatility are not changed.

Additives may be added to diesel fuel at three different stages: (1) at the refinery, (2) in the fuel distribution system, and (3) after the fuel has left the terminal. Additives of the latter group, added by the end user or a reseller, are called *aftermarket additives*.

Refinery Additization. Fuel refiners must ensure that their products meet specifications and are suitable for the intended use. This can be achieved through such means as the choice of crude oil, refinery processing, blending, or the use of additives. The final choice of methods is driven by economics. Some refineries may rely on additives, while others may be able to provide high quality fuel with no additives. Since refiners do not publish such information, the exact extent of additive usage remains unclear.

Fuel manufacturers use multiple effect additive packages, rather than single additives. In the USA, common additives include pour point reducers and fuel stability additives [Chevron 1998]. Cetane improvers are especially common in California, to achieve the emission reductions mandated for the CARB diesel. Cloud point is usually controlled by processing changes, rather than by additives. In Europe, on the other hand, low temperature operability is often enhanced through the use of CFPP improving additives. Antifoam additives are used in Europe and Asia to prevent spills when consumers fill their tanks. Foaming is a lesser problem in North America, due to the lower distillation point of diesel fuel and different design of tanks and fuel dispensing systems. Lubricity additives are used worldwide in fuels with ultra low sulfur content.

Distribution System Additization. Pipeline operators sometimes inject drag reducing additives (to increase the pipeline capacity) and/or corrosion inhibitors. Fuel properties may be also upgraded at the terminal—such as from a regular to a "premium" diesel grade—by treating the fuel with additives. An example additive package may include a detergent/dispersant, stabilizing additives, a cetane number improver, a low temperature operability additive (flow improver or pour point reducer), and a biocide [Chevron 1998]. Of course, the additive package must be always tailored to the fuel properties.

Aftermarket Additives. Some users use additives to further improve the fuel to meet their particular needs, for instance cold climate operation, or because they believe they need a higher quality fuel. A wide range of aftermarket additives are available from a number of suppliers. Some of these additives may have legitimate uses. For instance, the use of de-icers may be warranted under cold weather conditions and/or when problems with fuel system icing are encountered. In many cases, however, aftermarket additives packages consist of compounds such as detergents, lubricity improvers and cetane enhancers that would normally be added at the refinery or fuel terminal by the fuel marketer.

Users should be cautious when considering the use of any aftermarket additives. Some aftermarket additives are aggressively marketed, with performance claims that are often too good to be true. Yet, in most cases, they are not needed and should be avoided. Quality commercial fuels from reputable marketers contain all the additives that a fuel needs and have been extensively tested to minimize the possibility of adverse interactions between different additive and/or fuel components.

If the user still feels that additives are needed, they should be chosen based on careful research, and used in accordance with the recommendations of the supplier and the engine manufacturer. Inappropriate use of additives may have adverse effects on the engine, and may affect engine warranties (for example, some engine makers require that alcohol based de-icers not be used).

Engine Performance Additives

Cetane Number Improvers. Diesel ignition improvers raise the cetane number and facilitate quieter combustion and lower emissions. 2-Ethylhexyl nitrate (EHN, octyl nitrate) has become the universal cetane number improver due to its good performance and low cost. EHN is thermally unstable and decomposes rapidly under the high temperatures in the combustion chamber. The products of decomposition help initiate fuel combustion and, thus, shorten the ignition delay period. A disadvantage of EHN is its detrimental effect on stability of some fuels.

EHN is used at dose levels typically varying from 0.05% to 0.4% (m/m), to yield about 3 to 8 cetane number improvement. The increase in cetane number is greater for a fuel whose natural cetane number is already high. The incremental increase becomes smaller as more EHN is added. Correlations to calculate the cetane number increase as a function of EHN concentration can be found in the literature [Thompson 1997].

Cetane number improvement is seen also with other alkyl nitrates, as well as ether nitrates and some nitroso compounds. Another category of cetane improvers are peroxide based compounds, for example di-tertiary butyl peroxide. Their effect is strongly dependent on fuel composition [Clothier 1993][Clothier 2000]. They have generally been more expensive and less effective than nitrate based cetane improvers.

Injector Cleanliness Additives. Fuel and lube oil can form deposits in the injector nozzle area, which is exposed to high combustion chamber temperatures. Excessive deposits may cause deformation in the injector spray pattern, or even completely clog some of the nozzle holes. The impaired air-fuel mixture formation may lead to increased emissions and decreased fuel economy. Injector deposits can be cleaned using ashless polymeric *detergent* additives, composed of a polar group that bonds to deposits and deposit precursors, and a non-polar group that dissolves in the fuel. Detergent additives typically are used in the concentration range of 50 - 300 ppm.

Lubricity Additives. Lubricity additives are needed to compensate for the poor lubricity of ultra low sulfur fuels, which loose their natural lubricating properties during hydrotreatment. They contain a polar group which is attracted to metal surfaces, causing the additive to form a thin surface film. The film acts as a boundary lubricant when two metal surfaces come in contact. Two additive chemistries are commonly used: organic acids (such as fatty acids) and esters. The acid type is typically used in the concentration range of 10 - 50 ppm. Esters, being less polar, require a higher concentration range of 50 - 250 ppm.

Smoke Suppressants. Black smoke emissions can be reduced through the addition of certain organometallic compounds that act as catalysts [Howard 1980]. Barium organometallics were used occasionally as smoke suppressants in the USA during the 1960s. They were later banned by the EPA, because of the potential health hazard of barium emissions. Other metals can be also used as smoke suppressants, including calcium, iron, cerium, or platinum. While they can be effective at reducing soot emissions, these additives can lead to significant deposits in the combustion chamber and have long term impacts on engine performance. Their ability to reduce soot emissions is at least partially offset by the fact that 85-95% of the additive is exhausted from the engine and therefore contributes to total PM (mass and number). These additives can be also used to support regeneration of diesel particulate filters. Their usage without filters is generally discouraged by environmental authorities due to the potential health impacts of the metal-based particle emissions.

Combustion Catalysts. Another class of combustion catalysts are various aftermarket additives, organometallic or organic, that are promoted to reduce fuel consumption and emissions through an improvement in combustion efficiency. It must be realized that the combustion efficiency in modern diesel engines is better than 99%, thus leaving very little potential for further improvement. Combustion catalyst additives are likely to bring higher benefit in older engines and in applications with poor quality fuels.

Several studies have shown that in some cases, these compounds can provide about a 5-7% improvement in fuel economy [Haring 1993][Kelso 1990][Valentine 2000]. Some authors found better response in older engines and in vehicles operating in busy city centers with low daily mileage [Hayat 2000]. However, other studies utilizing very old technology engines reported that the use of various combustion catalysts made almost no change in fuel economy or exhaust soot levels [Moulton 1984].

Considered a trade secret by most suppliers, the formulation of combustion catalysts often remains unknown. Many organometallic compounds are based on platinum. It is also believed that some organic combustion catalysts are peroxide based (in similarity to some cetane improvers).

Many organometallic combustion catalysts require several hundred hours of engine operation with the fuel additive before significant benefits are experienced. They appear to coat the inside of the combustion chamber with the catalyst. The net result seems to be a reduction in ignition delay and their benefits are largely explained through this mechanism. They do not show any significant impact on heat release rate after ignition [Caton 1991]. Some have even classified these organometallic compounds simply as cetane improvers [Suppes 1996], as suggested by the fact that they reduce ignition delay. The fuel consumption benefits and emission reduction benefits are also very similar to those sometimes reported for cetane improver additives. The main drawback over conventional cetane improvers is that several hundred hours of operation are required before the impact of combution catalysts is observed.

Due to the long engine pre-conditioning period required for combustion catalysts, their net benefit is very difficult to determine. Pt based additives can also add significantly to a vehicle's operating cost. At treatment rates of 0.2 ppm mass, about 0.17 mg of Pt would be required per liter of fuel. At Pt prices of $1,200/troy ounce, this would require 0.7 cents worth of Pt per liter of fuel (2.5 cents/US gallon). Considering the additional costs associated with making, distributing and selling the additive, it is apparent that the cost of the additive can offset any savings from the modest fuel consumption decrease.

Another mechanism suggested by a combustion catalyst supplier is to facilitate chemical reactions that deposit polymer complexes of phosphorus and nitrogen on the surface of ferrous and non-ferrous metals (in addition to catalyzing the combustion process). These complexes are claimed to smooth and passivate the metal surface, increase reflectivity and reduce oxygen reactivity. While the actual mechanism of the additive has not been clarified, tests on an EMD locomotive engine showed fuel consumption improvements of 8-15%, some NO_x reductions at notches 2, 3 and 4 but also significant PM increases at all notch settings ranging from 40-170% [EPA 2005]. The PM increased despite significant decreases in exhaust opacity. Duty-cycle weighted PM results did however remain below the Tier 0 locomotive emission standard despite the large increase.

One interesting observation from this study was that SO_2 emissions increased by 50% after the engine was run with the additive. Since the fuel sulfur level did not change, this would suggest that either engine oil consumption increased by more than 50% (this is the only other source of sulfur) or that the lubricating oil was changed to one with a higher sulfur level in the time between tests. The fact that PM emissions increased substantially while opacity decreased would be consistent with an increase in oil consumption. Opacity is mainly affected by combustion generated soot, while PM would represent combustion generated soot and organic carbon (the latter being known to originate largely from the lubricating oil).

The formation of phosphate deposits in the combustion chamber resulting from any additives would be a significant concern over the long term. Deposit formation in the upper land and ring groove area of the piston can interfere with the ring action and eventually lead to ring sticking. Phosphates from the engine oil are known to contribute to deposits in the upper land and top ring groove area of the piston [Smith 2002]. These deposits can result in increased oil consumption [Burnett 1992][McGeehan 1983][Schetelich 1986] and eventually in reduced engine durability and performance. The presence of phosphorous—a known catalyst poison—in additives would also be of concern for engines using catalytic aftertreatment devices.

Significant reductions in CO and HC emissions are also claimed for many combustion catalysts. CO and HC emissions from diesel engines are generally low (and well below the regulated limits) and are therefore not usually of major concern. Some emission benefits have also been reported that seem to result from these additives providing a Pt coating on the inside surfaces of the exhaust system—much the same as a catalytic converter [Kelso 1990].

Fuel Handling Additives

Low Temperature Operability Additives. These additives—which can lower the pour point, cloud point, or improve the cold flow properties—are usually polymers that interact with the wax crystals formed in diesel fuel which was cooled below the cloud point. The polymers modify the size, shape, and/or degree of agglomeration of the wax crystals. The additives must be blended into the fuel before any wax has formed, when the fuel is above its cloud point. Different additives are effective for different fuels, and their effectiveness must be determined experimentally. The benefits from different types of low temperature operability additives are listed in Table 8 [Chevron 1998].

Table 8
Low Temperature Operability Additive Benefits

Additive Type	Typical Treat Rate	Typical Benefit	
	ppm	°C	°F
Cloud point	200-2000	3-4	5-7
LTFT	50-2000	8-12	15-25
CFPP	100-2000	15-20	25-35
Pour point	100-300	30-40	50-70

De-Icing Additives. Free water in diesel fuel is a major source of low temperature operability problems. It can appear in the fuel when the temperature drops, even if proper handling procedures and precautions have been taken to keep water out of all points of the fuel handling chain. Diesel fuel is not entirely hydrophobic and can disolve small amounts of water—typically less than 100 ppm. As the temperature of the fuel drops, the water solubility in the fuel decreases and free water can appear in the fuel as tiny droplets. Over time, these droplets settle to the bottom of the tank where a layer of water can build up. This water can freeze at low temperatures, plugging fuel lines or filters and blocking fuel flow.

Two different types of additives are used to prevent icing problems: (1) surfactants and (2) freezing point depressants (antifreezes). Surfactants—such as amines, diamines, amides, or glycol esters of fatty acids—help keep the water droplets that first form as the temperatures drop dispersed. While they may not prevent the water droplets from freezing, they are kept small enough to pass through the fuel filter. Surfactants are effective at concentrations from 10-60 ppm. Other surface-active substances added to fuels such as detergents also have anti-icing properties. Freeze point depressants include alcohols, glycols, dimethylformamide, and other water-soluble polar substances. Depending on the type, they are used in concentrations ranging from 0.02-2 vol %. Isopropanol is a common alcohol that is found in many de-icing additives.

Antifoam Additives. Foaming of diesel fuel can interfere with filling the fuel tank and/or cause spills. Antifoam additives are typically organosilicone compounds, usually used at concentrations of 10 ppm or less.

Drag Reducing Additives. Pipeline operators sometimes use drag reducing additives to increase the pipeline capacity. These additives are high molecular weight polymers that reduce the turbulence of fluids in the pipeline, which can increase the maximum flow rate by 20 - 40%. Drag reducing additives are typically used at dose rates below 15 ppm. The additive is broken down (sheared) into smaller molecules when the additized product passes through a pump, thus, it has no effect on fuel performance in engines.

Antistatic Additives. Additives can be added to diesel fuel to avoid the risk of an explosion due to a charge of static electricity building up during fast rates of pumping.

Fuel Stability Additives

Antioxidants. Antioxidants block certain oxidation processes in the fuel to interrupt the chain of reactions that leads to fuel instability. The most commonly used antioxidants are hindered phenols and certain amines, such as phenylenediamine. They typically are used in the concentration range of 10 - 80 ppm.

Stabilizers. Additives of this class block acid-base reactions—another type of processes that can cause fuel instability. The stabilizers typically are strongly basic amines, which react with weakly acidic compounds to form products that remain dissolved in the fuel, but do not react further. Stabilizers are used in the concentration range of 50 - 150 ppm.

Metal Deactivators. Metal deactivators chelate metals dissolved in fuel (copper, iron) that can catalyze reactions involved in fuel instability. They typically are used in the concentration range of 1 - 15 ppm.

Dispersants. Dispersants do not prevent the fuel instability reactions, but they disperse the formed insoluble products, preventing them from clustering into aggregates that could harm engine components. Dispersants typically are used in the concentration range of 15 - 100 ppm.

Contaminant Control

Biocides. The growth of microorganisms in diesel fuel can be stopped by using biocides. The additive should be soluble in both the fuel and the water, so it can attack the microbes in both phases. Even if the biocide effectively stops biogrowth, it still may be necessary to drain and clean the tank to remove accumulated biomass. Since biocides are toxic, the biomass and water that contain biocides must be disposed of appropriately. Biocides typically are used in the concentration range of 200 - 600 ppm.

Demulsifiers. Under certain conditions, in the presence of compounds that act as surfactants, emulsions can be formed from the fuel and water. These emulsions are stabilized by operations that subject the mixture to high shear force, like pumping. Demulsifiers and dehazers are surfactants that break up the emulsion and allow the fuel and water phases to separate. They typically are used in the concentration range of 5 - 30 ppm.

Corrosion Inhibitors. These compounds attach to metal surfaces and form a barrier that prevents attack by corrosive agents. They are added primarily to prevent the corrosion of petroleum tanks and pipes by water. Corrosion inhibitors typically are used in the concentration range of 5 - 15 ppm.

Typical Specifications

There are several grades of diesel fuel that meet the various demands of different applications. Fuel properties must be also tailored for the given climate conditions; in many areas, diesel fuel of different properties is supplied during winter and summer seasons. There are also petroleum products for non-diesel applications, whose properties are similar to those of diesel fuel. In the USA, the primary type of diesel fuel used in transportation is *Grade No. 2-D*, a middle distillate fuel for diesel engine applications. Similar to No. 2-D diesel fuel are No. 2 fuel oil and No. 2-GT gas turbine fuel oil. *Grade No. 1-D* diesel is a light middle distillate fuel for use in diesel engine applications, which has higher volatility than that provided by No. 2-D diesel. The No. 1-D grade is similar to kerosene, 1-GT gas turbine fuel, and Jet A aviation turbine fuel.

There are also differences in the average quality of diesel fuel in different parts of the world. These differences arise from several reasons, such as crude oil type, balance between gasoline, jet fuel and diesel fuel demand, as well as local climatic conditions. One of the most striking differences is the cetane quality of US diesel fuel which is lower than that in other parts of the world. The main reason for the low cetane number is the high demand for gasoline relative to diesel fuel in the USA. Thus, US refineries have been configured for maximum gasoline production. As a result, diesel fuel in the USA contains higher fraction of cracked components of inherently low cetane quality (which are by-products of gasoline manufacture) and has lower distillation point than diesel in Europe or Japan.

Since the 1990s, fuel quality is further influenced by national and local regulations aimed at reducing emissions. Many countries introduce tax incentives for cleaner burning, better quality fuels (primarily lower sulfur, but also lower density, aromatics, higher cetane) to offset their higher production costs. Examples of fuel specifications and tax incentives in the 1990s are listed in Table 9 [Lee 1998].

Table 9
Diesel Fuel Specifications

	Sulfur	Cetane No.	Total Aromatics	Density	T90/95	Tax Incentive
	max ppm	min	max % vol.	g/cm^3	max °C	\$/ton
US No.2 (ASTM D975)	500	40	-	-	338	-
CARB[a]	500	40	10	-	338	-
EU 1996 (EN 590)	500	49	-	0.82-0.86	370	-
Japan No.2	500	45[b]	-	-	350	-
Japan No.3	500	45[b]	-	-	330	-
Sweden Class I	10	50[b]	5	0.80-0.82	285	97[c]
Sweden Class II	50	47[b]	20	0.80-0.82	295	54[c]
Finland Sw II	50	47[b]	20	0.80-0.82	295	34
Denmark Sw I	10	50/47[b]	5	0.80-0.82	285	85
Denmark City Bus	500	50	-	0.82-0.855	325	50
UK City Diesel	10	49[b]	-	0.80-0.83	-	37.5

a - or fuel must show emissions equivalent or better compared to CARB reference fuel of 500 ppm S, 48 cetane number, 10% aromatics, 1.4% polyaromatics, 0.83-0.86 g/cm^3 density, max T90 of 321°C.
b - cetane index
c - initial tax incentive at introduction (1991), current tax incentive lower (e.g. \$76/ton Swedish Class I in 1998)

Table 10 shows typical diesel fuel characteristics found in the USA, Japan and Germany during a fuel quality survey carried out in Winter 1994 [Owen 1995]. The survey values (“min”, “mean” and “max”) were generated from 20 (USA and Germany) to 26 (Japan) fuel samples. The survey data is compared with diesel fuel standards in the respective countries.

Table 10
Diesel Fuel Standards and Survey Data (1994)

Property	US East Coast				Japan Grade 2				Germany			
	ASTM D975	min	mean	max	JIS K 2204	min	mean	max	DIN 51601	min	mean	max
Density, kg/m^3 @15°C		833.2	846.4	851.9		823.1	835.0	844.5	820-860	824.9	834.3	844.6

Viscosity, mm^2/s @20°C									2.0-8.0	3.278	3.953	5.120
@30°C					2.5 min	3.092	3.859	4.872				
@40°C	1.9-4.1	2.066	2.348	2.711								
Sulfur, % m/m	0.05 max	0.013	0.027	0.036	0.2 max	0.068	0.154	0.194	0.2 max	0.051	0.124	0.196
Cetane number	40 min	41.7	44.9	49.8	45 min	47.0	54.9	59.0	45 min	48.0	51.6	53.6
Cetane index 1980 equation		43.5	45.1	50.2		52.8	55.7	58.0		47.8	50.2	53.9
1988 equation		43.3	45.2	50.1		52.7	56.5	59.9		48.2	50.2	53.8
Cloud point, °C		-19	-14	-7		-11	-5	-1		-13	-9	-6
Pour point, °C		-45	-29	-24	-7.5 max	-33	-16	-8		-41	-32	-26
CFPP, °C		-36	-22	-16	-5 max	-12	-9	-6	-15 max	-32	-28	-21
Wax*, % m/m		1.0	1.6	2.1		2.8	4.0	6.1		0.7	1.4	2.8
Distillation, °C									see **			
IBP		148	174	206		151	172	209		150	173	186
20%		209	221	229		215	242	260		198	216	235
50%		242	253	264		274	285	298		241	257	280
90%	282-338	305	312	322	330-350	318	336	347		309	328	363
FBP		340	344	352		339	360	375		329	355	388

* - 10°C below cloud
** - 65% max @250°C, 85% min @350°C

Effective 2005 (a year and a half before the switch to ultra low sulfur diesel in the USA), a diesel fuel lubricity specification of 520 microns wear scar diameter over the HFRR test has been added to the ASTM D975 diesel fuel standard.

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Ford Diesel HP FIE and Bio-diesel

6/21/2006

Ford Diesel Products and Biodiesel

What is Biodiesel?

Biodiesel fuel is a mixture of petroleum diesel fuel and fatty acid methyl esters (FAME) that were produced from a transesterification process of either vegetable oils and/or animal fats.

What are biodiesel fuel blends?

Biodiesel fuel is used in blends of 2% to as high as 100% biodiesel. These blends are signified by the what is commonly called the “B” factor, ex. B20 is fuel containing 20% biodiesel / 80% petroleum diesel and B100 is pure biodiesel.

Ford Diesel Products and Biodiesel

Biodiesel Fuel Properties to be aware of:

- Biodiesel requires special care at low ambient temperatures due to the excessive rise in viscosity and reduced fluidity properties
- Biodiesel is hygroscopic, indicating it tends to store more water than diesel fuel and water is not completely miscible in biodiesel
- Higher water content leads to increased corrosion of the internal components of the fuel system
- Higher water content can lead to microbial contamination and growth in the fuel resulting in increased filter clogging
- Higher water content during cold operation leads to ice crystallization providing a nucleation site for fuel gelling causing filter plugging in cold temperatures
- Biodiesel has a higher cloud point than petroleum diesel and can have issue with operation in cold weather
- Biodiesel has solvent properties that can release deposits in diesel fuel systems that were previously run on mineral based diesel fuels
- Biodiesel operation increases the amount of engine deposits

Ford Diesel Products and Biodiesel

Biodiesel vs. Fossil Fuels

Biodiesel fuels have both superior and inferior fuel qualities and properties compared to US Fossil Fuels

- **Cetane Number (Biodiesel > US Fossil Fuel)**
- **Aromatic % (Biodiesel < US Fossil Fuel)**
- **Water Content (Biodiesel > US Fossil Fuel)**
- **Lubricity (Biodiesel > US Fossil Fuel)**
- **Cold Properties (Biodiesel > US Fossil Fuel)**
- **Oxidation Stability (Biodiesel < US Fossil Fuel)**
- **Biological Growth (Biodiesel > US Fossil Fuel)**

Biodiesel challenges increase the technical challenge already encountered with fossil fuel development

Ford Diesel Products and Biodiesel

Steps taken to help development of Bio-Diesel Robust Engine

- Development of a Biodiesel specification for B20 that includes required fuel properties
- Request Bio-diesel compatibility of the HP Fuel system to levels of B20 in Fuel System specifications
- Submission of the Bio-diesel material compatibility sheet to the fuel system supplier and monitor material compatibility to those requirements
- Continue to work with the regulating agencies to improve fuel quality and help determine methods of industry regulation for fuel quality
- Communication with customers and fleets about Bio-diesel and usage in Ford products

Ford Diesel Products and Biodiesel

Recommendations for operation on biodiesel fuel:

- Verify that fuel supply meets the latest fuel specifications (EN14214 and ASTM D6751)
- Recommendation that fuel supplies and storage tanks are checked and maintained to verify the fuel meets the required fuel specifications listed above
- Follow the Owners Manual recommended service intervals and oil types for Biodiesel fuel operation:
  - Increased fuel filter change intervals in the vehicle
  - Increased water separator draining intervals
  - Oil type and change interval
  - Special cold weather storage and vehicle operation to ensure that the biodiesel fuels do not gel in the vehicle fuel system
  - Do not allow vehicle to sit off with B20 fuels for extended periods of time.

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• **Water Content**	**(Biodiesel > US Fossil Fuel)**
• **Lubricity**	**(Biodiesel > US Fossil Fuel)**
• **Cold Properties**	**(Biodiesel > US Fossil Fuel)**
• **Oxidation Stability**	**(Biodiesel < US Fossil Fuel)**
• **Biological Growth**	**(Biodiesel > US Fossil Fuel)**

Biodiesel challenges increase the technical challenge already encountered with fossil fuel development

Ford Diesel Products and Biodiesel

Steps taken to help development of Bio-Diesel Robust HP FIE Equipment

- Development of a Biodiesel specification for B20 that includes required fuel properties
- Request Bio-diesel compatibility of the HP Fuel system to levels of B20 in Fuel System specifications
- Submission of the Bio-diesel material compatibility sheet to the fuel system supplier and monitor material compatibility to those requirements
- Continue to work with the regulating agencies to improve fuel quality and help determine methods of industry regulation for fuel quality
- Communication with customers and fleets about Bio-diesel and usage in Ford products

Ford Diesel Products and Biodiesel

This materials compatibility sheet applies to the components and materials that come into contact with Bio-diesel.

Compatible	**Incompatible / Not Recommended**
Metals Stainless Steel Aluminium Iron Carbon Steel	**Metals** Brass Bronze Copper Lead Tin Zinc
Polymers / Elastomers Polyethylene Acryl & Epoxy (paints) PTFE – e.g. Teflon Polyamide Nylon Fluorocarbons – e.g. Viton	**Polymers / Elastomers** Hypalon (chlorosulphonated polyethylene) Polyurethane Polyvinyl Nitrile – e.g. Buna-N Natural rubber Polyvinylchloride - e.g. Tygon Fluorosilicone Polypropylene

Best knowledge to date. CPMT's are advised to discuss material selections / compatibility with biodiesel and biodiesel blends directly with their suppliers.

Ford Diesel Products and Biodiesel

If you choose to operate biodiesel fuels at your own discretion, taking these preventive steps can help avoid costly vehicle repairs and potential safety issues involving vehicle performance:

- Verify that fuel supply meets the latest fuel specifications (EN14214 and ASTM D6751)
- Recommendation that fuel supplies and storage tanks are continuously checked and maintained to verify the fuel meets the required fuel specifications listed above
- Installation of a low pressure fuel system pressure sensor in the fleet vehicles to warn the driver of fuel system pressure loss due to fouling/clogging of fuel system components especially filters
- Increased fuel filter change intervals in the vehicle
- Increased Water separator draining intervals
- Special cold weather storage and vehicle operation to ensure that the biodiesel fuels do not gel in the vehicle fuel system
- Do not allow vehicle to sit off with B20 fuels for extended periods of time.

Ford Diesel Products and Biodiesel

Current Product Summary

- 7.3L operation on Bio-diesel
  - LPFS pressure sensor up to 2002
  - HP fuel system more robust to low pressure conditions
- 6.0L operation on Bio-diesel
  - HP fuel system less robust to low pressure conditions
  - No ability to currently alert the customer to a low pressure condition in the LPFS
- 6.4L actions to improve operation on Bio-diesel
  - WIF alert to the customer (message center)
  - LPFS pressure switch (alert customer to low pressure condition)
  - Considered active alert to customer and active protection
  - Considering tracking customer WIF light on and pressure sensor low time

From: Ladd, John (J.R.)
Sent: Thursday, June 22, 2006 3:24 PM
To: Fulton, Brien (B.L.)
Subject: Ford Diesel Products and Biodiesel.ppt

Attachments: Ford Diesel Products and Biodiesel.ppt

My edits. I'm gone until after shutdown. Hopefully you will have gotten this through OGC for service.

Ford Diesel
Products and Biodi..

Ford Diesel Products and Biodiesel

6/21/2006

Ford Diesel Products and Biodiesel

What is Biodiesel?

Biodiesel fuel is a mixture of petroleum diesel fuel and fatty acid methyl esters (FAME) that were produced from a transesterification process of either vegetable oils and/or animal fats.

What are biodiesel fuel blends?

Biodiesel fuel is used in blends of 2% to as high as 100% biodiesel. These blends are signified by the what is commonly called the “B” factor, ex. B20 is fuel containing 20% biodiesel / 80% petroleum diesel and B100 is pure biodiesel. ***It is critical that this nomenclature does not get confused with the “E” system or E-diesel nomenclature and E-diesel in any form is not used in any Ford diesel product.***

Current Status

Recently efforts by the Engine Manufacturers Association (EMA) and American Society for Testing and Materials (ASTM) are underway to develop specifications for Biodiesel fuels and to gain acceptance for operation of these fuels in the marketplace. These specifications are currently being written, but If the ASTM specification or other specifications do not match manufacturers' requirements, then it is critical that customers or fleets are aware that compliance to these specifications does not assure manufacturer warranty.

Ford Diesel Products and Biodiesel

Biodiesel Fuel Properties to be aware of:

- Biodiesel requires special care at low ambient temperatures due to the excessive rise in viscosity and reduced fluidity properties (Cloud Point).
- Biodiesel oxidation stability is not controlled. Under prolonged time and temperature, it may breakdown resulting in fuel system issues.
- Biodiesel is hygroscopic, indicating it tends to store more water than diesel fuel and water is not completely miscible in biodiesel
  - Higher water content leads to increased corrosion of the internal components of the fuel system, including fuel tank.
  - Higher water content can lead to microbial contamination and growth in the fuel resulting in increased filter clogging
  - Higher water content during cold operation leads to ice crystallization providing a nucleation site for fuel gelling causing filter plugging in cold temperatures
- Biodiesel has solvent properties that can release deposits in diesel fuel systems that were previously run on mineral based diesel fuels
- Biodiesel operation increases the amount of engine deposits

Ford Diesel Products and Biodiesel

There have been many Biodiesel Initiatives and fleet tests that have resulted in field concerns. The most recent calamity was in Minnesota, December 2005, involving B2 (2% biodiesel) fuel:

- LAWS OF MN 2002 - CHAPTER 244 [S.F.No. 1495] requiring that diesel fuel sold in Minnesota contain at least 2% by volume of biodiesel (B2)
- The Minnesota Law was suspended due to the number of vehicle/engine problems resulting from the use of biodiesel.
- 62 percent of the Minnesota Trucking Association's fleet managers who responded to a December survey reported clogged fuel filters, engines failing to start, power loss on hills and roadside breakdowns.

Ford Diesel Products and Biodiesel

Biodiesel production and quality is completely uncontrolled, current specifications are deficient and almost completely unenforceable.

- Farm co-ops, local entrepreneurs and individual owners are starting production facilities all over the country, these facilities are currently unregulated.
- Even if proper fuel specifications were in place they would be unenforceable due to the diverse nature of the production infrastructure currently developing in the biodiesel industry.
- To date, Federal government agencies have not shown any desire to try and regulate this emerging industry infrastructure.

Ford Diesel Products and Biodiesel

If an operator chooses to operate biodiesel fuels, it is at their own discretion. Taking these preventive steps can help to avoid costly vehicle repairs and potential safety issues involving vehicle performance:

- Verify that fuel supply meets the latest fuel specifications (EN14214 and ASTM D6751)
- Recommendation that fuel supplies and storage tanks are continuously checked and maintained to verify the fuel meets the required fuel specifications listed above
- Installation of a low pressure fuel system pressure sensor in the fleet vehicles to warn the driver of fuel system pressure loss due to fouling/clogging of fuel system components especially filters
- Increased fuel filter change intervals in the vehicle from once every 2 oil changes to at least every oil change or less
- Increased Water separator draining intervals
- Special cold weather storage and vehicle operation to ensure that the biodiesel fuels do not gel in the vehicle fuel system

Ford Diesel Products and Biodiesel

Summary

Ford Motor Company recognizes the potential benefits that may be associated with the expanded use of high quality biodiesel fuel blends, but before Ford approves increased biodiesel content of the diesel fuel supply, Ford and biodiesel producers must:

- Ratify an industry specification and fuel quality control plan.
- Evaluate the aforementioned biodiesel fuels, in Ford vehicles to verify that these fuel blends do not have a negative impact on:
  - Performance
  - Durability
  - Compliance with emissions limits set by the regulating government agencies U.S. EPA and CARB.

Biodiesel by itself cannot meet Tier II emissions requirements without the addition of particulate filters and catalysts. Biodiesel fuel is not a key enabler to meet Tier II emissions standards.

Ford Diesel Products and Biodiesel

Summary cont.

- Ford supports use of up to B5 (5% Biodiesel) in Ford diesel products.
- Ford does not support operation of biodiesel content above B5 in any Ford diesel product.
- Biodiesel used in any Ford diesel products must, at a minimum, comply with the most recent specifications available (EN14214 and ASTM 6751).
- Manufacturers, including Ford, are determining what fuel specifications are required for B20 operation.
- Ford is studying product revisions required to support the use of Biodiesel up to B20 in future diesel products.
- Operation of biodiesel fuels greater than B5 is solely at the risk and discretion of the customer. Warranty is void if claim is associated with B20 use.
- Compliance of a Biodiesel fuel to an ASTM specification does not assure manufacturer warranty. B5 is the maximum permissible concentration.

From: Eeley, Scott (A.)
Sent: Thursday, February 24, 2011 8:10 AM
To: Fulton, Brien (B.L.)
Cc: Heggie, Forest (F.); Culler, Mary (M.E.)
Subject: FW: Compatibility of automotive materials in biodiesel

Attachments: sdarticle[2].pdf

Brien,

Are you familiar with this article?

Scott

From: Heggie, Forest (F.)
Sent: Thursday, February 24, 2011 8:05 AM
To: Eeley, Scott (A.)
Subject: Compatibility of automotive materials in biodiesel

Compatibility of automotive materials in biodiesel: A review
Fuel, Volume 90, Issue 3, p. 922-931, March 2011
A.S.M.A. Haseeb, M.A. Fazal, M.I. Jahirul, H.H. Masjuki
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Use of biodiesel in automobile can significantly reduce our dependence of fossil fuel and help reduce environmental pollution. However, there are concerns over the compatibility of currently used automotive materials in biodiesel. A few automobile manufacturers extended their warranty only to lower blends of biodiesel (e.g. B5). Higher blends (e.g. B50 or B100) are still not covered by warranty. In automobile fuel system, metallic materials like ferrous alloy and non-ferrous alloys, and elastomers come in contact with fuel. Biodiesel, having different chemical characteristics from diesel, can interact with materials in a different way. It can cause corrosive and tribological attack on metallic components and degrade elastomer parts. This paper attempts to present an overview of the work done so far on the compatibility of biodiesel with automotive materials.

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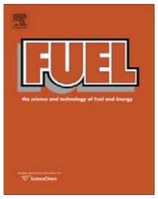

Review article

Compatibility of automotive materials in biodiesel: A review

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ABSTRACT

Use of biodiesel in automobile can significantly reduce our dependence of fossil fuel and help reduce environmental pollution. However, there are concerns over the compatibility of currently used automotive materials in biodiesel. A few automobile manufacturers extended their warranty only to lower blends of biodiesel (e.g. B5). Higher blends (e.g. B50 or B100) are still not covered by warranty. In automobile fuel system, metallic materials like ferrous alloy and non-ferrous alloys, and elastomers come in contact with fuel. Biodiesel, having different chemical characteristics from diesel, can interact with materials in a different way. It can cause corrosive and tribological attack on metallic components and degrade elastomer parts. This paper attempts to present an overview of the work done so far on the compatibility of biodiesel with automotive materials.

Contents

1. Introduction

Increasing population and growing demand of energy in the transportation sector are causing rapid depletion of fossil fuel reserve. High consumption of fossil fuel in automobile engine also causes environmental pollution. These facts have encouraged researchers to look for alternative fuels which promise a harmonious correlation with sustainable development, energy conversion, efficiency and environmental preservation. Biodiesel is such type of promising fuel which can meet all these necessaries.

There are many potential feedstocks available for use in biodiesel. These include various types of vegetable oils as well as animal fats. Common sources of biodiesel currently under investigation include soybean oil [1,2], sunflower, corn, used fried and olive oil [3,4], rapeseed oil [5–7], castor, lesquerella oil [8], milkweed (Asclepias) seed oil [9], *Jatropha* curcas [10], *Pongamia* glabra (Karanja), *Madhuca* indica (Mahua) and *Salvadora* oleoides [11], palm oil [12–14], linseed oil [15] etc. In general, biodiesel derived from these sources can be defined as mono-alkyl esters of long chain fatty acids [16]. The mono-alkyl esters that are the main chemical species of biodiesel, give its properties similar to diesel

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fuel [17]. It can be used in modern diesel engines in its pure form (B100) or may be blended with petroleum diesel [18].

Besides being renewable sources, biodiesel offers a number of distinct advantages. It is biodegradable, non-toxic, has higher flash point, causes reduced exhaust emission, eco-friendly with petroleum diesel fuel [19–21]. But at the same time, it also has some unfavorable characteristics like oxidative instability, poor-low temperature properties, solvent like property etc. It can provide slightly lower power and torque, and higher fuel consumption [22]. Distinctions between petrodiesel and biodiesel may be attributed to their variation of chemical nature. Petrodiesel is composed of hundreds of compounds boiling at differing temperatures (determined by the petroleum refining process and crude oil raw material) where as biodiesel contains a few compound-primarily C16–18 carbon chain length alkyl esters (determined entirely by the feedstock) [23]. Besides the major fatty ester components, minor constituents of biodiesel include intermediary mono- and di-glycerides and residual triglycerides resulting from the transesterification reaction, methanol, free fatty acids, sterols etc. [24].

The inherent characteristics of biodiesel have been found to cause a number of operational problems including materials incompatibility, severe engine deposits, injector coking, filter plugging, piston ring sticking [25,26]. Studies [27,28] shows that several characteristics of biodiesel like thermal instability, oxidation, polymerization, water absorption, increasing acid are the prime concern to ensure stable fuel properties during its application. Biodiesel compatibility with the currently used automotive materials is one of major concerns. Although a number of studies have been done to investigate the materials incompatibility issues, our understanding of interactions between biodiesel and automotive materials is far from being complete. The present paper attempts to review the results available in the literature on the compatibility of different types of metal in biodiesel.

In automobile applications, biodiesel comes in contact with a wide variety of materials which can be grouped in three major categories: (i) ferrous alloys, (ii) non-ferrous alloys, and (iii) elastomers. Metallic materials can undergo corrosion (chemical/electrochemical attack) and wear in biodiesel. Tribo-corrosion, which is the combined effect of corrosion and wear, may also affect metallic materials in biodiesel. Polymers like plastics and elastomers can undergo degradation in contact with biodiesel. In this paper, corrosion, wear and degradation of different automotive materials in biodiesel are reviewed. After the Introduction, chemistry of biodiesels which has important bearing on their interactions with materials is summarized (Section 2). This is followed by a section (Section 3) that outlines different types of materials that are used in automotive fuel systems. Section 4 reviews the studies on the corrosion of metals in biodiesel. Material wear in biodiesel is discussed in Section 5. Section 6 presents an overview of the degradation of elastomer materials in biodiesel. Finally some conclusions based on this review are presented.

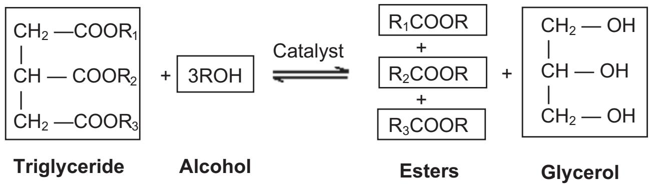


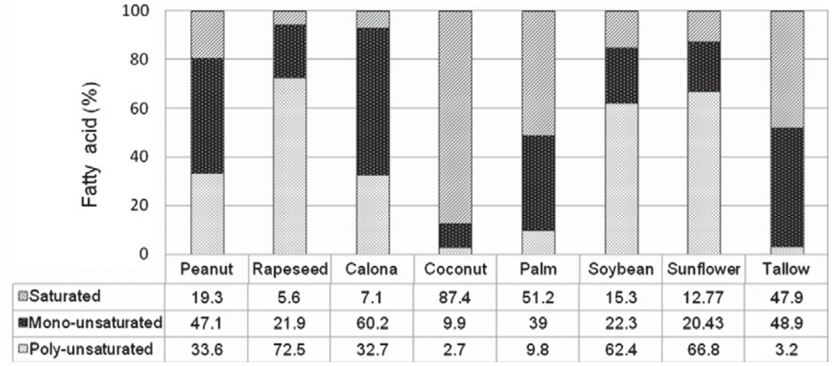
Fig. 1. Transesterification reaction for producing biodiesel (esters) from oil (triglyceride).

2. Chemistry of biodiesel

Vegetable oils/animal fats mainly consist of triglyceride molecules. The structure of one such molecule is shown schematically in Fig. 1 (left side).

R_1, R_2, and R_3 represent the hydrocarbon chains (more than 10 carbon atoms) of the fatty acid of the triglyceride. Glycerides make the oil thick and sticky with higher viscosity. In order to reduce the viscosity to make the fuel usable in a diesel engine, pure oil is converted from natural oil triglyceride into three mono-alkyl esters (three separated long chain carbon molecules) by transesterification as shown in Fig. 1. Glycerol is removed as by-product and esters are known as biodiesel. These esters have several acronyms to describe the short chain biodiesel fuels as SME (soyabean oil methyl ester), RME (rapeseed methyl ester), FAME (fatty acid methyl ester, encompasses oils from many sources: all types of vegetable oils and animal fats), POME (palm oil methyl ester) etc. The total ester content is a measure of the completeness of the transesterification reaction [17]. The content of esters for different types of biodiesel depends on the type of feedstock used to produce biodiesel. Fuel properties such as cetane number (CN), viscosity, cloud and pour points, degree of saturation depend on the verities and amounts of esters. The presence of impurities remaining after processing also affects the fuel properties. Therefore, properties of biodiesel are generally affected by the choice of feedstock and by degree of refinement. For biodiesel, as an alternative to diesel fuel, a higher CN is desirable whereas higher viscosity and higher cloud and pour points are undesirable.

The fatty acid profile of biodiesel is identical to that of its parent oil or fat [18]. Biodiesels obtained from different sources contain different types and amounts of unsaturated and saturated fatty acids. Unsaturated fatty acids with double bonds in their structures are more susceptible to oxidation. Fig. 2 shows the bar diagram of total amount of saturated and mono- and poly-unsaturated fatty acids in different types of biodiesel. It is seen that biodiesel from



	Peanut	Rapeseed	Calona	Coconut	Palm	Soybean	Sunflower	Tallow
▨Saturated	19.3	5.6	7.1	87.4	51.2	15.3	12.77	47.9
■Mono-unsaturated	47.1	21.9	60.2	9.9	39	22.3	20.43	48.9
▧Poly-unsaturated	33.6	72.5	32.7	2.7	9.8	62.4	66.8	3.2

Fig. 2. Saturated, mono- and poly-unsaturated fatty acid contents for different biodiesel. (Adapted from Ref. [29–31]).

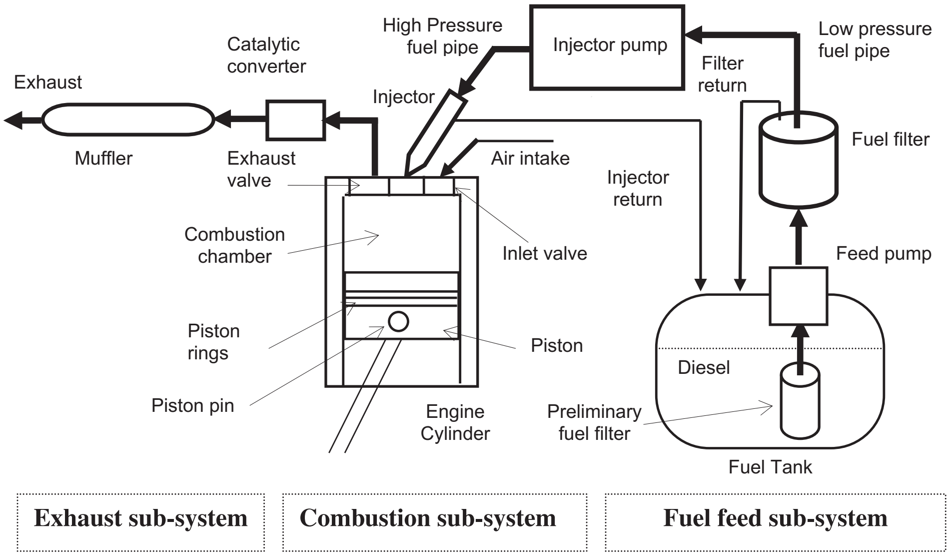


Fig. 3. Schematic diagram of a typical diesel engine fuel system.

Table 1
Comparison of oxidation properties of different biodiesels. (Adapted from Ref. [32]).

Property	Unit	Palm oil methyl ester (POME)	Rapeseed methyl ester (RME)	Soybean methyl ester (SME)
Oxidation stability	Hour	6.65	4.5	1.28
Iodine number		5.2	110	128
Methyl linoniate	Mass%	0.3	7.7	7.2

coconut oil, palm oil and tallow contain more saturated acids whereas biodiesel from soybean, sunflower, rapeseed, calona etc. contain more unsaturated fatty acids. Thus coconut or palm oil based biodiesel is expected to be less prone to oxidation than biodiesel from soybean or rapeseed. This has been verified in a recent study (Table 1) which shows that palm biodiesel remains stable for longer period during oxidation test.

3. Diesel engine fuel system materials

In diesel engine fuel system, fuel passes through three sub-systems: fuel feed, combustion and exhaust sub-system. Basic components of these sub-systems are shown in Fig. 3.

The fuel feed sub-system helps to draw fuel from the tank and to deliver it to the injectors of various cylinders. It consists of diesel tank, preliminary fuel filter, feed pump, filter, an injector pump, injectors and connecting lines. From tank, fuel feed pump delivers fuel to the injection pump through filter. The injection pump feeds high-pressure lines to the fuel nozzles for injection into the cylinders [33]. In in-line pumps and injectors, there is less reliance on the fuel for lubrication, however there are some sliding components at where fuel itself provides lubricity (e.g. plunger and barrel). In combustion zone, fuel is burnt once it is injected. This sub-system consists of cylinder block, cylinder liner, cylinder head, inlet valve, exhaust valve, piston, piston rings, piston pin and connecting rod. The piston compresses the air and raises its temperature above 500 °C. The diameter of the piston is slightly smaller then cylinder which allows the piston to slide up and down in the cylinder. To prevent the gap between piston and cylinder wall, piston rings are installed around the piston. The rings are split at single point. Engine exhaust system consists of mainly exhaust manifold, catalytic converter and muffler. After combustion the exhaust gas flows through the catalytic converter and the muffler. The catalytic converter converts most of the pollutant in the exhaust gas to harmless substances. The muffler reduces exhaust noise.

During the flow of fuel in different sub-systems, fuel comes in contract with a wide verity of metallic and non-metallic materials. Table 2 shows the types of materials commonly used in diesel engine fuel system. Metallic materials include ferrous like steel, cast irons and non-ferrous like aluminum alloys and copper alloys. Elastomer, plastics, paints, paper etc. are the most common non-metallic materials. Fuel comes in contact with these materials under different temperature, velocity, load as well as in different

Table 2
Typical materials used in the construction of diesel engine fuel system components [34,35].

Main parts	Components	Materials
Fuel tank	Housing	Steel, plastic, paint, coating
	Gasket	Elastomer, paper, cork, copper
Fuel feed pump		Aluminum alloy, iron based alloy, copper based alloy
Fuel lines	High pressure	Steel
	Low pressure	Plastics, rubber
Fuel filter	Filter cartridge	Paper
	Housing	Aluminum, plastic
Fuel pump		Aluminum alloy, iron based alloy, copper based alloy
Fuel injector		Stainless steel
Cylinder	Cylinder head	Gray cast iron, cast aluminum, forged aluminum
	Cylinder barrels	Gray cast iron, steel, cast aluminum
	Cylinder liner	Gray cast iron, aluminum
	Valves	Steel casting
Piston assembly	Piston	Sand-cast aluminum, die-cast aluminum, forged aluminum, gray cost iron
	Piston pin	Steel
	Piston ring	Special cast iron, steel
	Bearing	Copper alloy
	Connecting rod	Steel, aluminum alloy
Exhaust system	Exhaust manifold	Cast iron
	Exhaust pipe	Steel
	Catalytic converter	Stainless steel, ceramic fiber, aluminum fiber
	Muffler	Steel

sliding and physical state and thereby causes corrosion, wear, and degradation of metals.

4. Corrosion

Corrosion is the chemical/electrochemical attack of metals by certain environment. It is generally known that biodiesel are more corrosive than diesel. Corrosive characteristics of biodiesel are very important for long term durability of engine parts. Corrosion of metals can also trigger/catalyze other undesirable reactions leading the instability and degradation of biodiesel. ASTM D130 is currently used to measure the corrosion of biodiesel by copper strip tarnish test. During the test, copper strips are immersed into the sample being evaluated. At the end of the exposure period, the strips are compared to standardized reference strips and rated on a scale of slight tarnish 1A, B to heavy tarnish 4A–C [36]. Some test results available in the literature are summarized in Table 3. In most cases, such tests in biodiesel indicate 1A which represents marginal corrosion. It is thus seen that the results cannot distinguish between different types of biodiesel as well as different concentration of biodiesel in blends. Similarly, TAN value is another parameter measured by titration to indicate the total acid number. For biodiesel, the standard calls for a maximum acid number of 0.80 mg KOH/g [36]. The acid number is directly related to the free fatty acid content. Higher the free fatty acid content and is considered as a measure of corrosiveness of biodiesel. For biodiesel, total acid content increases as it is oxidized specially while in service. Besides, the acid number can become a serious issue when feedstocks with high free fatty acids are used to produce biodiesel.

It has been suggested that both of these indicators are not reliable indicators of the corrosiveness of biodiesel [43,44]. The corrosive nature of biodiesel can also stem from impurities like water, methanol, free glycerol, free fatty acid, catalyst (Na and K) remaining after processing and also from the reversibility of the chemical reaction which produces the esters. Under certain conditions, absorbed water can convert some of the esters back to fatty acid plus methanol. These acids can then react with metals and causes [43].

Very few research studies are available on the corrosion of metals in biodiesel. Haseeb et al. [45] investigated corrosion characteristics of copper and leaded bronze in palm biodiesel. They found that in biodiesel, copper was more susceptible to corrosion than leaded bronze. They also added that oxidized biodiesel was more corrosive than as-received biodiesel. Tsuchiya et al. [43] investigated corrosion of terne sheet steel by immersion in diesel and 5% FAME blended diesel fuel at 80 °C. Terne sheet is a Pb–8% Sn coated rolled steel sheet which is commonly used to fabricate fuel tank. After 500 h, they found pitting corrosion on the surface of the sample immersed in 5% FAME blended diesel (Fig. 4). They observed that corrosion occurred even in 2% FAME biodiesel. They opined that TAN value was not enough to explain the corrosive nature of FAME. They suggested that oxidation process reconverts esters into fatty acids such as formic acid, acetic acid, propionic acid, caproic acid which are highly corrosive.

Kaul et al. [11] have carried out static immersion test (300 days at 15–40 °C) to observe corrosion on piston metal and piston liner metal by using diesel and biodiesel derived from *J. curcas*, *P.* glabra (Karanja), *M.* indica (Mahua), *S.* oleoides (Pilu). They found that higher corrosion occurred in both *Salvadora* and *J. curcas* as compared with diesel. Corrosion in other biodiesel was similar to that in diesel. It was shown that liner metal was comparatively more affected than piston metal. However, the compositions of both components were not given in the paper. Based on the density given in the paper, it appears that the piston metal (density: 2.22 g/cm^3) is an aluminum alloy whereas the piston liner metal (density: 6.0 g/cm^3) is a ferrous alloy, probably a cast iron. It thus appears this study that aluminum alloy is more corrosion resistant in all the biodiesel tested. However, the corrosion rates of both metals were found to be within permissible limits.

Geller et al. [44] investigated the corrosion of a number of metals e.g. carbon steel, 316 stainless steel, gray cast iron, copper

Table 3
Cu strip corrosion test results.

Fuel	Experimental results	Test method	Ref.
Diesel	1A	ASTM D130	Kanneth Proc [37]
B20 (feedstock is not mentioned)	1A	ASTM D130	
B20 and B100 (feedstock is not mentioned)	1A for both B20 and B100	ASTM D6751	Mazzoleni et al. [38]
B100 (rapeseed oil based)	1A	ASTM D-130	Rashid et al. [16]
B100 (cottonseed oil based)	1A	ASTM D-130	Rashid et al. [39]
B20 (soybean oil based; oxidized)	1A	ASTM D130 (IP 154)	Terry [40]
B100 (rapeseed oil based)	1A	EN ISO 2160	Dinkov et al. [41]
B100 (ethyl soyate, methyl soyate)	1A	ASTM D-130	Clark et al. [42]

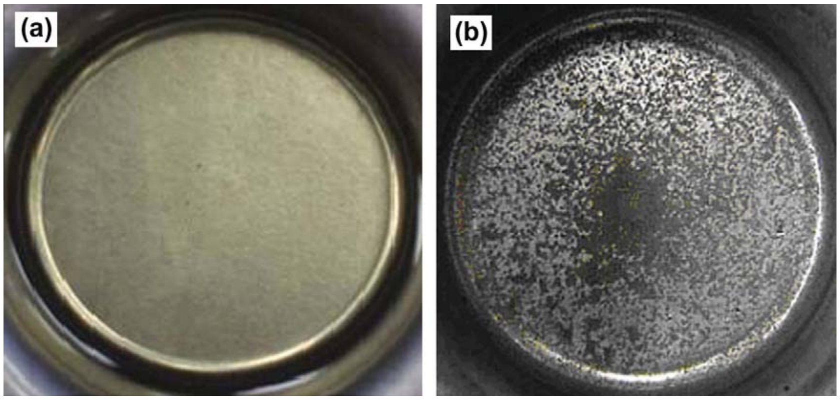


Fig. 4. Appearance of terne cup after immersion in (a) diesel and (b) 5% FAME for 500 h [43].

and admiralty brass in poultry fat–diesel mixture of different composition. They performed static emersion test at 38 °C for 10 months and observed that carbon steel and stainless steel did not undergo any weight loss during corrosion tests. Gray cast iron showed no weight loss in 20% biodiesel but moderate loss in 80% biodiesel. Among the materials tested, copper exhibited maximum weight loses followed by brass. Pitting was observed in copper and brass. Sgroi et al. [46] reported on the corrosive effect of biodiesel on sintered bronze filter of an oil nozzle. They observed that pitting corrosion occurred on bronze when the nozzle operated at 70 °C for several hours. Corrosive nature of biodiesel seems to be attributed to its free fatty acid components and impurities remaining after processing. In addition, biodiesel is hygroscopic in nature and can absorb moisture from air and thereby can increase the water content [47]. Free water in biodiesel is undesirable because it may promote microbial growth and corrode fuel system components [48]. Diaz-Ballote et al. [49] studied the corrosion of pure aluminum in canola based biodiesel by electrochemical technique. They observed that the corrosion rate of aluminum strongly depended on the level of impurities in biodiesel that originated from the transesterification process. Cleaning of biodiesel by washing greatly decrease the corrosion rate. A couple of studies [11,50] reported that the corrosiveness of biodiesel can be reduced by using additives.

In addition to the scientific literature, reports on materials compatibility issues are also available which are mainly produced by industrial stakeholders and government agencies. In one such report it has been suggested [51] that copper, brass, bronze, lead, tin and zinc are corroded by biodiesel. These elements accelerate oxidation of biodiesel and hence should be avoided in fuel system. Stainless steel, carbon steel and aluminum, on the other hand, have been suggested to be used in biodiesel.

Based on the studies done so far, it can be said that biodiesel is more corrosive than diesel. The corrosiveness of biodiesel increases with the concentration of biodiesel in the blend. Copper alloys are more susceptible to corrosion than ferrous alloys and aluminum alloys. Lead alloys on terne steel sheet are also affected by biodiesel. The presence of impurities and water increases the corrosion tendency of biodiesel. There are concerns that the currently used indicators of corrosiveness of biodiesel e.g. copper strip corrosion and TAN value that are prescribed by different standards are not effective enough. Clearly at present, there is a serious lack of scientific data on corrosion of automotive metals and alloys in biodiesel based on which confident decisions could be made. Corrosive nature of biodiesel under wide spectrum of compositional, environmental and operating variables should be investigated.

5. Wear analysis

Wear of materials in biodiesel received more attention of researchers than corrosion. Wear means removal of metal from the surface due to tribological contact. Abrasion, adhesion, corrosion, scuffing and additive depletion are the main mechanisms of wear in diesel engine. While abrasion, adhesion, scuffing involve mechanical damage of surfaces; corrosive wear or tribo-corrosion and additive depletion involve a series of chemical reactions resulting in wear. The most critical wear points in engine are cylinder liner, bearing, cam, tappet, crankshaft journals, pistons and piston pins, valve guides, valve systems etc. To investigate the comparative wear components in diesel and biodiesel, several laboratory investigations as well as wear tests in static engine and field trial have been done with various types and blend of biodiesel. The following laboratory wear test data will be discussed which will be followed by static engine tests and field trial data.

5.1. Laboratory wear test data

In order to understand the comparative wear in diesel and biodiesel, laboratory investigations were done by several researchers by using four-ball wear machine, pin-on-disk wear testing machine, high frequency reciprocating wear rig (HFRR) etc. Masjuki and Maleque [52] investigated the anti-wear characteristics of palm oil methyl ester (0%, 3%, 5%, 7%, and 10%) in lubricant. A conventional four-ball wear testing machine with different loads has been used at 1500 rev min^{-1} for 1 min at ambient temperature (∼28 °C). Results show less wear of EN31 steel ball at 5% POME (act as lubricant) as compared with 0% POME. But, more than 5% POME blended lubricant caused higher wear damage due to oxidation and corrosion.

In order to investigate the effect of biodiesel components on lubricity, Anastopoulos et al. [53] conducted an experiment with high frequency reciprocating rig (HFRR) in acetoacetic esters and di-carboxylic acid esters blended diesel. They observed that the wear scar diameter decreased with an increase in concentration of esters in diesel. Fazal et al. [54] investigated the effect of speed and palm biodiesel concentration on wear scar diameter and friction coefficient by four-ball wear machine. They found that wear scar diameter and friction coefficient increase almost linearly with increasing speed. On the other hand both wear scar diameter and friction coefficient decreased as concentration of palm biodiesel in the blend increased. Maleque et al. [55] showed the effect of temperature on the wear behavior under 5% POME blended lubricant. The specific wear rate (SWR) was found to increase as the test temperature increases. They also found that TAN number was increased with increasing temperature. According to Haseeb et al. [56], wear rate is comparatively decreased with increase of the concentration of biodiesel in diesel blends. However, lubricity of biodiesel at higher temperature is relatively decreased. This could be attributed to increase of oxidation rate as well as water content which may cause corrosive wear.

Lower wear rate in biodiesel is suggested to be due to the presence of fatty compounds in biodiesel [9,57]. Components found in biodiesel including fatty acid methyl esters, free fatty acids, monoglycerides were reported to improve the lubricity of biodiesel [58,59]. Oxygenated moieties [57], degree of unsaturation [58], long chain molecules [53] in biodiesel play an important role in increasing lubricity. According to Knothe and Steidley [57], the sequence of oxygenated moieties in enhancing lubricity is $COOH > CHO > OH > COOCH_3 > C{=}O > C{-}O{-}C$. Under normal condition, biodiesel offers higher lubricating property as compared to that in diesel due to its higher viscosity.

It has been reported that viscosity may be also increased due to oxidation and polymerization of the fuel constitutes [60]. Fuel dilution as a result of oxidation can also cause higher wear and friction loss in automotive parts [61]. Wain [62] investigated wear under both normal and oxidized conditions in low sulfur diesel and B20 (soybean) by four ball (steel ball) machine at 60 °C, 75 °C with sliding speed 600, 1200 rpm and load 1, 10, 40 kg. Under normal condition, they found that biodiesel showed less wear but in oxidized condition biodiesel possessed poor anti-wear property as compared to diesel fuel. Increasing oxygen content in low sulfur diesel fuel has shown reduced friction and wear properties than that in biodiesel. Normally, under oxidized condition, sulfur containing compounds serve as natural lubricity enhancers in fuels by forming lubricating film. But biodiesel contains very little or no sulfur and this might be one of the causes that are behind its poor anti-wear property under oxidized condition [62]. According to another explanation, oxidation can lead to the formation of corrosive acids which may cause increased wear of components [25].

Terry [40] investigated the wear of rotary pump components in rapeseed methyl ester (B5, B20) and soybean methyl ester (B5, B20, oxidized B5, oxidized B20) for 500 h. He reported that the rotary pump test in B20 oxidized soy biodiesel failed to reach full duration for test, stopping after 66 h. It was observed that at very high levels of oxidation biodiesel blends can separate into two phases causing fuel pump and injector operation problems. But the wear rate in B5 RMS and B5 SME was similar to that in diesel. However, for B5 SME oxidized, B20 RME and B20 SME, the wear rates were higher than that in diesel fuel.

Studies discussed above are mostly based on short term tests intended to investigate effect of biodiesel on lubricity. It is observed that in short term tests biodiesel offers beneficial properties in terms of lower wear and friction. Oxidation of the biodiesel and test temperature had been found to adversely affect the tribological properties of biodiesel. Currently very little laboratory data are available on the long term tribological properties of biodiesel. Effect of impurities in biodiesel needs special attention. Availability of scientific data as indicated above are expected to provide a basis for the effective prediction of the life for automotive components in biodiesel.

5.2. Wear test by static engine and field trial

Components used in diesel engine fuel system can be divided into following two groups. One is static components which include fuel tank, filter, fuel pump injector housing, fuel line, exhaust system, cylinder liner etc. Another one is dynamic components which include piston, piston rings, inlet and exhaust valve, fuel pumps and filters plunger, connecting rod etc. Dynamic components are usually metallic. These components slide on each other and also on static components during engine operations. Sliding contact between these metallic components is always accompanied by wear, which results in the generation of minute particles of metal. In a lubricated diesel engine system, wear particles are washed away by lubricating oil and remain in suspension in the lubricating oil. By analyzing the concentration of the metallic particle in the lubricant oil after running engine, sufficient information about wear rate, source of element and engine condition can be predicted. Since many sliding components are involved, various contaminant metals present in lubricating oil might have various source in engine. The most common metallic elements found in lubricating oil are aluminum (Al), chromium (Cr), copper (Cu), iron (Fe) and lead (Pb). Investigation of wear in automobile engine can be categorized into two types. (1) Static engine test in which, experiments are conducted in laboratory for a definite periods of time (h). After the test, oil is collected to investigate the wear debris. (2) On-road engine test in which, on-road diesel engine vehicles are run for a definite length of time or road distance (miles or km). At the end of test, oil is collected from oil sump for wear investigation [42,61–71]. Results obtained from different experiments for static engine and on-road vehicle are summarized in Tables 4 and 5 respectively. Including comparative wear rate in diesel and biodiesel, these tables also provide the information on biodiesel feedstock, types of biodiesel blend as well as engine/vehicle operating conditions. Elemental analysis based on different wear metals is presented in following sections.

Aluminum (Al): Source of aluminum in lube oil can be piston, cylinder. From Table 4, it is evident that biodiesel mainly causes similar or less Al wear in engine components as compared to that caused by petro diesel. Higher wear has also been reported for Al by several researchers. After 200,000 km field trial test with palm oil based biodiesel, Raadnui and Meenak [63] found more Al wear compared to that with diesel. Prateepchaikul and Apichato [64] run single cylinder diesel engine with B100 (100% palm biodiesel) in laboratory and found higher Al wear. Clark et al. [42] also observed higher wear in 100% ethyl soyate.

Chromium (Cr): Chromium debris may come from wear of cylinder wall/liner, piston, ring, valve, shaft, gear. Except the study conducted by Prateepchaikul and Apichato [64], all other studies

Table 4
Static engine test results on wear in biodiesel as compared with diesel.

Biodiesel	Sources	Engine operation hours	Wear elements					Ref.
			Al	Cr	Cu	Fe	Pb	
B100	Ethyl soyate	200	H	L	H	L	H	Clark et al. [42]
B100	Methyl soyate	200	L	S	L	L	H	
B20	Rapeseed	512	L	L	L	L	L	Agarwal et al. [61]
B100	Rapeseed	1000	L	L	–	L	L	Peterson et al. [68]
B50	Rapeseed	1000	L	L	–	L	L	
B100	Palm oil	1000	H	H	H	S	H	Prateepchaikul and Apichato [64]
B7.5	Palm oil	100	L	–	L	L	L	Kalam and Masjuki [70]
B15	Palm oil	100	L	–	L	L	L	

H = Higher, L = Lower, S = Similar wear, compared to that in diesel.

Table 5
On-road engine test results on wear in biodiesel as compared with diesel.

Biodiesel	Sources	Engine operation (km)	Wear elements					Ref.
			Al	Cr	Cu	Fe	Pb	
B100	Palm	200,000	H	L	H	L	H	Raadnui and Meenak [63]
B50	Palm	200,000	S	L	L	L	L	
B1	Soybean	166,000	L	L	H	S	L	Schumacher [65]
B2	Soybean	243,400	L	L	H	L	L	
B20	Rapeseed	164,000	L	L	H	L	L	
B50	Soybean	326,200	L	L	H	L	L	
B100	Soybean	161,000	L	L	H	L	L	
B100	Rapeseed	160,100	L	L	H	L	L	
B100	Rapeseed	30,000	–	–	–	L	–	Agarwal et al. [71]
B20	Soybean	161,000	–	S	S	S	–	Mazzoleni et al. [38]
B20	Soybean	965,606	L	L	L	L	L	Fraer et al. [66]
B100	Rapeseed	45,000	S	S	S	H	S	Daryl and Peterson [67]

H = High, L = Low, S = Similar wear, compared to that in diesel.

showed that wear of Cr in biodiesel was similar or less than that in diesel (Tables 4 and 5).

Copper (Cu): Copper in wear debris could be because of wear of the bearings, bronze, and bushing. Cu wear is one of the most significant issues for biodiesel run engine. Schumacher [65] presented wear data for B1 (1% biodiesel in diesel), B2, B20, B50 and B100 by field trial test. This study found higher Cu wear in soybean-diesel blend. Opposite result was reported by Fraer et al. [66] where low copper wear was observed in B20 soybean biodiesel. On the other hand, a couple of studies [38,66] reported no significant change of Cu wear in biodiesel. Raadnui and Meenak [63] used B100and B50 palm biodiesel to run diesel engine vehicles. After conducting 200,000 km test, they found more Cu wear in B100 biodiesel but less Cu wear in B50 biodiesel blend compared with that in petrodiesel. Similar to on-road vehicle test, contradictory results have also been reported on static engine test as shown in Table 5. Prateepchaikul and Apichato [64] found higher wear in B100 palm oil. Agarwal et al. [61] have found lower Cu wear in lower biodiesel blend. Clark et al. [42] reported higher Cu wear in methyl soyate but low wear in ethyl soyate as compared to that in diesel.

Iron (Fe): Iron in wear debris originated from wear of piston ring, cylinder head, piston, rings, valves, gears, shafts, rust and crankshaft. Daryl and Peterson [67] used 100% rapeseed biodiesel as replacement of petro diesel in field trial test. After 45,000 km run, this study found higher Fe wear as compared to that in petro diesel. Except this, no other studies found excessive Fe wear in biodiesel run diesel engine in both static engine and on-road vehicle test.

Lead (Pb): The probable source of lead in wear debris can be bearings, paint, coating and greases. In on-road vehicle test, Raadnui and Meenak [63] used B100 palm biodiesel and found higher concentration of Pb in lube oil. All other studies presented in Table 5 reported less or similar Pb wear in on-road vehicle tests in different biodiesel. In static engine tests, Clark et al. [42]; Prateepchaikul and Apichato [64] found higher Pb wear in 100% biodiesel.

It is seen that Fe, the main constituents of the most critical components in automobiles shows less or similar wear except one study conducted by Daryl and Peterson [67]. On the other hand, Cu shows higher wear in many cases. Similar or less wear is found for the metal Pb and Al in biodiesel. It is evident that non-ferrous metals suffer from higher wear loss compared with ferrous metals.

6. Elastomer degradation

The compatibility of seal and hose materials commonly used in automotive fuel systems using conventional hydrocarbon fuels (petrodiesel) has long been established. However, there is less information available on the compatibility of fuel system elastomers with biodiesel fuels. Concern arises from the fact that petrodiesel and biodiesel have much different chemical structures and consequent different effects on elastomers. Besides, biodiesel is susceptible to oxidation upon exposure to air as well as storage conditions and the amount of unsaturation of fatty acids. Being oxidized, it produces hydroperoxides at the unsaturated points of the fatty acids and these hydroperoxides later decompose to aldehydes, ketones, shorter chain carboxylic acids [57]. Esters, the main components of biodiesel, can also be easily hydrolyzed in the presence of water to form carboxylic acids. All these products including the chemical composition of biodiesel affect the swelling characteristic of elastomer depending not only on its composition but also on the formulation of the compound [72].

For diesel engine, usually hoses are produced from rubber modified polyolefin whereas gaskets are produced from gasket paper, non-asbestos, rubber, ethylene–propylene–diene monomer (EPDM), nitrile, Buna, neoprene, flexible graphite, viton, silicone, metal, mica, felt or plastic polymer, like Teflon® (PTFE), ethylene polymer etc. The common seal materials are polyurethane, nitrile rubber, Buna-N, EPDM, silicon rubber, virgin polytetrafluoroethylene (PTFE), aluminum etc. Many of these materials used in diesel engine are not compatible with biodiesel. Trakarnpruk and Porntangjitlikit [73] carried out immersion tests with six types of elastomers like nitrile rubber (NBR), hydrogenated nitrile butadiene rubber (HNBR), NBR/PVC, acrylic rubber, co-polymer fluoroelastomer (FKM), and terpolymer FKM in B10 (palm biodiesel) for upto 1008 h at 100 °C. They showed that mass and volume increased with respect to time for all test samples except NBR and NBR/PVC. Only for these two (NBR and NBR/PVC) mass and volume were decreased with time.

Materials compatibility may also vary depending on feedstock of biodiesel. Frame and McCormick [74] investigated the degradation characteristics of elastomers like peroxide-cured nitrile rubber (N1059), nitrile rubber (N674), high aceto-nitrile content rubber (N0497), fluorocarbon filled with carbon black (V747) and fluorocarbon without carbon black (V884) in diesel, diesel blend with 15% ethanol and 20% soy-derived biodiesel. They observed that these elastomers were fully compatible with B20 and diesel but not in 15% ethanol blend. Haseeb et al. [75] investigated the degradation behavior of different elastomers in palm biodiesel. After immersion, they found that tensile strength, elongation and hardness were significantly reduced for both nitrile rubber and polychloroprene while very negligible changes were found for fluoro-viton. In order to investigate the oxidation effect, Terry [40] conducted experiments with different types of elastomers like sulfur cured acrylonitrile butadiene nitrile rubber (NO674-70), peroxide cured acrylonitrile butadiene nitrile rubber (NB104-75), hydrogenated nitrile polymer (KB162-80), fluorocarbon polymer with 67% fluorine content (VB153-75), fluorocarbon polymer with 66% fluorine content (V1164-75) in different types of feedstock blends like rapeseed methyl ester (B5, B20) and soybean methyl ester (B5, B20, oxidized B5, oxidized B20). He found that NB104-75, NO674-70 and KB162-80 showed higher volume swell and little decrease in hardness in B20 oxidized SME. Dimensional changes were higher in oxidized B5 and B20. These results most likely proved that oxidized products caused comparatively more degradation of elastomers. Tensile strength was decreased for each elastomer only little in all the fuels. According to Baranescu [76] most of the elastomers used with conventional diesel swell by absorption of aromatic compounds. It is also reported in his study that biodiesel may leach aromatics as well as additives designed to prevent hardening and cracking.

Methylesters have been shown to swell trilobutyldilene and nitrile rubber, common automotive seal and gasket materials [77]. Fluorine containing elastomers do not exhibit significant swelling. Bessee and Fey [78] examined the effect of exposure to methyl soyester and diesel blends on the tensile strength, elongation, hardness and swelling of several common elastomers. They reported that nitrile rubber, nylon 6/6, and high-density polypropylene all exhibited changes in physical properties whereas Teflon®, viton® 401-C and viton® GFLT are unaffected. The general agreement is that fluorinated elastomers are hardly affected by biodiesel [72]. Based on the experimental data and field experience gained so far, some guidelines concerning the compatibility of different elastomer have been compiled in different sources. Some of these are presented in Table 6.

All these guideline suggest that fluorocarbon (e.g. PTFE), acetal etc. are compatible for use in biodiesel. Viton, EPDM etc. can also be used depending upon conditions. However, some common types of elastomer like nitrile rubber NBR, SBR, chloroprene, neoprene, natural rubber etc. are not suitable for use in biodiesel. Mechanisms of degradation of polymer in biodiesel are not well

Table 6
Elastomer compatibility.

Compatible	Medium compatible	Incompatible	Ref.
Teflon, carbon-filled acetal (CFA)	Viton	Wil-Flex, Buna-N, Nordel, polyurethane	Chem. Regis. Guide [79]
Fluorocarbon (FKM), Hiflur FKM, perfluoroelastomer (FFKM)	Ethylene propylene EPDM, butyl IIR, fluorosilicone (FVMQ)	Nitrile NBR, hydrogenated nitrile NBR, chloroprene CR/neoprene, styrene–butadiene rubber (SBR), hypalon CSM, butadiene rubber (BR), natural rubber	Parker O-Ring Handbook [80]
Chemraz, virgin, fluorocarbon, Teflon	Fluorosilicone, butyl, ethylene–propylene	Nitrile, styrene–butadiene rubber (SBR), Buna-N, natural rubber, hypalon, neoprene	O-ring Chem. Compa. Guide [81]

understood yet. The effects of fatty acid structure (e.g. degree of saturation and biodiesel purity) on elastomer compatibility do not appear to have been examined. Highly unstable free fatty acids as well as unreacted mono-, di-, and triglycerides, glycerol, and methanol may have a great impact on elastomers which require systematic investigations. These aspects of compatibility with elastomers are a topic for future research.

7. Summary and conclusions

Biodiesel has chemical characteristics that are distinct from that of petroleum diesel. It is therefore expected that they will interact with materials differently. Compositional differences of biodiesel derived from different feed stocks complicate the situation. In automobile fuel systems, numerous materials come in contact with fuel. These can be mainly grouped into ferrous alloys, non-ferrous alloys and elastomers. Among these groups of materials, elastomers undergo degradation to a greater extent in biodiesel. Common elastomers like natural rubber, nitrile, chloroprene/neoprene etc. are not suitable for use in biodiesel. Fluorocarbons have shown good resistance and are recommended for used in biodiesel. Exact mechanisms of degradation of elastomers in biodiesel and the effects of different biodiesel constituents require systematic investigations. Between the other two groups of materials, viz. ferrous alloys and non-ferrous alloys, the former are more resistant to attack in biodiesel. Among non-ferrous alloys, copper alloys and lead alloys are the most vulnerable which appear to be followed by aluminum.

Metallic components in automobiles can undergo corrosive, tribological or both forms (tribo-corrosion) of attacks depending on their functionality. Corrosion studies done so far suggest that biodiesel is more corrosive than diesel. However, there is no conclusive evidence as to whether the extent of corrosion encountered in biodiesel is within limits acceptable for automotive components. The corrosiveness of biodiesel increases with the concentration of biodiesel in the blend and the extent of oxidation. Copper alloys are more susceptible to corrosion than ferrous alloys and aluminum alloys. Lead alloy coating on terne steel sheet which is used for automotive fuel tanks is severely affected by biodiesel. The presence of impurities and water increases the corrosion tendency of biodiesel. There are concerns that the currently used indicators of corrosiveness of biodiesel e.g. copper strip corrosion and TAN value that are prescribed by different standards are not effective enough. Corrosive nature of biodiesel under wide spectrum of compositional, environmental and operating variables should be investigated.

As for the tribological degradation of metallic components in biodiesel, short term laboratory studies have shown that biodiesel offers beneficial properties in terms of lower wear and friction. However, oxidation of the biodiesel and higher test temperatures adversely affect its tribological properties. A number of long term wear durability tests have been conducted using static engine as well as on-road tests. Most of these studies mainly evaluated engine component wear in biodiesel in terms of the contents of different elements in lubricants. In general, these studies show low or similar wear for many elements in biodiesel compared with diesel. Fe, the main constituents of the most critical components in automobiles, shows less or similar wear, except for one study which involved higher blend (100%). On the other hand, Cu shows higher wear in many cases. Pb and Al follow copper in terms of decreasing trend in the number of studies where higher wear was reported for these metals. The lubricant analysis technique for wear evaluation provides only overall indication of the extent of wear. It does not furnish information on the extent of damage of individual components which is important in the prediction of component life. Such information can be obtained by examining the individual wear components in an engine. A handful of studies involving such engine teardown investigations did not find excessive in lower blends (⩽B20) of biodiesel as compared with diesel. However, higher wear was reported for piston rings in 100% biodiesel.

Clearly, at present, there is a serious lack of scientific data based on which confident decisions about the durability of automotive components particularly in higher blends could be made. Laboratory test and on-road vehicle test data available so far suggest that the metallic components made from ferrous alloys are perhaps not incompatible with lower blends of biodiesel. More data are necessary to comment on the long term durability of metallic components in higher blends. Systematic laboratory studies should be carried out under wide spectrum of experimental conditions that are likely to be encountered in practical conditions. Future studies should take into account the effects of metal–biodiesel interactions on the stability of biodiesel and vice versa.

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From: Harrison, Mike (M.J.)
Sent: Friday, August 05, 2005 3:43 PM
To: Koszewnik, John (J.J.); Waszczenko, Ed (E.W.); Bautz, Jeffrey (J.E.); Czapski, Mark (M.G.); Divakaruni, Ramana (R.); Eekhoff, Jeff (J.); Fulton, Brien (B.L.); Gomes, Enio (E.D.); Gryglak, Adam (A.J.); Hansen, Randy (R.F.); Ives, David (D.C.); Ladd, John (J.R.); Lingg, Dan (D.J.); Morgan, Patrick (P.B.); Ramey, Blaine (B.D.); Raquepau, Alden (A.P.)
Subject: FW: Information about refiner's plans for 15 ppm S Highway Diesel Fuel

Attachments: EPA 2004 summary.pdf

FYI

Mike Harrison
Chief Engineer, North American Diesel
Ford Motor Company
Desk/Cell (313) 805 4744

-----Original Message-----
From: Raney-Pablo, Beth (H.E.)
Sent: Thursday, August 04, 2005 5:44 PM
To: Harrison, Mike (M.J.); Davidson, Daniel (D.E.); Pearce, Steve (S.L.); Probus, Carla (C.A.); Herbert, Steve (S.A.); Kulik, Ed (E.C.); Trajnowski, John (J.T.); Beltramo, Joel (J.J.); Rocco, Julie (J.E.)
Cc: Misangyi, Pete (P.W.)
Subject: Information about refiner's plans for 15 ppm S Highway Diesel Fuel

At today's meeting I was asked to investigate refiners' plans for compliance with the 2007 highway diesel fuel rule and the impacts on the availability of 15 ppm sulfur diesel fuel.

As part of that regulation, EPA requires that "any refiner or importer planning to produce or import highway diesel fuel in 2006 must submit annual pre-compliance reports". These reports are due on June 1 of a given year with the final pre-compliance report due on June 1, 2005. EPA then publishes their analysis and summary of those pre-compliance reports.

Here are a few key points from EPA's analysis and summary of the 2004 pre-compliance reports.

- 95% of the highway diesel fuel produced in 2006 (or 2.6 million bbls/day) is anticipated to be 15 ppm sulfur highway diesel fuel. In the 2003 reports, the estimate was 96% or 2.8 million bbls/day. (Page 12)
- Most refineries will be producing 15 ppm highway diesel fuel exclusively or a mix of 15 and 500 ppm fuel. A few refineries plan to produce 100% of the 500 ppm sulfur fuel. However EPA's analysis indicates that all "of these refineries are in markets where 15 ppm fuel will be readily available from other sources. As a result, they should not create any 15 ppm availability problems." (Page 19)
- Approved small refiners may be allowed to continue "to produce and sell highway diesel fuel meeting the 500 ppm sulfur standard through May 31, 2010, provided that the refiner supplies information showing that sufficient alternate sources of 15 ppm sulfur highway diesel fuel will exist in the marketing area(s) that the refiner serves…If after 2004 the sources of 15 ppm sulfur highway diesel fuel decrease, the pre-compliance reports for 2005 must identify this change and must include a supplementary showing that the sources of 15 ppm sulfur highway diesel fuel are still sufficient." (Page 9)

EPA's analysis indicates that 15 ppm sulfur highway diesel fuel should be widely available. In addition, EPA's regulatory requirements for pump labeling further decreases the potential for incorrect vehicle fueling with 500 ppm sulfur fuel.

If you're interested in more detailed information about the pre-compliance reports, please refer to the EPA Summary and Analysis of Highway Diesel Fuel 2004 Pre-Compliance Reports (attached) or viewed directly from the EPA website at http://www.epa.gov/otaq/regs/hd2007/420r04014.pdf.

EPA 2004
summary.pdf

Regards,

Beth Raney-Pablo

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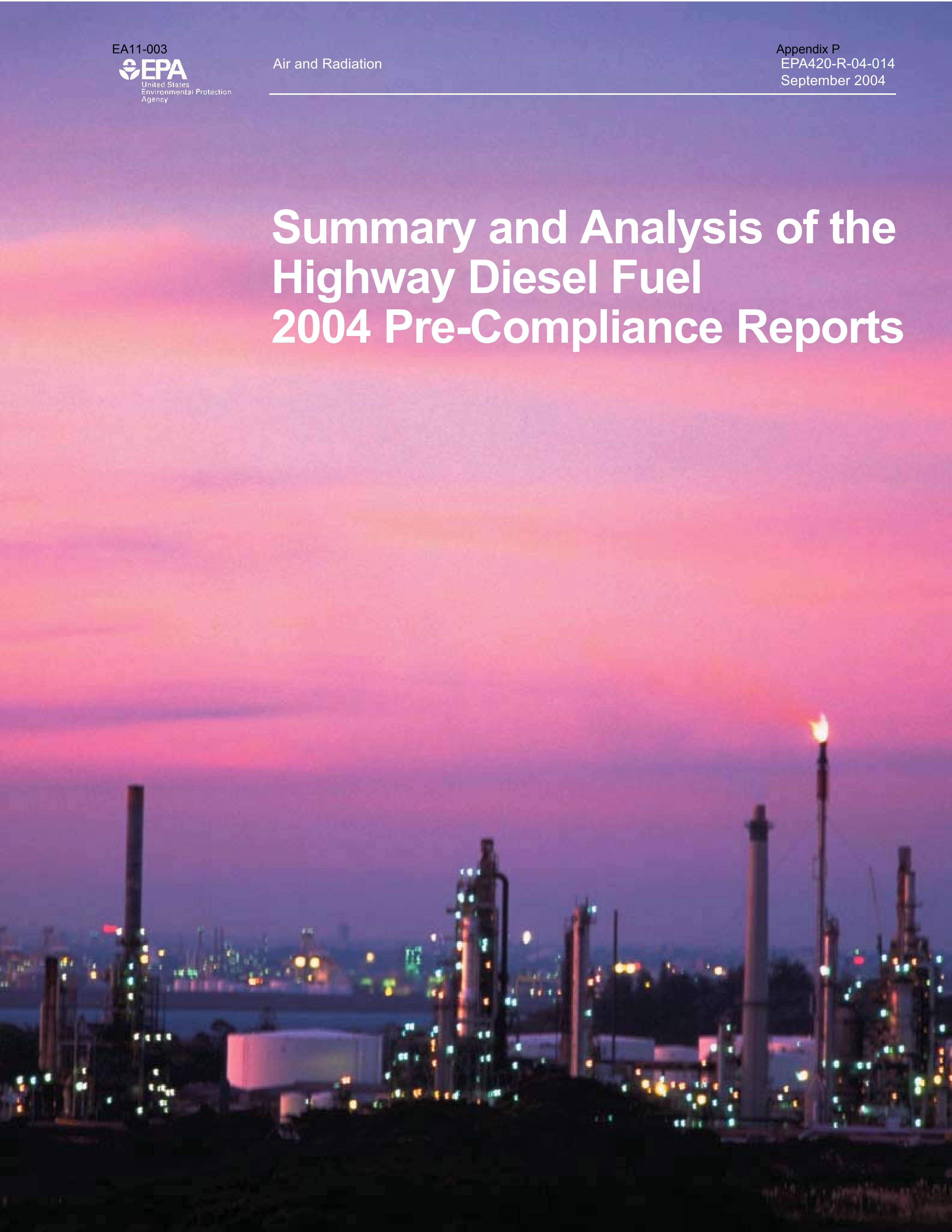
EA11-003

EPA
United States
Environmental Protection
Agency

Air and Radiation

Appendix P
EPA420-R-04-014
September 2004

Summary and Analysis of the Highway Diesel Fuel 2004 Pre-Compliance Reports



EPA420-R-04-014
September 2004

Summary and Analysis of the Highway Diesel Fuel 2004 Pre-compliance Reports

Assessment and Standards Division, Transportation and Regional Programs Division
Office of Transportation and Air Quality
Office of Air and Radiation
U.S. Environmental Protection Agency

NOTICE

This technical report does not necessarily represent final EPA decisions or positions. It is intended to present technical analysis of issues using data that are currently available. The purpose in the release of such reports is to facilitate the exchange of technical information and to inform the public of technical developments which may form the basis for a final EPA decision, position, or regulatory action.

Executive Summary

Any refiner or importer planning to produce or import highway diesel fuel in 2006 through 2010, is required to submit to the U.S. Environmental Protection Agency ("EPA" or "the Agency") pre-compliance reports by June 1 of each year. This report summarizes the results of the June 2004 pre-compliance reports. The first reports were due in June 2003; the final set of highway diesel reports will be due next June.

While individual refiners made a number of changes in their 2004 reports relative to their 2003 reports, on balance there was little overall change at both the nationwide and PADD level. The same general conclusions as in our 2003 summary report can be drawn this year. Specifically, the 2004 reports continue to indicate: 1) that refiners are on target for complying with the 15 ppm sulfur standard by June 2006, 2) that 15 ppm sulfur diesel fuel will be widely available nationwide with 95 percent of highway diesel fuel produced to the 15 ppm sulfur standard, and 3) that highway diesel fuel production will be sufficient to meet demand – refiners projected production exceeds the Department of Energy's Energy Information Administration's (EIA) projected demand. As shown in the report, planned total highway diesel fuel production appears to be in line with, or slightly above, projected demand. Hence, it appears that the refining industry as a whole is adequately planning for projected highway diesel demand through 2010.

The pre-compliance reports must contain estimates of the volumes of 15 parts-per-million (ppm) sulfur highway diesel fuel and 500 ppm sulfur highway diesel fuel that will be produced at each refinery or imported by each importer from June 2006 through May 2010. For those refineries planning to participate in the credit trading program, the reports must contain a projection of how many credits will be generated or used by each refinery. The pre-compliance reports must also contain information outlining each refinery's timeline for compliance with the 15 ppm sulfur standard and provide information regarding engineering plans (e.g., design and construction), the status of obtaining any necessary permits, and capital commitments for making the necessary modifications to produce 15 ppm sulfur highway diesel fuel. Similarly, for the new nonroad diesel rule, annual pre-compliance reports will be due on June 1 of each year beginning in 2005 and continuing through 2011.

This year, we received pre-compliance reports and/or information for all refineries that produced highway diesel fuel in the year 2003. Our conclusions here are based on the information provided in these reports which project data on fuel volumes, credit generation, and credit use plans as of June 1, 2004. The reports submitted for 2003 were projections that were based on more preliminary plans and several refiners changed their plans this year. While this year's pre-compliance reports may still reflect some preliminary information, as not all refineries have made final decisions on compliance plans at this point in time, we expect that most refinery plans are generally final or will be finalized in the very near future. Therefore, the 2004 pre-compliance reports should provide a more accurate prediction than the 2003 reports. Our summary and analysis of the pre-compliance reports for 2005 will be based on the pre-compliance reports that are submitted in 2005, and will therefore reflect updated information relative to the information that we received this year. However, given the status of most refiners, we expect fewer changes than occurred this year.

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I. Pre-compliance Report Requirements

The 2007 highway diesel final rule (66 FR 5002, January 18, 2001) requires that any refiner or importer planning to produce or import highway diesel fuel in 2006 must submit annual pre-compliance reports to the Agency.[a] Reports were due on June 1, 2003 and June 1, 2004; the final highway diesel pre-compliance reports will be due on June 1, 2005. Similarly, pre-compliance reports will be due annually on June 1 for the new nonroad diesel final rule (69 FR 38958, June 29, 2004), with the first of these reports also being due on June 1, 2005.[b]

The pre-compliance reports must contain the following information:

1. Any changes in the refiner's or importer's basic company or facility information since registration.
2. Estimates of the volumes of 15 parts-per-million (ppm) sulfur diesel fuel and 500 ppm sulfur (if applicable) diesel fuel to be produced from crude oil by each refinery and/or imported by each importer, as well as the volumes of each grade of highway diesel fuel produced from other sources.
3. Estimates of the numbers of credits to be generated and/or used, if at all.
4. Information regarding engineering plans (e.g., design and construction), the status of obtaining any necessary permits, and capital commitments for making the necessary modifications to produce ultra-low sulfur highway diesel fuel, and actual construction progress. Additionally, the reports summarized here, as well as the 2005 reports, are required to provide an update of the progress in each of these areas.

We recognize that the pre-compliance reports may still contain some preliminary information, as final decisions on desulfurization plans may not have been made in all cases as of the June 1 reporting deadline. Our conclusions from these reports are based on this preliminary information, and reflect some updated information from the 2003 pre-compliance reports.[1] Likewise, the Summary and Analysis of the Pre-compliance Reports for 2005 will be based on the pre-compliance reports that are submitted in 2005 and will reflect any new or updated information relative to the information that we received this year. While we expect that some information in this year's pre-compliance reports may still be somewhat preliminary, we do expect that the 2005 reports will contain finalized information for refiners plans for complying

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[a] The primary purpose of these reports is to help facilitate the market for credit trading under the highway diesel fuel program's temporary compliance option (TCO) which is described in the preamble to the 2007 highway diesel final rule at 66 FR 5065, January 18, 2001.

[b] The nonroad diesel fuel pre-compliance reports will be due beginning June 1, 2005, and will continue annually until June 1, 2011, or until the entity produces/imports nonroad (NR) or nonroad, locomotive, and marine (NRLM) diesel fuel meeting the 15 ppm sulfur standard.

with the rule. Given the lead time remaining and the status of most refiners, we anticipate fewer changes in the 2005 reports than are reflected in the 2004 reports.

In addition to the information listed above that is required for all refiners, small refiners and Geographic Phase-in Area (GPA) refiners must provide additional information in their pre-compliance reports. For small refiners, the required information varies according to which small refiner option the refiner plans to use. The following paragraphs summarize the supplementary information required for small and GPA refiners.

Small Refiners

In the highway diesel fuel regulations, a small refiner is defined as a refiner who 1) processes highway diesel fuel from crude oil; 2) employs no more than 1,500 people, based on the average number of employees for all pay periods for 1999; and, 3) has an average crude oil capacity less than or equal to 155,000 barrels per calendar day (bpcd).

The highway diesel final rule provided three alternative compliance options for refiners that qualify for small refiner status: 1) 500 ppm sulfur option, 2) small refiner credit option, and 3) diesel/gasoline compliance date option. A description of the additional reporting requirements for each of these options follows.

500 ppm Sulfur Option

The 500 ppm sulfur option allows an approved small refiner to continue to produce and sell highway diesel fuel meeting the 500 ppm sulfur standard through May 31, 2010, provided that the refiner supplies information showing that sufficient alternate sources of 15 ppm sulfur highway diesel fuel will exist in the marketing area(s) that the refiner serves.

The pre-compliance report for a small refiner planning to use this option must make a showing that sufficient sources of 15 ppm sulfur highway diesel fuel will likely exist in the area. If after 2004 the sources of 15 ppm sulfur highway diesel fuel decrease, the pre-compliance reports for 2005 must identify this change and must include a supplementary showing that the sources of 15 ppm sulfur highway diesel fuel are still sufficient.

Small Refiner Credit Option

Under the small refiner credit option, an approved small refiner that chooses to produce 15 ppm sulfur highway diesel fuel prior to June 1, 2010, may generate and sell credits under the TCO. Since small refiners have no requirement to produce 15 ppm sulfur highway diesel fuel prior to June 1, 2010, any fuel that they produce at or below the 15 ppm sulfur standard will qualify for credits under this option. (Additionally, the small refiner could then sell its remaining highway diesel fuel under the 500 ppm sulfur option described above.)

I. Pre-compliance Report Requirements

The pre-compliance reporting requirements for small refiners choosing this option are the same as those for the 500 ppm sulfur option (that is, if the small refiner is also producing 500 ppm sulfur highway diesel fuel), with the additional requirement that the refiner must also report on any credits it expects to generate and sell.

Diesel/Gasoline Compliance Date Option

Under the diesel/gasoline compliance date option, approved small refiners that are also subject to the Tier 2/Gasoline Sulfur program (40 CFR Part 80, Subpart H) may extend the duration of their applicable interim gasoline sulfur standards by three years (until January 1, 2011), provided that all of the highway diesel fuel that they produce meets the 15 ppm sulfur standard as of June 1, 2006.

Pre-compliance reports from any small refiners expecting to use this option must provide information showing that diesel desulfurization plans are on track for compliance with the 15 ppm sulfur standard by June 1, 2006. In addition to the information required above for all refiners regarding the expansion of desulfurization capacity, the pre-compliance reports for small refiners expecting to use this option need to reasonably show that the refiner will be in a position by June 1, 2006 to produce 95[c] percent its highway diesel fuel at the 15 ppm sulfur standard. Further, the refiner must show that its total highway diesel fuel production will be at least 85 percent of its highway diesel fuel baseline volume.

<u>GPA Refiners</u>

The GPA refiner option under the Tier 2/Gasoline Sulfur program, allows such refiners to extend the duration of their applicable interim gasoline sulfur standards by two years (until January 1, 2009), provided that they produce all of their highway diesel fuel at the 15 ppm sulfur standard beginning June 1, 2006.

Similar to the pre-compliance reports requirements for small refiners that choose to use the diesel/gasoline compliance date option described above, pre-compliance reports from refiners or importers expecting to use the GPA refiner option must provide information showing that their diesel desulfurization plans are on track. In addition to the information about the expansion of desulfurization capacity required above for all refiners, the pre-compliance reports for prospective GPA refiners need to reasonably show that the refiner will be in a position by June 1, 2006 to produce 95 percent of its highway diesel fuel that is compliant with the 15 ppm

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[c] In the nonroad diesel final rule, we changed the volume requirement (for small refiners and GPA refiners choosing the diesel/gasoline compliance option) from 100 percent to 95 percent to account for the change in volume determination from the point of production to the point of delivery. Consequently, refiners that were previously required to produce 100 percent of their highway diesel fuel to the 15 ppm sulfur standard are now provided with an allowance to deliver a small amount of 500 ppm sulfur diesel fuel to the next downstream party (e.g., pipeline).

sulfur standard and that its total highway diesel fuel production will be at least 85 percent of its highway diesel fuel baseline volume.

II. Summary Statistics

A. Nationwide Analysis

According to the Energy Information Administration (EIA), 160 refineries reported producing either high or low sulfur distillate (or both) fuels in 2000. Of these distillate-producing refineries, 115 produced highway-compliant diesel fuel (less than or equal to 500 ppm sulfur) in the year 2003.[d] This number includes data for four refinery/importers that are located outside of the continental United States (i.e., in the U.S. Virgin Islands, Puerto Rico, and Eastern Canada) whose production is targeted to the U.S. market. We received pre-compliance reports or information for all of the 115 refineries that produced highway-compliant diesel fuel in 2003.

In addition to the reports that we received from current highway diesel fuel producers, we received reports from six refineries that plan to enter the market at some point before 2010. Of these six refineries, four will be entering the market in 2006, one in 2007, and the last will be entering the market in 2009.

The reported totals for all refineries and importers planning to produce highway diesel during and after the first year of the TCO (2006) are presented and summarized in Tables 1 and 2, below. These tables show that for 2006, 110 refineries reported that they intend to produce an estimated total volume of 2.8 million barrels per day (bbls/day)[e] of highway diesel fuel (15 ppm sulfur + 500 ppm sulfur). Over 2.6 million bbls/day, or 95 percent of the national total, is anticipated to be 15 ppm sulfur highway diesel fuel, with the remaining five percent meeting the 500 ppm sulfur highway diesel fuel standard. This projection is just slightly less than what was projected in the refinery pre-compliance reports for 2003. In last year's reports, it was anticipated that 111 refineries would produce 2.9 million bbls/day of total highway diesel fuel, with 96 percent of that fuel meeting the 15 ppm sulfur standard.

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[d] In our Summary and Analysis of the Highway Diesel Fuel 2003 Pre-compliance Reports, we reported 114 refineries producing highway diesel fuel in 2003. Subsequent to the publication of that report, we received a late pre-compliance report from an additional refinery that had been producing highway diesel fuel in 2003. In this report, the number of refineries for 2003 has been adjusted from 114 to 115 to reflect that late submission.

[e] Diesel fuel volume information was submitted in units of gallons per year pursuant to the pre-compliance reporting requirements under § 80.594. Since the compliance periods in 2006 and 2010 are not full years, we converted the reported values which were in units of gallons per year to equivalent barrels per calendar day to compare the aggregated volumes and credits on an equal basis from 2006 through 2010. Volumes and credits were converted from an annual basis to a daily basis by dividing by the number of days in each compliance period, and then converted from gallons to barrels by dividing by 42 gallons/barrel. The aggregated volumes and credits for 2006 were divided by 214 days (the 2006 compliance period is from June 1, 2006 through December 31, 2006), and the aggregated volumes and credits for 2010 were divided by 151 days (the 2010 compliance period is from January 1, 2010 through May 31, 2010).

Over the duration of the TCO, refineries plan to generate approximately 1.7 million bbls/day of credits. They have plans to use over 264 thousand credits. The remainder of the credits would be available to respond to any unplanned compliance difficulties.

The following sections discuss this information in more detail.

1. Number of Refineries and Importers

In the highway diesel final rule, we evaluated compliance costs for refiners to produce 15 ppm sulfur highway diesel fuel under two scenarios: 1) all current producers of highway diesel fuel continue to do so, and 2) some refineries increase production of highway diesel fuel while some refineries shift out of the highway diesel fuel market due to relatively high desulfurization costs. To be conservative, our cost projections for the highway diesel final rule were based on the first scenario. However, we also performed a sensitivity analysis based on the second scenario. Under this scenario, some refineries that currently produce relatively small volumes of highway diesel fuel would face relatively high costs per gallon to desulfurize a given volume of diesel fuel. At the same time, other refineries that currently produce no (or a relatively small volume of) highway diesel fuel could convert their diesel production from high sulfur (i.e., greater than 500 ppm sulfur) down to 15 ppm sulfur at a relatively low cost. Consequently, in our sensitivity analysis we projected that a number of refineries would shift into or significantly expand their presence in the highway diesel fuel market. The pre-compliance reports appear to be supporting this projection.

As shown in Table 1, below, 110 refineries reported that they intend to produce highway diesel fuel in 2006 (this is down one refinery from the 111 refineries that were projected in the 2003 pre-compliance reports). It is anticipated that four refineries will enter the highway diesel fuel market and nine will shift out of the highway diesel fuel market in 2006; for an overall decrease in the number of refineries, but an overall increase in volume, as shown in Table 2.

Of the nine refineries that anticipate shifting out of the market, one refinery reported that it intends to transport and desulfurize their fuel at another location. As such, its highway diesel production will not be lost from the market. An additional refinery, the Shell Bakersfield refinery, is being shut down due to declining crude oil supplies for the refinery.[2] Five refineries noted that they are studying options on whether or not to desulfurize their higher sulfur fuel to 15 ppm. The remaining two refineries did not state their intentions for desulfurization, though it is likely that these refineries will shift into the nonroad diesel fuel market.

While some refineries may be shifting out of the highway diesel fuel market, others are planning to shift into the market. The pre-compliance reports project that some refineries will shift into the market during the TCO (four in 2006 and two more by 2010), resulting in a total of 114 refineries that will be producing highway diesel fuel in 2010. Though small refiners have the option to delay desulfurization until the year 2010, the reports indicate that currently only five refineries owned by small refiners plan to utilize this option.

Approximately two-thirds of the reporting refineries are planning to increase production of highway diesel fuel in 2006 compared to their 2000 production (based on EIA), and one-third of refineries are planning to decrease production.

Table 1.
U.S. Aggregated Report Information
Highway Diesel Fuel Refinery Statistics 2006-2010

Year	2003	2006	2007	2008	2009	2010
# refineries producing highway diesel fuel	115	110	112	112	113	114
# refineries at 100% 15 ppm		87	89	88	91	97
# refineries at 100% 500 ppm	115	12	12	12	11	9
# refineries with 15/500 ppm mix		11	11	12	11	8
# refineries increasing production (vs. 2003)		76	81	80	80	86
# refineries shifting into the highway market		4	5	5	6	6
# refineries decreasing production (vs. 2003)		43	39	40	41	35
# refineries shifting out of the highway market		9	8	8	8	7
# refineries generating credits		57	58	58	60	
# refineries using credits		6	5	5	4	3

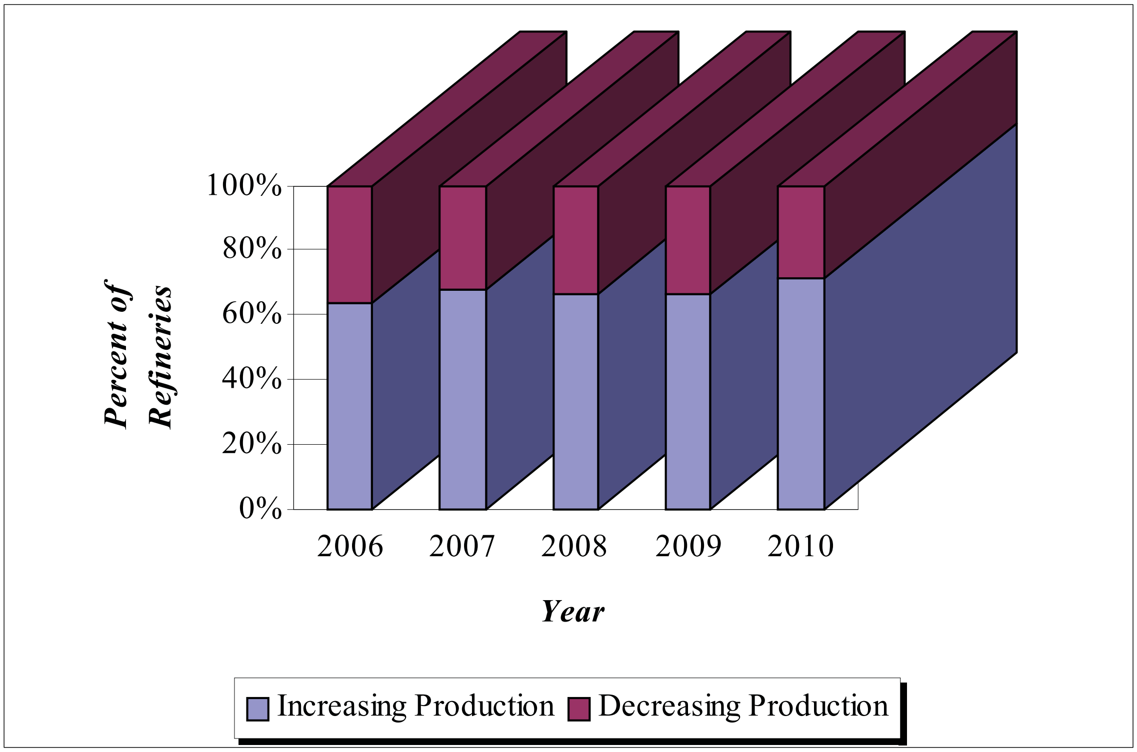

Figure 1. Number of Refineries Increasing or Decreasing Production Relative to the Year 2003

2. Production Versus Consumption

Table 2, below, shows the projected total production of highway diesel fuel for 2006 through 2010. The pre-compliance reports project that approximately 2.8 million bbls/day of highway diesel fuel will be produced in 2006. This volume increases to just over 3.0 million bbls/day for 2010. These volume projections are likely conservative given the fact that not all imported highway diesel fuel has been accounted for due to lack of reporting from spot market importers. We estimate that approximately two percent of the total highway diesel fuel supply is currently unaccounted for based on the pre-compliance information received to date.[f]

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[f] In 2000, approximately 2.6 million bbls/day of highway-compliant (less than or equal to 500 ppm sulfur) diesel fuel were supplied in the U.S. Of that total supply, imports accounted for 134 thousand bbls/day or 5.2 percent. The refineries located outside of the U.S. from which we received pre-compliance reports produced approximately 76 thousand bbls/day, or 57 percent of the total volume of highway-compliant diesel fuel that was imported in 2000 and about three percent of the total volume of highway-compliant diesel fuel that was supplied in the U.S. in 2000. Therefore, approximately 43 percent of imports or two percent of the total supply of highway

(continued...)

II. Summary Statistics - Nationwide Analysis

For 2006, on a volume basis, the 76 refineries that anticipate increasing their production of highway diesel fuel reported a cumulative increase in their highway diesel fuel production volume of approximately 699 thousand bbls/day, and the 43 refineries planning to decrease production of highway diesel fuel reported a cumulative decrease in their highway diesel fuel production volume of over 466 thousand bbls/day. This results in a projected net increase of 233 thousand bbls/day of highway diesel fuel produced in 2006. As shown in Figure 2, this growth continues into the future, reaching a projected net increase of 544 thousand bbls/day in 2010.

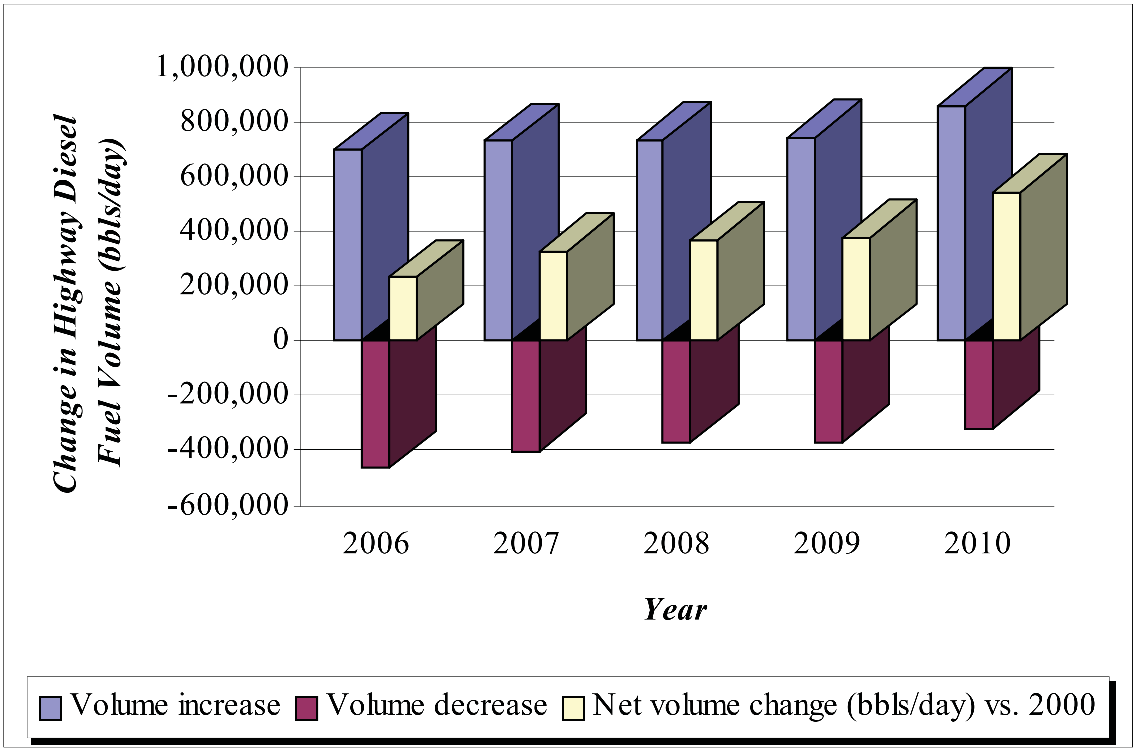

Figure 2. Nationwide Highway Diesel Fuel Volume Change vs. 2000

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[f](...continued)
diesel fuel is currently unaccounted for based on the pre-compliance information received to date.

Table 2.
U.S. Aggregated Report Information
Highway Diesel Fuel Volume and Credits 2006-2010[g]

Year	2006	2007	2008	2009	2010
Total 15 ppm, bbls/day	2,637,120	2,730,429	2,767,278	2,808,308	3,022,236
Total 500 ppm, bbls/day	140,928	144,764	146,604	113,780	67,311
Total 15 + 500 ppm, bbls/day	2,778,048	2,875,193	2,913,882	2,922,087	3,089,547
Net volume change vs. 2000 bbls/day	232,544	329,689	368,377	376,583	544,043
% change from 2000 highway volume	9.1	13.0	14.5	14.8	21.4
% 500 of total 15 + 500 ppm	5.1	5.0	5.0	3.9	2.2
Credit generation, bbls/day	415,245	420,006	424,627	433,476	
Credit usage, bbls/day	68,985	67,008	67,019	41,088	20,225

While the pre-compliance reports and this summary report are focused on projected highway diesel fuel production values, EIA's Annual Energy Outlook (AEO) reports projected energy consumption values by sector and source in quadrillion British Thermal Units (Btu) per year. In AEO 2004,[3] consumption values were projected for distillate fuel in the transportation sector for the years 2005 and 2010. We assumed a linear growth rate from 2005 until 2010 to estimate values for 2006 through 2009. We then converted these values to bbls/day by dividing by 138,700 Btu/gal[4] and 365 days per year. Results of this analysis are shown in Table 3, below. The resulting EIA-based consumption projections are compared against the pre-compliance report production projections in Table 3 and Figure 3, below. As shown below, planned total highway diesel fuel production appears to be in line with, or slightly above, projected demand. Hence, it appears that the refining industry as a whole is adequately planning for projected highway diesel demand through 2010.

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[g] The base year for the highway diesel fuel refinery statistics is 2003 as shown in Table 1, above. However, consistent with the Summary and Analysis of the Highway Diesel Fuel 2003 Pre-compliance Reports, the base year for the highway diesel fuel volume statistics is 2000, as shown in Table 2, above, because refinery distillate production data were not yet available to the Agency for calendar year 2003 at the time of publication of this report.

II. Summary Statistics - Nationwide Analysis

Table 3.
Projected Production of Highway Diesel Fuel vs. Estimated Demand

Year	2004 Total Reported Production (000 bbls/day)	Estimated Demand 2004 AEO (000 bbls/day)
2000	2,560	
2006	2,778	2,711
2007	2,875	2,788
2008	2,914	2,864
2009	2,922	2,941
2010	3,090	3,017

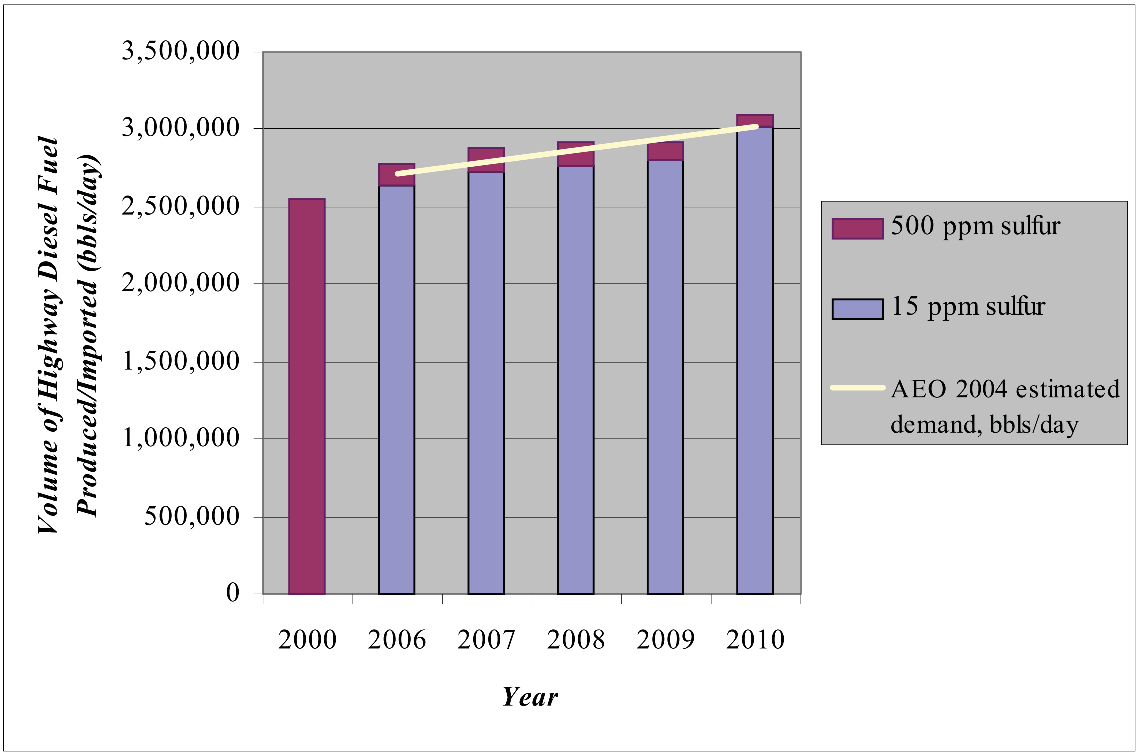

Figure 3. Projected U.S. Diesel Fuel Production and Demand, 2006-2010

3. Availability of 15 ppm sulfur Highway Diesel Fuel

The pre-compliance reports show that 15 ppm sulfur diesel fuel will be widely available. As shown in Figure 4, of the 110 refineries planning on producing highway diesel fuel in 2006, 87 refineries will be producing 100 percent 15 ppm highway diesel fuel. Another 11 plan to produce a mix of 15 and 500 ppm fuel, and three refineries will be using credits until May 31, 2010 to meet the standard. Only 12 are planning on producing exclusively 500 ppm fuel. Upon analyzing the data, we found that all 12 of these refineries are in markets where 15 ppm fuel will be readily available from other sources. As a result, they should not create any 15 ppm availability problems.

As shown in Figure 5, on a volume basis, it is anticipated that 95 percent of the volume of highway diesel fuel that will be produced in 2006 will meet the 15 ppm sulfur standard which is virtually identical to the volume predicted in the 2003 pre-compliance reports.

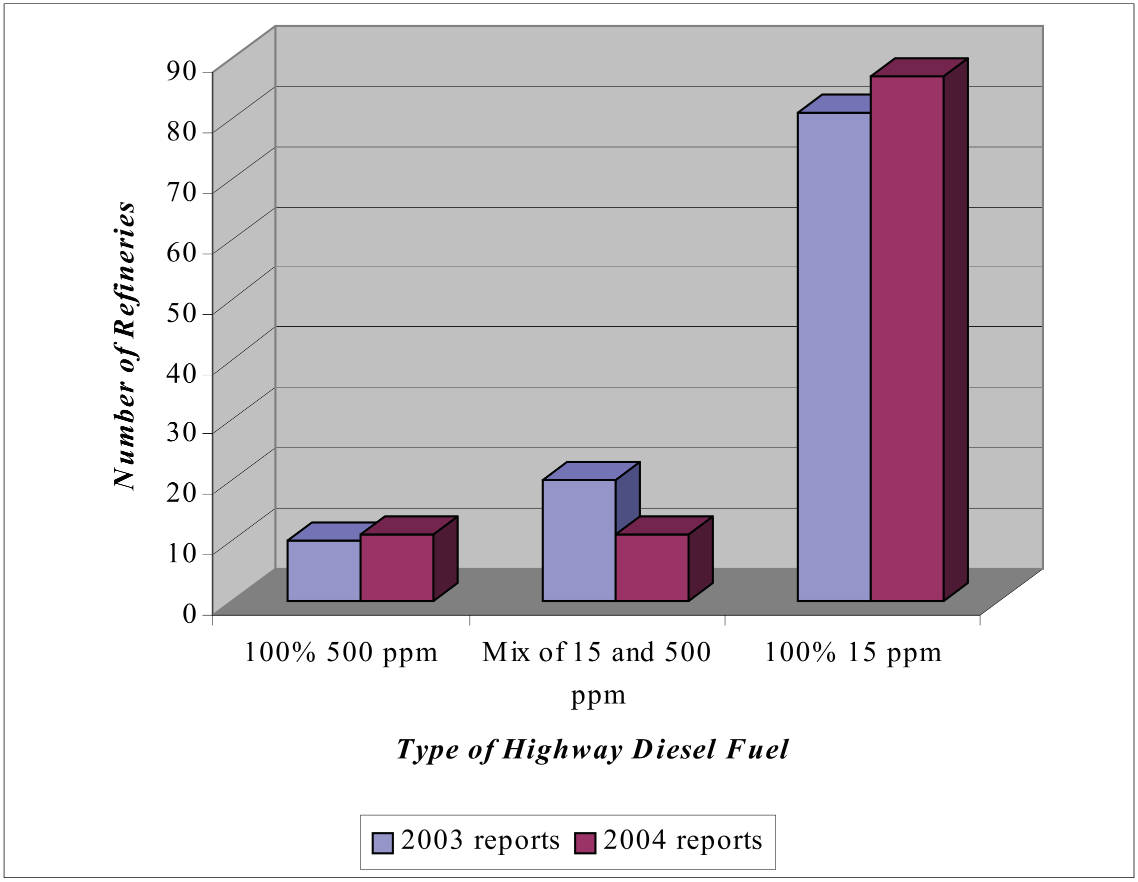

Figure 4. Number of Refineries Producing Highway Diesel Fuel in 2006

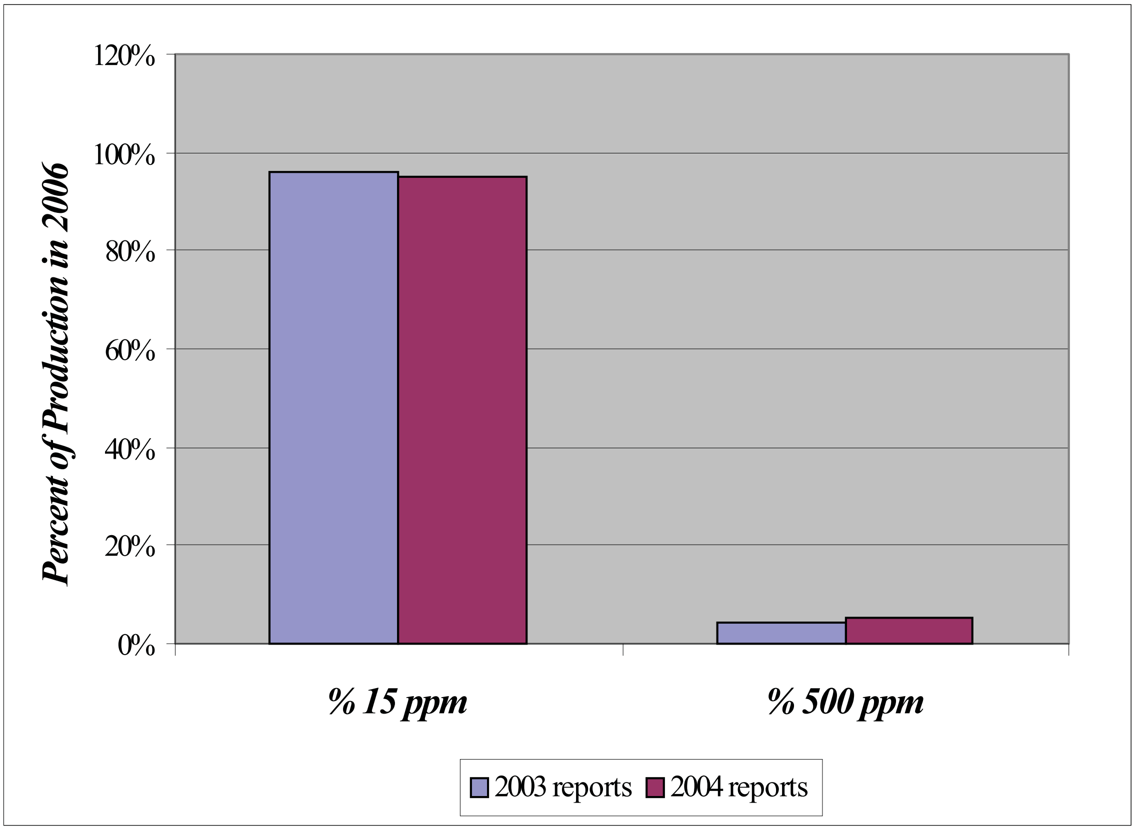

Figure 5. Highway Diesel Fuel Grades by Percent of Production Volume, 2006

In the highway diesel final rule, we projected that 15 ppm sulfur highway diesel fuel would be available nationwide with 80 percent of the highway diesel fuel market converted to the 15 ppm sulfur level. With 95 percent of the market projected to be 15 ppm sulfur highway diesel fuel, we can have even greater confidence in the fuel's nationwide availability.

4. Projected Credit Generation and Use

Given that the majority of highway diesel fuel is anticipated to meet the 15 ppm sulfur standard, a large credit volume is expected within each PADD, as shown in Table 4. This large credit volume will help to accommodate off-spec distillate material and will also provide a supply "safety valve" by allowing for an additional volume of 500 ppm sulfur highway diesel fuel without violating the TCO requirements. In 2006 a total credit generation of 415 thousand bbls/day is expected to be generated, while approximately 69 thousand bbls/day are expected to be used. The projected volume of credits used decreases to 20 thousand bbls/day by 2010. Over the course of the TCO, credit generation (1,693,354) continues to far exceed credit use (264,327).

Table 4.
Projected Volume of Credits (bbls/day)
Generated and Used by PADD, 2006-2010

Credits (*bbls/day*)	PADD 1	PADD 2	PADD 3	PADD 4	PADD 5	Total US
Generated	211,353	429,101	959,731	22,455	70,716	1,693,354
Used	0	(27,617)	(216,483)	0	0	(264,327)
Net	**211,353**	**401,484**	**743,246**	**22,455**	**70,716**	**1,429,029**

At this point in time, it is too early to reach any definite conclusions regarding the extent to which refineries will use credits for compliance purposes or the extent to which they will make the credits that they generate available for purchase by other refineries. This information will become clearer with time as the program's implementation date becomes closer. However, from the reported data that we received, a total of six refineries anticipate that they will be using credits in 2006 to meet the standards. This number decreases to three refineries by 2010.

5. Project Timing

In addition to providing highway diesel fuel volume and credit projections, refineries must also include information outlining both their timeline for compliance with the 15 ppm sulfur standard and their engineering plans (e.g., design and construction) in their pre-compliance reports. The 2003 pre-compliance reports indicated that most companies were in the planning stage and expected to make final decisions before the first quarter of 2004.

For this year's pre-compliance reports, we requested that refineries report more specific information to us on the status of their highway diesel fuel compliance plans. We provided refineries with the following five stages on which to report: 1) strategic planning, 2) planning and front-end engineering, 3) detailed engineering and permitting, 4) procurement and construction, and 5) commissioning and start-up. As this new reporting requirement was not requested until May (via the nonroad diesel final rule), not all refineries were able to report their data according to these five stages.

Of the 104 refineries that reported some information on their project timing, nearly 80 percent reported that they have completed the strategic planning stage, while the remaining few were still in this stage at the time of reporting.

As with the strategic planning stage, the majority of the refineries reported that they had either completed the planning and front-end engineering stage or would be doing so in the very near future (third or fourth quarter of 2004). Various reasons were reported for the remaining refineries that had not yet completed this stage, such as: no additional work would be needed at the refinery (already producing 15 ppm sulfur diesel fuel), the refinery will be importing 15 ppm sulfur diesel fuel, or the refinery will only be producing high sulfur (over 500 ppm) diesel fuel.

Of the refineries that reported information for the detailed engineering and permitting stage, roughly half are in the midst of this stage and will likely be finished by early 2005. For the 25 refineries that reported information on permits, most had submitted their permit applications at the time of reporting. Roughly half of these permits are pending approval. The remaining refineries reported that they had either received their approvals, or, in the case of four refineries, had not yet submitted their permit applications.

The majority of the refineries that reported procurement and construction dates projected that this stage would be complete by the first quarter of 2006. Some of these refineries reported that they would be done earlier in 2005 (and three refineries are already producing 15 ppm sulfur highway diesel fuel). A few refineries reported that they would be completing this stage after the June 2006 deadline, as they will either be using the Small Refiner Delay option or credits to comply.

Finally, with respect to the commissioning and start-up stage, Figure 6 shows projected start-up dates by quarter. Three refineries are already producing 15 ppm and another nine currently have operational desulfurization units that are capable of producing 15 ppm sulfur highway diesel fuel. Another 11 refineries anticipate having their desulfurization units up and running before January 2006. Figure 6 also shows the breakdown of these early refineries by PADD. As a result, in many places 15 ppm sulfur diesel fuel will be available early to prove out the distribution system, as well as supply fuel to retrofit fleets.

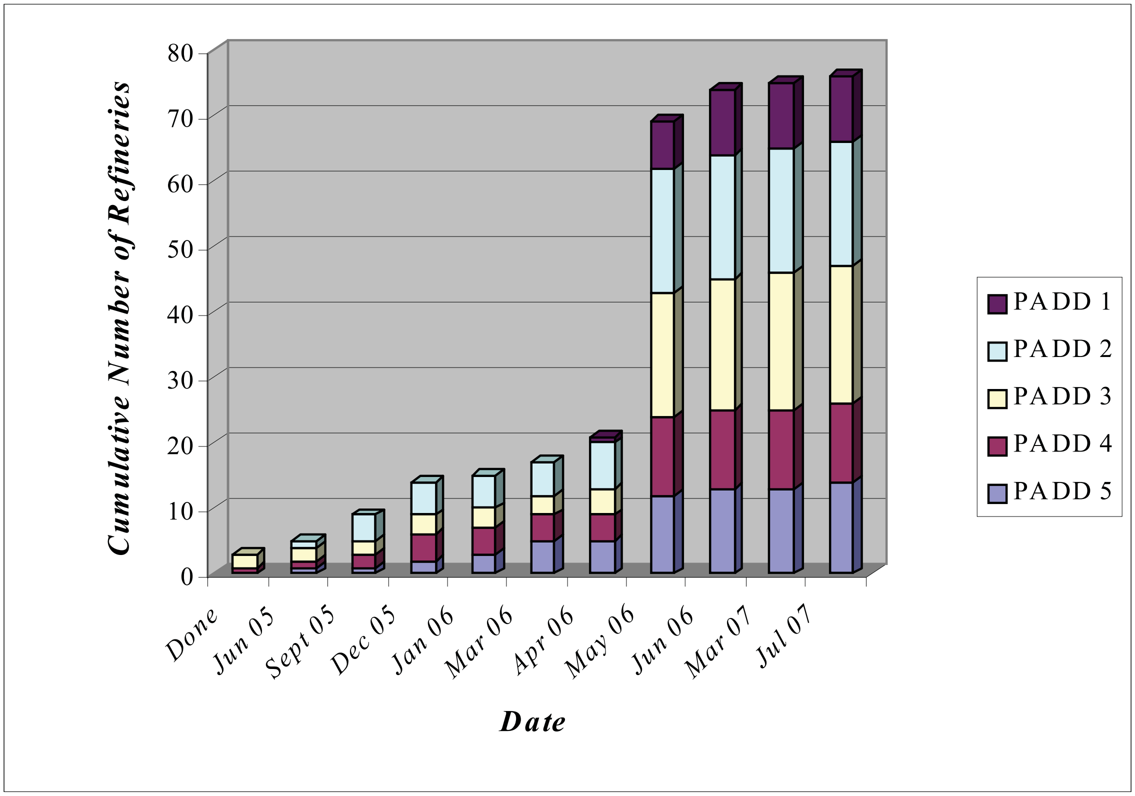

Figure 6. Projected Start-up Dates for Producing 15 ppm Highway Diesel Fuel[h]

6. Revamped Versus Grassroots Projects

In the final highway diesel rule, we projected that, in order to meet the 15 ppm sulfur standard, refiners would use similar hydrotreating technology to that which is currently being used to meet the 500 ppm sulfur standard. In doing so, refiners would either need to install new

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[h] While some refineries reported their projected start-up date on a monthly basis, others reported on a quarterly basis. For those that reported on a quarterly basis, we assumed the month that would correspond with the end of the quarter to be conservative.

hydrotreating equipment or revamp their current hydrotreaters/desulfurization equipment.

Seventy-nine refineries reported that they would either be revamping existing equipment or constructing new facilities, 50 (73 percent) refineries reported plans for revamping existing equipment, 19 (24 percent) refineries reported that they would be installing new equipment, and 10 (13 percent) refineries reported they would be doing both. This is roughly in line with the projections that we made in the highway diesel final rule, and also the anticipated plans that refiners reported last year. In their 2003 pre-compliance reports, 75 percent reported anticipated plans for revamping existing equipment, 15 percent were anticipating installing a new unit, and 10 percent reported that they would be doing both.

Twelve refineries reported they either did not need to install new desulfurization capacity or revamp existing desulfurization units, including two refineries that plan to transport part of their distillate to other refineries for desulfurization. Another six refineries have that they are still evaluating options and another 14 refineries are currently unsure of their future desulfurization plans. Some of these refineries are owned by small refiners, some are anticipating using credits to comply, some refineries expect to refine their high-sulfur diesel fuel at other facilities, and others reported that they would not be producing 15 ppm sulfur fuel. The remaining 21 refineries are still in the process of finalizing their plans.

7. Small and GPA Refiner Options

Small Refiners

As discussed in greater detail above, the highway diesel fuel regulations contain three options which provide qualified small refiners with additional flexibilities to the TCO. Option A, the 500 ppm Sulfur Option, allows a refinery owned by an approved small refiner to delay production of 15 ppm sulfur fuel until the end of the TCO (May 2010). This option would enable a refinery to continue to produce all of its highway diesel fuel at the 500 ppm sulfur standard during the TCO years, provided the refiner shows in its pre-compliance report that adequate supplies of 15 ppm sulfur highway diesel fuel will be available in the refinery's marketing area. Option A was chosen by six refineries. Based on the reports received from these refineries, it is expected that their total production for 2006 will be five thousand bbls/day of 500 ppm highway diesel fuel.

Option B, the Small Refiner Credit Option, allows a small refiner to generate credits for any 'early' (since small refiners have until 2010 to comply with the 15 ppm standards under the highway diesel rule) volume of 15 ppm sulfur highway diesel fuel produced. This option was chosen by six refineries. Refineries using this option will likely have a mix of 500 ppm and 15 ppm highway diesel fuel in 2006. Based on reported data, it is anticipated that in 2006 the six refineries choosing this option will produce a total of 33 thousand bbls/day, of which 15 ppm sulfur fuel is 96 percent of the total production volume.

Lastly, option C, the Diesel/Gasoline Compliance Date Option, allows a refinery owned by a small refiner the ability to delay its compliance date for the Tier 2 gasoline sulfur standards for up to three years if the refinery produces 95 percent of its highway diesel fuel (above a minimum volume limit tied to the refinery's baseline volume) at the 15 ppm sulfur standard by June 1, 2006. Nine refineries have chosen this option. These refineries reported that they expect to produce 99 thousand bbls/day of 15 ppm sulfur highway diesel fuel in 2006.

The volumes reported by refineries regarding the small refiner options are shown in Table 5 below.

Table 5.
Intended Small Refiner Compliance Options by Number of Refineries and Highway Diesel Fuel Production Capacity

Option	Description	Number of Refineries	2006 Highway Diesel Fuel Production Capacity (000 bbls/day)
A.	500 ppm sulfur Option	6	5
B.	Credit Option	9	33
C.	Diesel/Gasoline Compliance Date Option	6	99
	Total	21	138

GPA Refiners

The highway diesel fuel regulations also contain an option that allows a GPA refinery to delay its compliance date for the final Tier 2 gasoline sulfur standards by two years provided that the refinery produces 95 percent of its highway diesel fuel (above a minimum volume threshold tied to the refinery's baseline volume) at the 15 ppm sulfur standard by June 1, 2006. Twelve of the 35 GPA refineries reported that they would be using this option with an anticipated production volume in 2006 of approximately 92 thousand bbls/day.

B. PADD Analysis

The following discussion presents information specific to each PADD. Tables 6 through 9 below show the reported number of refineries and anticipated highway diesel fuel volumes for each PADD for 2006 and 2010. A total of four refineries will be shifting into the highway diesel fuel market in 2006, and an additional two will shift into the market by the end of the TCO. At the start of the TCO in 2006, over 415 thousand bbls/day of credits will be generated, though only six refineries anticipate that they will need to use those credits.

As shown in the tables, a decrease in production (relative to the year 2000) is projected for PADD 1 (from slightly over 10 percent in 2006 to less than two percent in 2010), and PADD 4 (less than one percent), and increases are projected in all of the other PADDs. Data from Table 32 of EIA's Petroleum Supply Annual for 2000-2003 show that PADDs 2 and 3 have historically transferred fuel to PADD 1 in relatively large quantities such that inter-PADD transfers should be able to offset the decrease in PADD 1. Similarly, the slight decrease that is predicted for PADD 4 in 2010, should be able to be offset by inter-PADD transfers as well.

More detailed information by PADD is shown in Tables 10 through 19, below.

Table 6.
Projected Number of Highway Diesel Fuel Refineries by PADD for 2006

PADD	1	2	3	4	5	Total U.S.
# refineries producing highway diesel fuel	11	23	39	15	22	110
# refineries at 100% 15 ppm	9	17	30	12	19	87
# refineries at 100% 500 ppm	0	3	6	2	1	12
# refineries with 15/500 ppm mix	2	3	3	1	2	11
# refineries increasing production (vs. EIA 2003)	7	19	25	8	17	76
# refineries shifting into the highway market	0	1	0	1	2	4
# refineries decreasing production (vs. EIA 2003)	6	6	17	7	7	43
# refineries shifting out of the highway market	2	2	3	0	2	9
# refineries generating credits	10	13	25	2	7	57
# refineries using credits	0	1	5	0	0	6

Table 7.
Projected Volumes of Highway Diesel Fuel by PADD for 2006

PADD	1*	2	3	4	5	Total U.S.
Total 15 ppm (*bbls/day*)	268,454	679,160	1,163,014	117,981	408,510	2,637,120
Total 500 ppm (*bbls/day*)	1,097	38,768	88,139	3,247	9,677	140,928
Total 15 + 500 ppm (*bbls/day*)	269,551	717,928	1,251,153	121,228	418,187	2,778,048
Net volume change vs. 2000 (*bbls/day*)	-30,951	63,791	132,604	354	66,745	232,544
% change from 2000 highway volume	-10.3	9.8	11.9	0.3	19.0	9.1
% 500 of total 15 + 500 ppm	0.4	5.4	7.0	2.7	2.3	5.1
Credit generation (*bbls/day*)	52,120	105,870	234,885	5,830	16,540	415,245
Credit usage (*bbls/day*)	0	6,905	62,081	0	0	68,985

* *The change that is projected for PADD 1 will be offset by imports and inter-PADD transfers. Historically, PADDs 2 and 3 have transferred fuel to PADD 1 in relatively large quantities.*

II. Summary Statistics - PADD Analysis

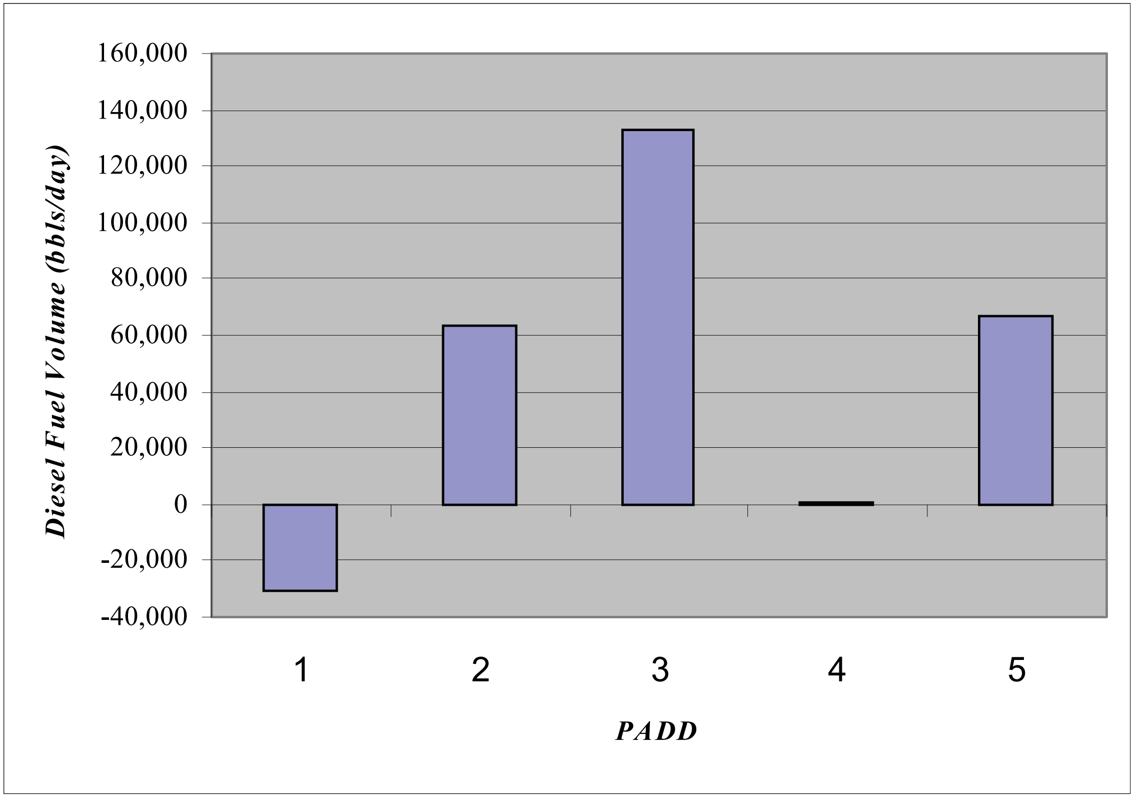


Figure 7. Highway Diesel Fuel Production Change 2006 vs. 2000 (by PADD)

Table 8.
Projected Number of Highway Diesel Fuel Refineries by PADD for 2010

PADD	1	2	3	4	5	Total U.S.
# refineries producing highway diesel fuel	12	25	39	15	23	114
# refineries at 100% 15 ppm	10	19	33	14	21	97
# refineries at 100% 500 ppm	0	3	4	1	1	9
# refineries with 15/500 ppm mix	2	3	2	0	1	8
# refineries increasing production (vs. 2003)	8	22	28	8	20	86
# refineries shifting into the highway market	1	1	0	1	3	6
# refineries decreasing production (vs. 2003)	6	3	14	7	5	35
# refineries shifting out of the highway market	2	0	3	0	2	7
# refineries generating credits						
# refineries using credits	0	1	2	0	0	3

Table 9.
Projected Volume of Highway Diesel Fuel by PADD for 2010

PADD	1[*]	2	3	4	5	Total U.S.
Total 15 ppm (*bbls/day*)	293,706	803,955	1,382,321	119,269	422,985	3,022,236
Total 500 ppm (*bbls/day*)	1,167	38,894	24,641	1,249	1,360	67,311
Total 15 + 500 ppm (*bbls/day*)	294,874	842,849	1,406,962	120,518	424,345	3,089,547
Net volume change vs. 2000 (*bbls/day*)	-5,629	188,712	288,413	-356	72,903	544,043
% change from 2000 highway volume	-1.9	28.8	25.8	-0.3	20.7	21.4
% 500 of total 15 + 500 ppm	0.4	4.6	1.8	1.0	0.3	2.2
Credit generation (*bbls/day*)	0	0	0	0	0	0
Credit usage (*bbls/day*)	0	6,954	13,272	0	0	20,225

* *The change that is projected for PADD 1 will be offset by imports and inter-PADD transfers. Historically, PADDs 2 and 3 have transferred fuel to PADD 1 in relatively large quantities.*

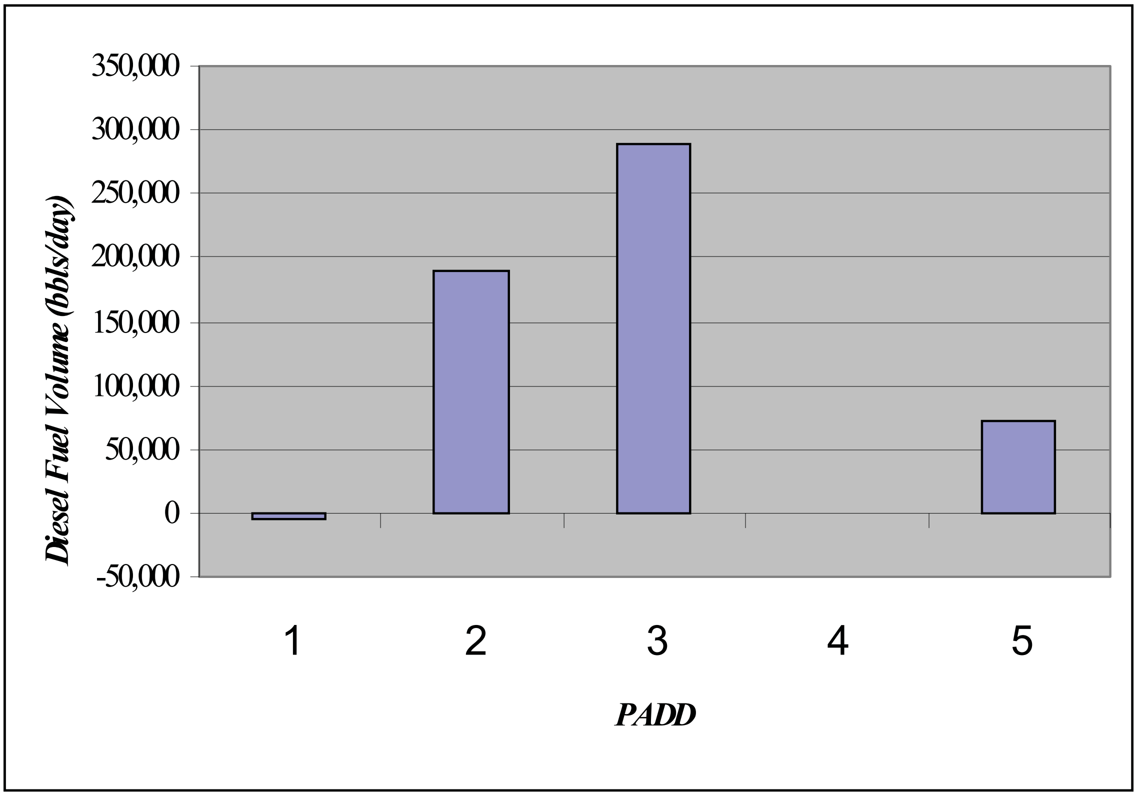
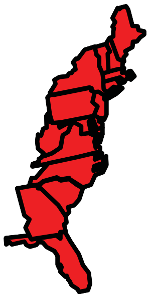


Figure 8. Highway Diesel Fuel Production Change 2010 vs. 2000 (by PADD)

1. PADD 1



Number of Refineries

Reported totals for all PADD 1 refineries and importers are summarized in Tables 10 and 11, below. These tables show that for the first year of the TCO (2006), 11 refineries projected the production of a volume of over 269 thousand bbls/day total (15 ppm sulfur + 500 ppm sulfur) highway diesel fuel. This projection is down slightly from the numbers reported in the 2003 pre-compliance reports of 12 refineries producing an estimated 285 thousand bbls/day of highway diesel fuel. More specifically, nine refineries reported that they intend to produce 100 percent of their highway diesel fuel with 15 ppm or less of sulfur in 2006, and no refineries intend to produce 100 percent of their highway diesel fuel at the 500 ppm sulfur level. Two refineries reported that they intend to produce a mix of 15 ppm and 500 ppm sulfur highway diesel fuel. Seven refineries reported that they intend to produce more highway diesel fuel than they did in 2000, while six refineries intend to produce less highway diesel fuel than they did in 2000. Four refineries intend to shift out of the highway diesel fuel market and one refinery intends to enter the highway diesel fuel market in 2010.

Highway Diesel Fuel Production[i]

As shown in Table 10, the seven refineries planning to produce more highway diesel fuel than in 2000 reported a cumulative increase in their highway diesel fuel production volume of approximately 79 thousand bbls/day, and the six refineries planning to produce less highway diesel fuel than in 2000 reported a cumulative decrease in their highway diesel fuel production volume of approximately 110 thousand bbls/day. This results in a projected net decrease of approximately 31 thousand bbls/day for 2006. However, in 2010, the projected net reduction in the volume of highway diesel fuel produced decreases to less than six thousand bbls/day.

While these results indicate that there will be a reduction in the production of highway diesel fuel in PADD 1, these reductions are not of great concern given the fact that the overall

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[i] As described above, the base volume of highway diesel fuel for the year 2000 (as shown in Table 11) that we for comparisons is slightly higher than the volume used in the Summary and Analysis of the Highway Diesel Fuel 2003 Pre-compliance Reports. One PADD 1 refinery submitted a pre-compliance report at such a time that it was not feasible to include its data in the 2003 pre-compliance report summary. Thus, we have included this data in today's Summary and Analysis of the Highway Diesel Fuel 2004 Pre-compliance Reports.

decline in net fuel volume (relative to 2000 volumes) decreases throughout the duration of the TCO, and the volume increases in PADDs 2 and 3, which historically transport diesel fuel to PADD 1, are much larger.

Availability of 15 ppm Sulfur Highway Diesel Fuel

As shown below in Figure 10, in 2006 more than 268 thousand bbls/day, or 99 percent of the PADD 1 total, are anticipated to be 15 ppm sulfur highway diesel fuel, and the remaining one thousand bbls/day are anticipated to be 500 ppm sulfur highway diesel fuel. The projections for 2010 also show that the amount of 15 ppm sulfur highway diesel fuel continues to be 99 percent of the total highway diesel fuel production for PADD 1.

Credit Generation and Use

In 2006 for PADD 1, 52 thousand bbls/day credits are anticipated to be generated, while no credits are anticipated to be used.

Table 10.
PADD 1 Highway Diesel Fuel Refinery Statistics 2006-2010

Year	***2003***	**2006**	**2007**	**2008**	**2009**	**2010**
# refineries producing highway diesel fuel	*13*	11	11	11	12	12
# refineries at 100% 15 ppm		9	9	8	9	10
# refineries at 100% 500 ppm	*13*	0	0	0	0	0
# refineries with 15/500 ppm mix		2	2	3	3	2
# refineries increasing production (vs. 2003)		7	7	7	8	8
# refineries shifting into the highway market		0	0	0	1	1
# refineries decreasing production (vs. 2003)		6	6	6	6	6
# refineries shifting out of the highway market		2	2	2	2	2
# refineries generating credits		10	10	10	11	
# refineries using credits		0	0	0	0	0
# refineries that were not able to provide volume data		2	2	2	2	2

Summary and Analysis of the Highway Diesel Fuel 2004 Pre-compliance Reports – September 2004

Table 11.
PADD 1 Highway Diesel Fuel Volume and Credit Statistics 2006-2010*

Year	*2000*	2006	2007	2008	2009	2010
Total 15 ppm (*bbls/day*)		268,454	268,186	272,180	293,397	293,706
Total 500 ppm (*bbls/day*)	*297,903*	1,097	1,159	2,815	2,815	1,167
Total 15 + 500 ppm (*bbls/day*)	*297,903*	269,551	269,345	274,995	296,212	294,874
Net volume change vs. 2000 (*bbls/day*)		-30,951	-31,157	-25,508	-4,291	-5,629
% change from 2000 highway volume		-10.3	-10.4	-8.5	-1.4	-1.9
% 500 of total 15 + 500 ppm	*100.0*	0.4	0.4	1.0	1.0	0.4
Credit generation (*bbls/day*)		52,120	52,014	51,488	55,731	
Credit usage (*bbls/day*)		0	0	0	0	0

* *The change that is projected for PADD 1 will be offset by imports and inter-PADD transfers. Historically, PADDs 2 and 3 have transferred fuel to PADD 1 in relatively large quantities.*

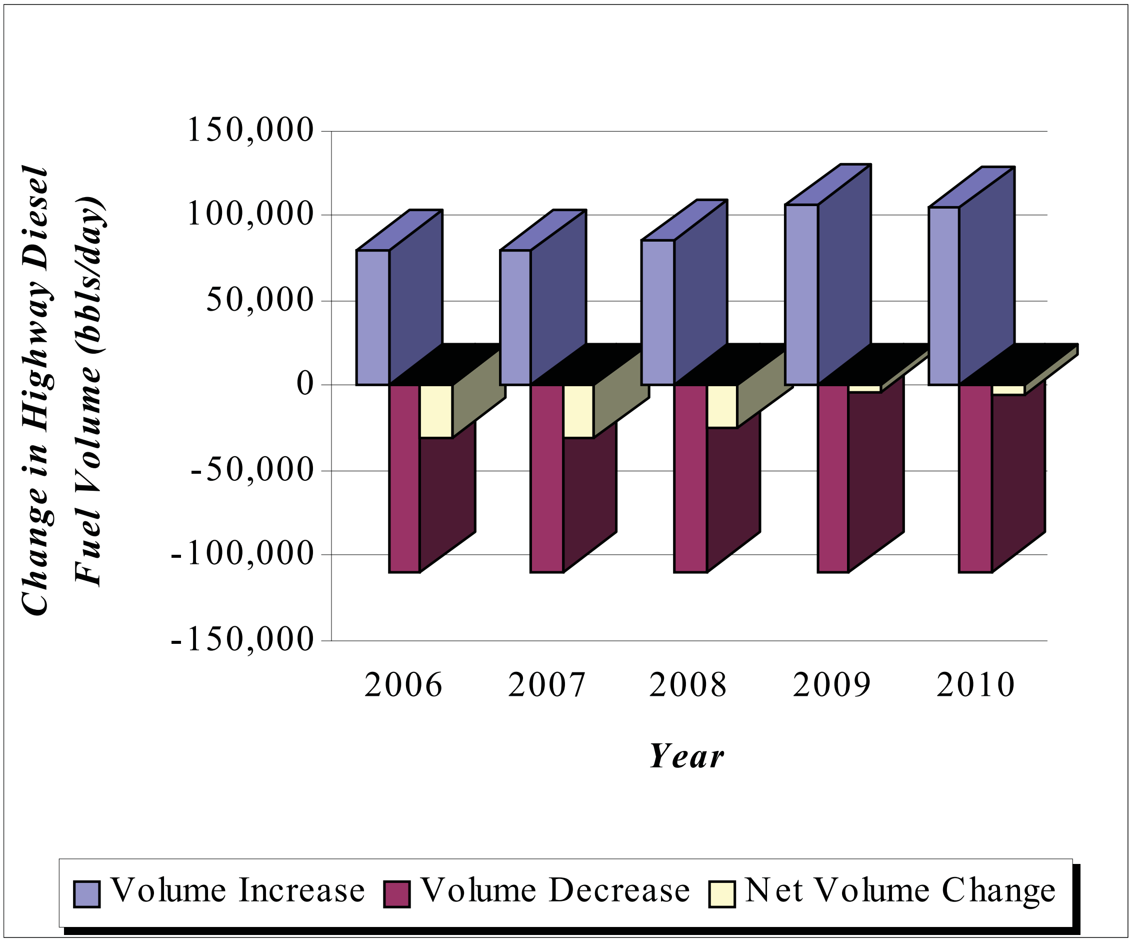


Figure 9. PADD 1 Highway Diesel Fuel Volume Change vs. 2000

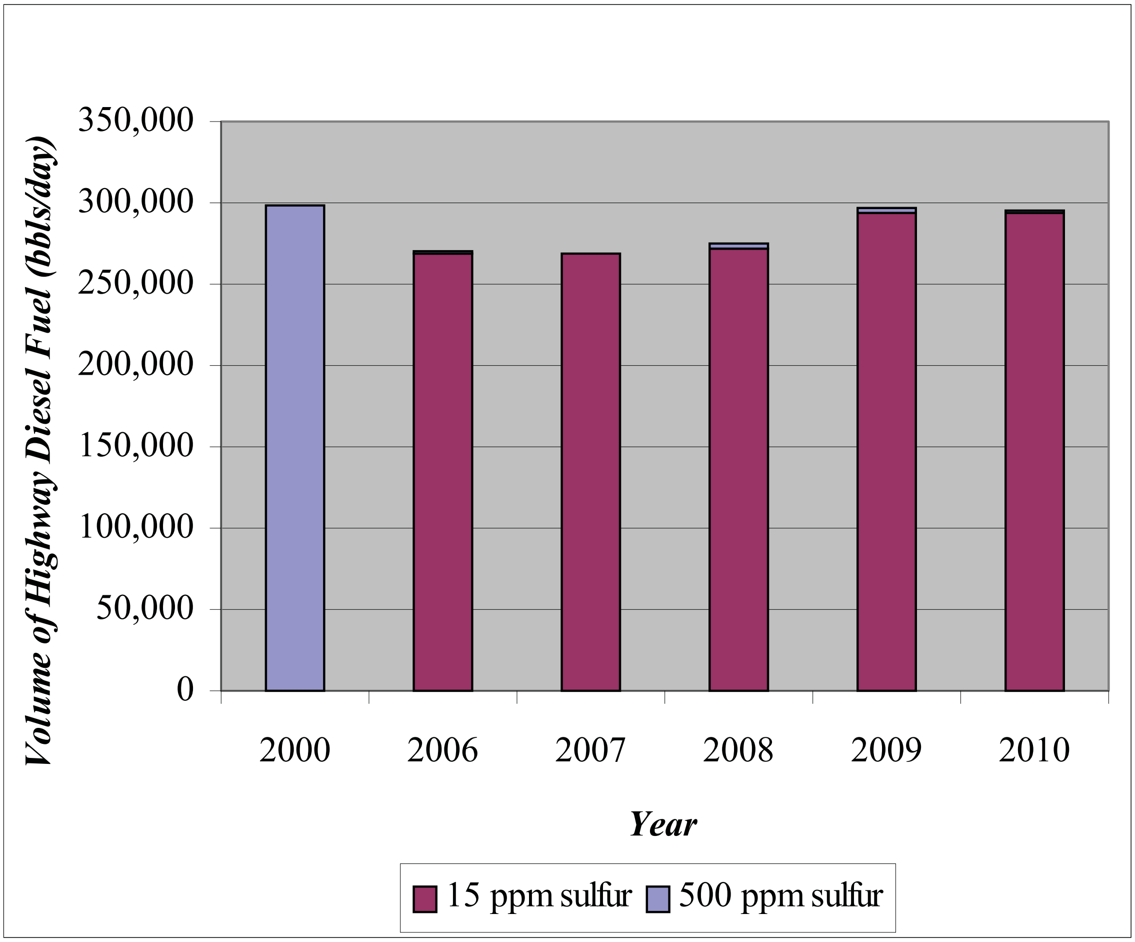
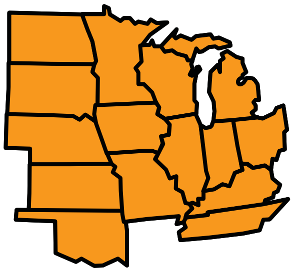


Figure 10. PADD 1 Projected Highway Diesel Fuel Production, 2006-2010

2. PADD 2



Number of Refineries

The reported totals for all PADD 2 refineries are summarized in Tables 12 and 13, below. These tables show that for 2006, the first year of the TCO, 23 refineries reported that they intend to produce an estimated volume of approximately 718 thousand bbls/day total (15 ppm sulfur + 500 ppm sulfur) highway diesel fuel. This projection is slightly down from the 739 thousand bbls/day that refiners estimated in the 2003 pre-compliance reports. In the 2004 pre-compliance reports 17 refineries reported that they intend to produce 100 percent of their highway diesel fuel with 15 ppm or less of sulfur. Additionally, three refineries intend to produce 100 percent of their highway diesel fuel at the 500 ppm sulfur level, and three refineries intend to produce a mix of 15 ppm sulfur and 500 ppm sulfur highway diesel fuel. Nineteen refineries reported that they intend to produce more highway diesel fuel than they did in 2000, including one refinery that produced no highway diesel fuel in 2000. Six refineries reported that they intend to produce less highway diesel fuel than they did in 2000, including one refinery that intends to temporarily shift out of the highway diesel fuel market. This is consistent with the projections in the 2003 pre-compliance reports.

In 2010, the last year of the TCO, the one refinery that produced highway diesel fuel in 2000 but will be shifting out of the highway market in 2006 expects to shift back into the highway diesel fuel market with all of its highway diesel fuel production meeting the 15 ppm sulfur standard.

Highway Diesel Fuel Production

As shown in Figure 11, below, the 19 refineries planning to produce more highway diesel fuel in 2006 than they did in 2000 reported a cumulative increase in their highway diesel fuel production volume of over 136 thousand bbls/day, and the five refineries planning to produce less highway diesel fuel than they did in 2000 reported a cumulative decrease in their highway diesel fuel production volume of approximately 72 thousand bbls/day. This results in a net increase of nearly 64 thousand bbls/day of highway diesel fuel production. In 2010, the net increase rises to approximately 188 thousand bbls/day.

Summary and Analysis of the Highway Diesel Fuel 2004 Pre-compliance Reports – September 2004

Availability of 15 ppm Sulfur Highway Diesel Fuel

As shown below in Table 13, 679 thousand bbls/day, or 95 percent of the PADD 2 total, are anticipated to be 15 ppm sulfur highway diesel fuel in 2006. The remaining five percent (almost 39 thousand bbls/day) is anticipated to be 500 ppm sulfur highway diesel fuel. Though the projected volume of total highway diesel fuel for 2006 is less than the amount anticipated in the 2003 pre-compliance reports, the projected volume increases during the TCO. In 2010, it is projected that over 842 thousand bbls/day will be produced, which is greater than the 818 thousand bbls/day volume that was projected in last year's pre-compliance reports.

Projected Credit Generation and Use

In 2006 for PADD 2, nearly 106 thousand bbls/day of credits are anticipated to be generated while approximately seven thousand bbls/day of credits are expected to be used. This will yield a net generation of 99 thousand bbls/day of credits.

Table 12.
PADD 2 Highway Diesel Fuel Refinery Statistics 2006-2010

Year	***2003***	**2006**	**2007**	**2008**	**2009**	**2010**
# refineries producing highway diesel fuel	*24*	23	24	24	24	25
# refineries at 100% 15 ppm		17	18	18	18	19
# refineries at 100% 500 ppm	*24*	3	3	3	3	3
# refineries with 15/500 ppm mix		3	3	3	3	3
# refineries increasing production (vs. 2003)		19	20	20	20	22
# refineries shifting into the highway market		1	1	1	1	1
# refineries decreasing production (vs. 2003)		6	5	5	5	3
# refineries shifting out of the highway market		2	1	1	1	0
# refineries generating credits		13	13	13	13	
# refineries using credits		1	1	1	1	1

Table 13.
PADD 2 Highway Diesel Fuel Volume and Credit Statistics 2006-2010

Year	***2000***	**2006**	**2007**	**2008**	**2009**	**2010**
Total 15 ppm (*bbls/day*)		679,160	735,075	729,093	734,578	803,955
Total 500 ppm (*bbls/day*)	*654,137*	38,768	38,768	38,778	38,524	38,894
Total 15 + 500 ppm (*bbls/day*)	*654,137*	717,928	773,843	767,871	773,102	842,849
Net volume change vs. 2000 (*bbls/day*)		63,791	119,706	113,734	118,965	188,712
% change from 2000 highway volume		9.8	18.3	17.4	18.2	28.8
% 500 of total 15 + 500 ppm	*100.0*	5.4	5.0	5.1	5.0	4.6
Credit generation (*bbls/day*)		105,870	108,174	106,882	108,174	
Credit usage (*bbls/day*)		6,905	6,904	6,904	6,904	6,954

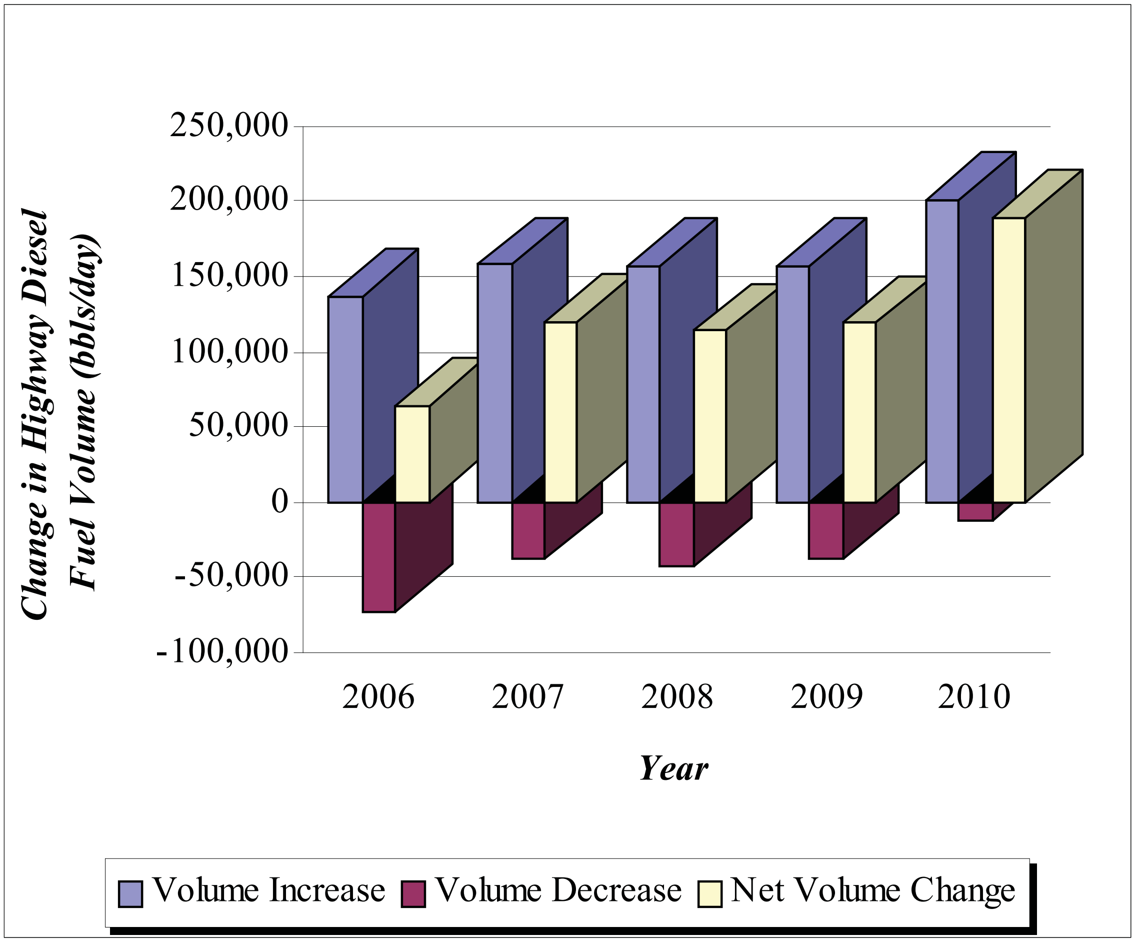


Figure 11. PADD 2 Highway Diesel Fuel Volume Change vs. 2000

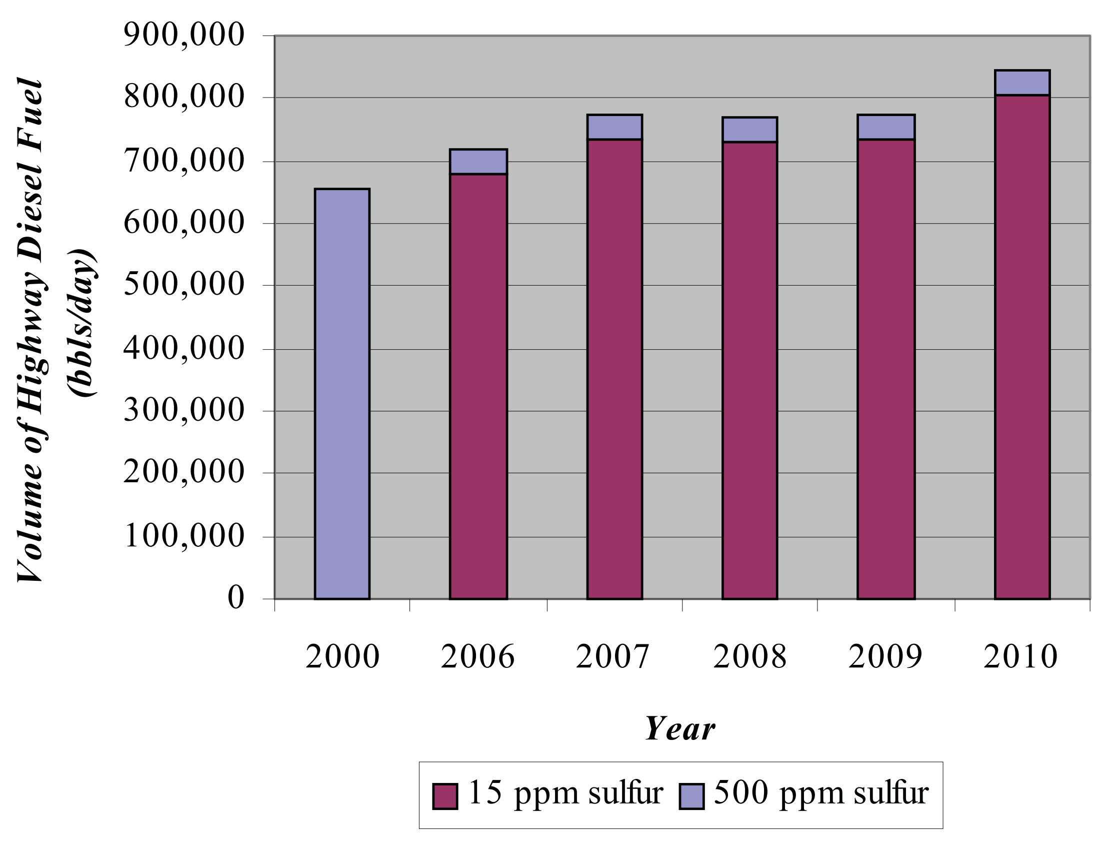
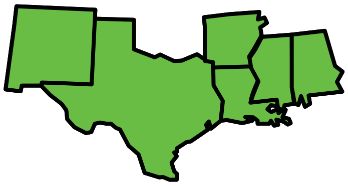


Figure 12. PADD 2 Projected Highway Diesel Fuel Production, 2006-2010

3. PADD 3



Number of Refineries

Reported totals for all PADD 3 refineries are summarized in Tables 14 and 15, below. These tables show that in 2006, the first year of the TCO, 39 refineries reported that they intend to produce an estimated volume of over 1.2 million bbls/day total (15 ppm sulfur + 500 ppm sulfur) highway diesel fuel. Specifically, 30 refineries (up from the 29 refineries reported in 2003) reported that they intend to produce 100 percent of their highway diesel fuel with 15 ppm or less of sulfur. Also, six refineries intend to produce 100 percent of their highway diesel fuel at the 500 ppm sulfur level, and three refineries intend to produce a mix of 15 ppm sulfur and 500 ppm sulfur highway diesel fuel. It was reported that 25 refineries intend to produce more highway diesel fuel in 2006 than they did in 2000, this is up from the 23 refineries that reported an expected increase in the 2003 pre-compliance reports. In the 2003 reports, one refinery that produced no highway diesel fuel in 2000 indicated its intention to enter the highway market; however, this year's reports show that there will not be any refineries entering the highway market during the TCO. Seventeen refineries intend to produce less highway diesel fuel than they did in 2000, including three refineries that intend to shift out of the highway diesel fuel market.

Highway Diesel Fuel Production

As shown in Figure 13, below, the 25 refineries planning to produce more highway diesel fuel than they did in 2000 reported a cumulative increase in their highway diesel fuel production volume of approximately 370 thousand bbls/day, and the 17 refineries planning to produce less highway diesel fuel than they did in 2000 reported a cumulative decrease in their highway diesel fuel production volume of approximately 237 thousand bbls/day. This results in a net increase of 132 thousand bbls/day of highway diesel fuel production. In 2010, the net increase is approximately 189 thousand bbls/day.

Availability of 15 ppm Sulfur Highway Diesel Fuel

Table 15 shows that in 2006 over 1.1 million bbls/day, or 93 percent of the PADD 3 total, are anticipated to be 15 ppm sulfur highway diesel fuel, the remaining percentage (88 thousand bbls/day) is anticipated to be 500 ppm sulfur highway diesel fuel.

II. Summary Statistics - PADD Analysis

Credit Generation and Use

In 2006, credit generation is anticipated to be approximately 235 thousand bbls/day, and only approximately 62 thousand bbls/day are anticipated to be used; yielding a net credit generation of almost 173 thousand bbls/day.

Table 14.
PADD 3 Highway Diesel Fuel Refinery Statistics 2006-2010

Year	***2003***	**2006**	**2007**	**2008**	**2009**	**2010**
# refineries producing highway diesel fuel	*42*	39	39	39	39	39
# refineries at 100% 15 ppm		30	30	30	31	33
# refineries at 100% 500 ppm	*42*	6	6	6	5	4
# refineries with 15/500 ppm mix		3	3	3	3	2
# refineries increasing production (vs. 2003)		25	26	26	24	28
# refineries shifting into the highway market		0	0	0	0	0
# refineries decreasing production (vs. 2003)		17	16	16	18	14
# refineries shifting out of the highway market		3	3	3	3	3
# refineries generating credits		25	25	25	26	
# refineries using credits		5	4	4	3	2

Table 15.
PADD 3 Highway Diesel Fuel Volume and Credit Statistics 2006-2010

Year	***2000***	**2006**	**2007**	**2008**	**2009**	**2010**
Total 15 ppm (*bbls/day*)		1,163,014	1,193,122	1,225,061	1,242,437	1,382,321
Total 500 ppm (*bbls/day*)	*1,118,549*	88,139	91,931	91,945	59,531	24,641
Total 15 + 500 ppm (*bbls/day*)	*1,118,549*	1,251,153	1,285,053	1,317,006	1,301,968	1,406,962
Net volume change vs. 2000 (*bbls/day*)		132,604	166,504	198,457	183,419	288,413
% change from 2000 highway volume		11.9	14.9	17.7	16.4	25.8
% 500 of total 15 + 500 ppm	*100.0*	7.0	7.2	7.0	4.6	1.8
Credit generation (*bbls/day*)		234,885	236,102	242,732	246,012	
Credit usage (*bbls/day*)		62,081	60,104	60,115	34,184	13,272

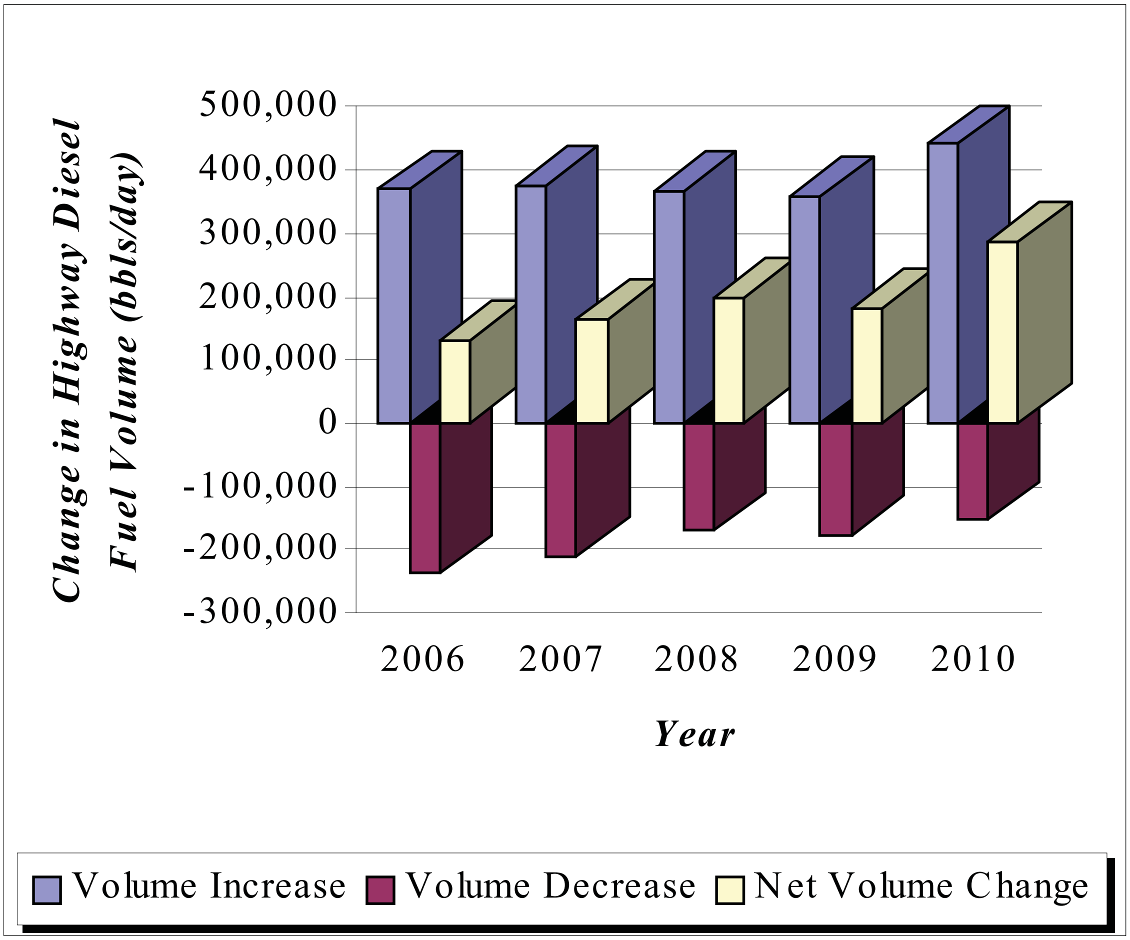


Figure 13. PADD 3 Highway Diesel Fuel Volume Change vs. 2000

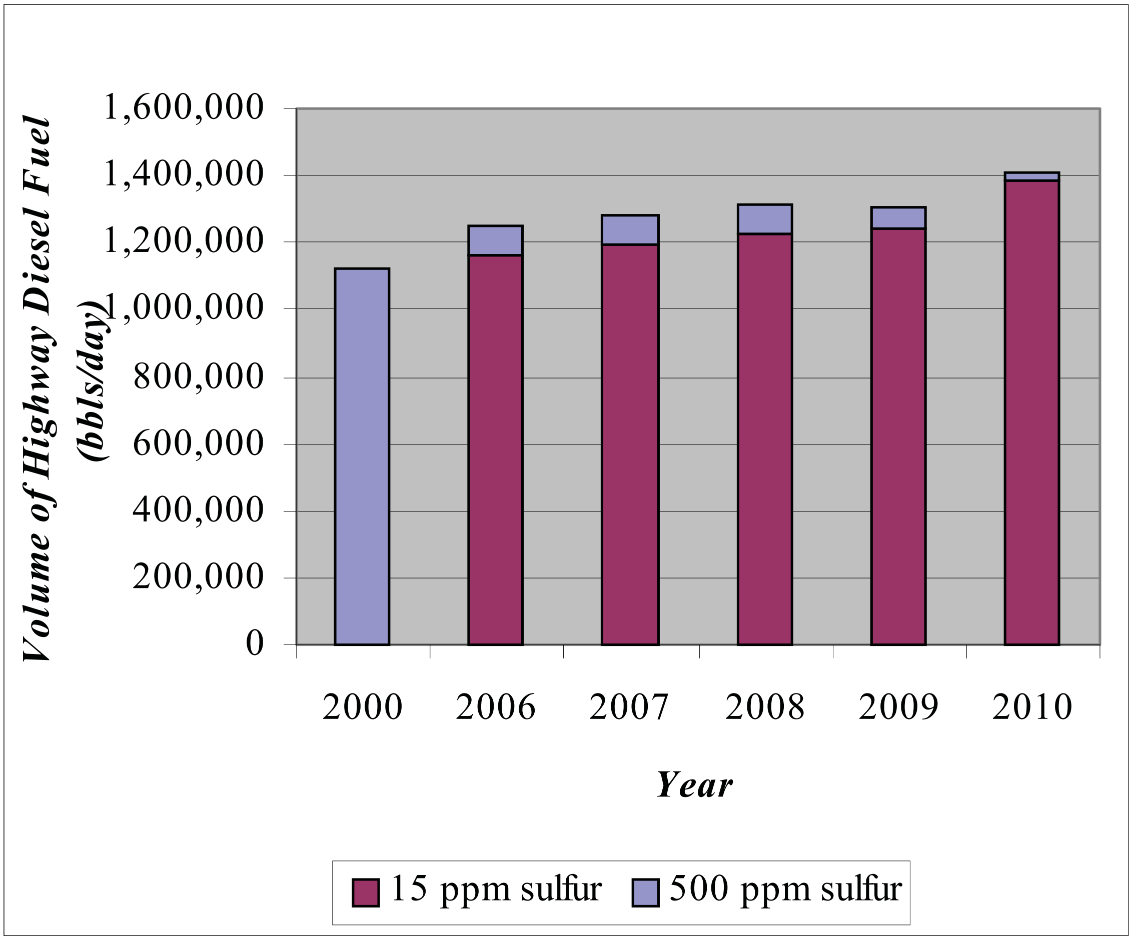
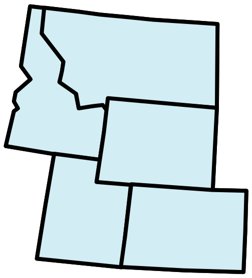


Figure 14. PADD 3 Projected Highway Diesel Fuel Production, 2006-2010

II. Summary Statistics - PADD Analysis

4. PADD 4



Number of Refineries

Reported totals for all PADD 4 refineries are summarized in Tables 16 and 17, below. These tables show that for the first year of the TCO (2006), 15 refineries reported that they intend to produce an estimated volume of 121 thousand bbls/day total (15 ppm sulfur + 500 ppm sulfur) highway diesel fuel. The 2004 reports show that 12 refineries intend to produce 100 percent of their highway diesel fuel with 15 ppm or less of sulfur and one refinery intends to produce a mix of 15 ppm sulfur and 500 ppm sulfur highway diesel fuel. Similar to the 2003 reports, two refineries still intend to produce 100 percent of their highway diesel fuel at the 500 ppm sulfur level. For 2006, eight refineries reported that they intend to produce more highway diesel fuel than they did in 2000, including one refinery that produced no highway diesel fuel in 2000. Seven refineries intend to produce less highway diesel fuel than they did in 2000.

Highway Diesel Fuel Production

As shown in Figure 15, below, in 2006, the eight refineries planning to produce more highway diesel fuel than they did in 2000 reported a cumulative increase in their highway diesel fuel production volume of approximately 22 thousand bbls/day, and the seven refineries planning to produce less highway diesel fuel than they did in 2000 reported a cumulative decrease in their highway diesel fuel production volume of just over 21 thousand bbls/day. This results in essentially no net change in production (a slight increase of approximately 350 bbls/day) Projected production in PADD 4 remains essentially constant through 2010, as shown in Figure 16.

Availability of 15 ppm Sulfur Highway Diesel Fuel

As shown in Table 17, below, in 2006, approximately 118 thousand bbls/day, or 97 percent of the PADD 4 total, are anticipated to be 15 ppm sulfur highway diesel fuel. Though the volume of highway diesel fuel is projected to decrease slightly in 2010, the percentage of highway diesel fuel at the 15 ppm sulfur standard is expected to increase to 99 percent of the total volume of highway diesel fuel produced in PADD 4.

Summary and Analysis of the Highway Diesel Fuel 2004 Pre-compliance Reports – September 2004

Credit Generation and Use

The volume of credits generated in 2006 are anticipated to be approximately 5,830 bbls/day for PADD 4. As with the projections from 2003, no credits are anticipated to be used in this PADD. Further, two refineries have indicated that they are planning to produce 100 percent of their highway diesel at the 500 ppm sulfur level until 2010.

II. Summary Statistics - PADD Analysis

Table 16.
PADD 4 Highway Diesel Fuel Refinery Statistics 2006-2010

Year	*2003*	2006	2007	2008	2009	2010
# refineries producing highway diesel fuel	*14*	15	15	15	15	15
# refineries at 100% 15 ppm		12	12	12	13	14
# refineries at 100% 500 ppm	*14*	2	2	2	2	1
# refineries with 15/500 ppm mix		1	1	1	0	0
# refineries increasing production (vs. 2003)		8	8	8	8	8
# refineries shifting into the highway market		1	1	1	1	1
# refineries decreasing production (vs. 2003)		7	7	7	7	7
# refineries shifting out of the highway market		0	0	0	0	0
# refineries generating credits		2	2	2	2	
# refineries using credits		0	0	0	0	0

Table 17.
PADD 4 Highway Diesel Fuel Volume and Credit Statistics 2006-2010

Year	*2000*	2006	2007	2008	2009	2010
Total 15 ppm (*bbls/day*)		117,981	116,856	117,132	116,657	119,269
Total 500 ppm (*bbls/day*)	*120,874*	3,247	3,232	3,232	3,197	1,249
Total 15 + 500 ppm (*bbls/day*)	*120,874*	121,228	120,087	120,364	119,854	120,518
Net volume change vs. 2000 (*bbls/day*)		354	-787	-510	-1,020	-356
% change from 2000 highway volume		0.3	-0.7	-0.4	-0.8	-0.3
% 500 of total 15 + 500 ppm	*100.0*	2.7	2.7	2.7	2.7	1.0
Credit generation (*bbls/day*)		5,830	5,537	5,520	5,568	
Credit usage (*bbls/day*)		0	0	0	0	0

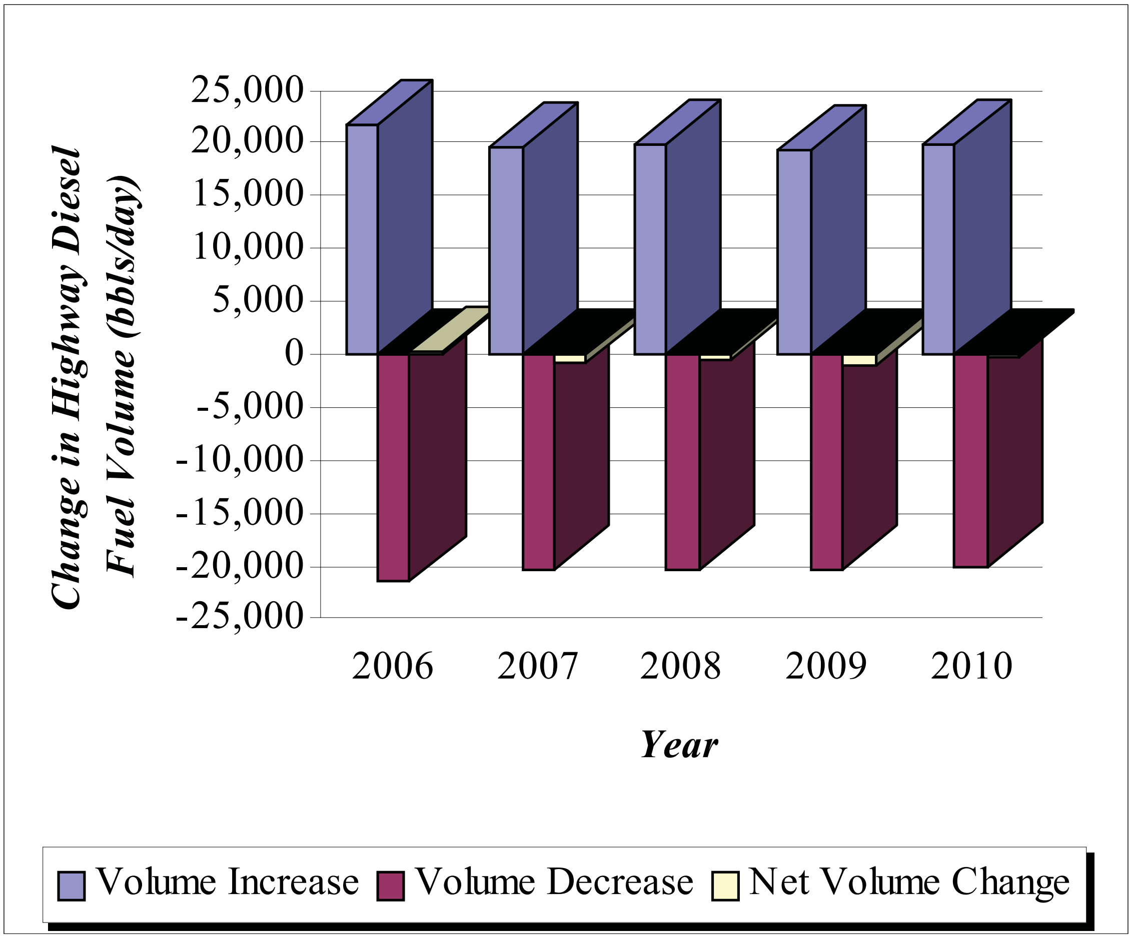


Figure 15. PADD 4 Highway Diesel Fuel Volume Change vs. 2000

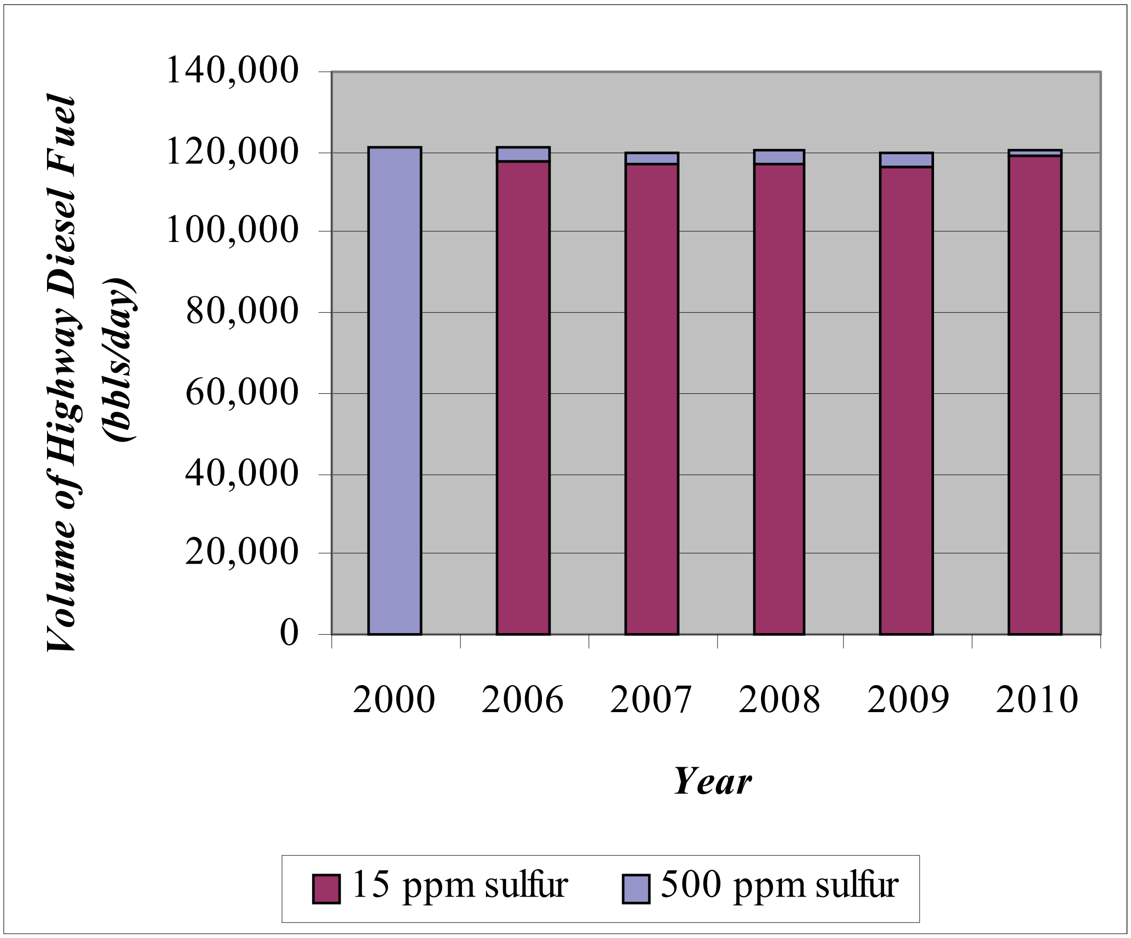
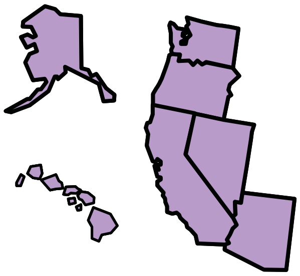


Figure 16. PADD 4 Projected Highway Diesel Fuel Production, 2006-2010

5. PADD 5[j]



Number of Refineries

Reported totals for all PADD 5 refineries are summarized in Tables 18 and 19, below. These tables show that in 2006, 22 refineries reported that they intend to produce a total volume of 418 thousand bbls/day of highway diesel fuel, 19 of which will be producing 100 percent of their highway diesel fuel at the 15 ppm sulfur standard. Furthermore, in 2006, two refineries expect to shift into the highway market, and one additional refinery will enter the market in 2007. In comparison, the 2003 pre-compliance reports only projected an increase of 351 thousand bbls/day with 16 refineries producing 100 percent of their highway diesel fuel at the 15 ppm sulfur standard. Only one refinery reported in its 2003 pre-compliance report that it would be entering the highway diesel market in 2006.

Highway Diesel Fuel Production

Seventeen refineries reported that they intend to produce more highway diesel fuel for 2006 than they did in 2000, including the two refineries that will be shifting into the highway diesel market in 2006. This will increase to 20 refineries increasing production over the duration of the TCO. Seven refineries intend to produce less highway diesel fuel in 2006 than they did in 2000, including two refineries that intend to shift out of the highway diesel fuel market. However, by 2010, only five refineries anticipate producing less highway diesel fuel than they did in 2000.

As shown in Figure 17, below, the 17 refineries planning to increase their highway diesel fuel production in 2006 reported a cumulative increase in their highway diesel fuel production volume of approximately 92 thousand bbls/day, and the five refineries planning to produce less highway diesel fuel in 2006 than they did in 2000 reported a cumulative decrease in their highway diesel fuel production volume of 25 thousand bbls/day. This results in a net increase in production of nearly 67 thousand bbls/day. In 2010, the net projected increase in production rises to 72 thousand bbls/day.

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[j] While the Summary and Analysis of the 2003 pre-compliance reports did not include the six refineries located in Alaska, we have included them in the analysis for 2004 Based on the pre-compliance reports that we received, some refineries in Alaska are planning to produce some 15 ppm sulfur diesel fuel beginning in 2006. Other refineries are still evaluating, but likely will elect to supply highway diesel fuel from refineries which may be located outside of Alaska.

II. Summary Statistics - PADD Analysis

Availability of 15 ppm Sulfur Highway Diesel Fuel

As shown in Table 19, below, in 2006, over 409 thousand bbls/day, or 98 percent of the PADD 5 total, are anticipated to be 15 ppm sulfur highway diesel fuel. Only 10 thousand bbls/day are expected to be 500 ppm sulfur highway diesel fuel. The percentage of highway diesel fuel at the 15 ppm sulfur standard is expected to increase to over 99 percent of the total volume of highway diesel fuel produced in PADD 5 in 2010. significant increase in projected production of highway diesel fuel over the duration of the TCO.

Credit Generation and Use

The reports for PADD 5 projected that for 2006, credit generation will likely total approximately 16 thousand bbls/day. On the other hand, no credits are expected to be used in PADD 5 during the TCO.

Table 18.
PADD 5 Highway Diesel Fuel Refinery Statistics 2006-2010

Year	***2003***	**2006**	**2007**	**2008**	**2009**	**2010**
# refineries producing highway diesel fuel	*22*	22	23	23	23	23
# refineries at 100% 15 ppm		19	20	20	20	21
# refineries at 100% 500 ppm	*22*	1	1	1	1	1
# refineries with 15/500 ppm mix		2	2	2	2	1
# refineries increasing production (vs. 2003)		17	20	19	20	20
# refineries shifting into the highway market		2	3	3	3	3
# refineries decreasing production (vs. 2003)		7	5	6	5	5
# refineries shifting out of the highway market		2	2	2	2	2
# refineries generating credits		7	8	8	8	
# refineries using credits		0	0	0	0	0

Table 19.
PADD 5 Highway Diesel Fuel Volume and Credit Statistics 2006-2010

Year	***2000***	**2006**	**2007**	**2008**	**2009**	**2010**
Total 15 ppm (*bbls/day*)		408,510	417,190	423,812	421,239	422,985
Total 500 ppm (*bbls/day*)	*351,442*	9,677	9,674	9,834	9,713	1,360
Total 15 + 500 ppm (*bbls/day*)	*351,442*	418,187	426,864	433,646	430,951	424,345
Net volume change vs. 2000 (*bbls/day*)		66,745	75,422	82,204	79,509	72,903
% change from 2000 highway volume		19.0	21.5	23.4	22.6	20.7
% 500 of total 15 + 500 ppm	*100.0*	2.3	2.3	2.3	2.3	0.3
Credit generation (*bbls/day*)		16,540	18,179	18,006	17,991	
Credit usage (*bbls/day*)		0	0	0	0	0

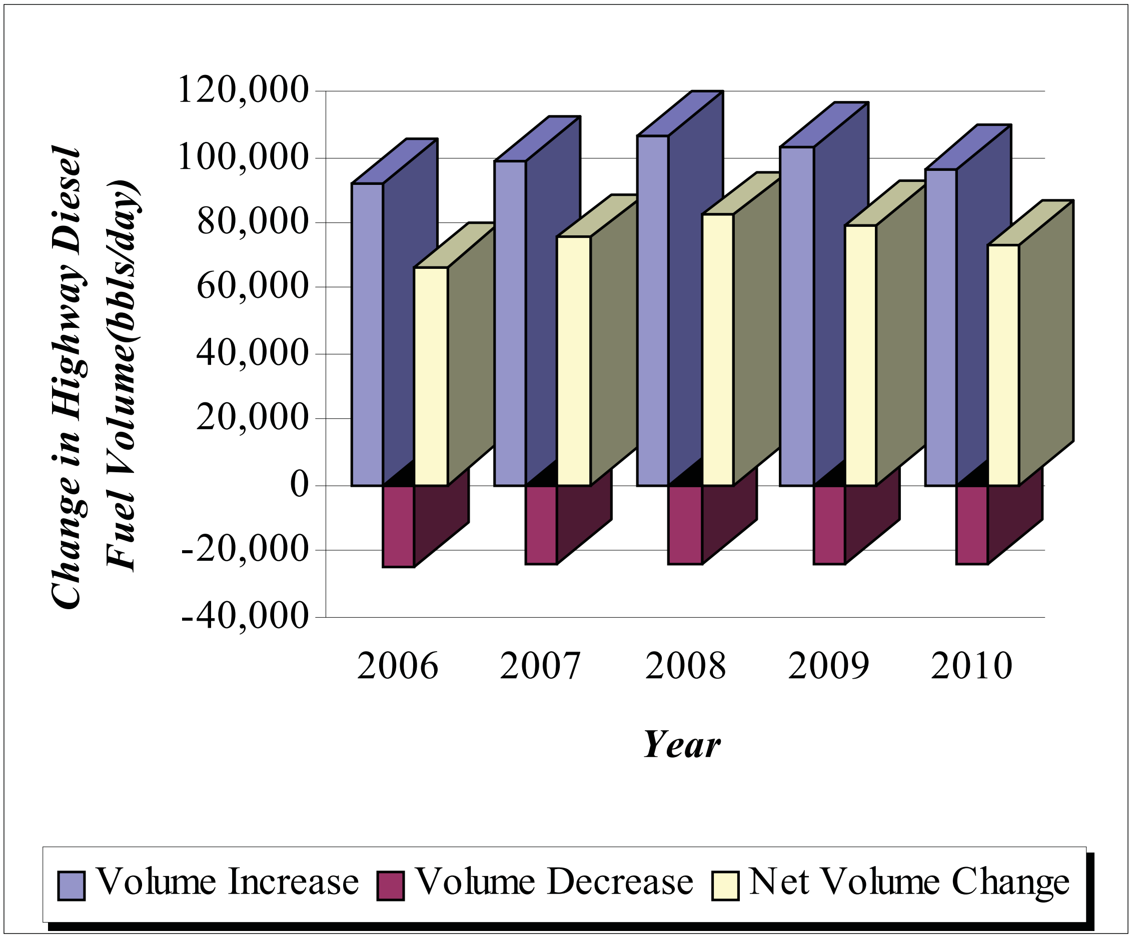

Figure 17. PADD 5 Highway Diesel Fuel Volume Change vs. 2000

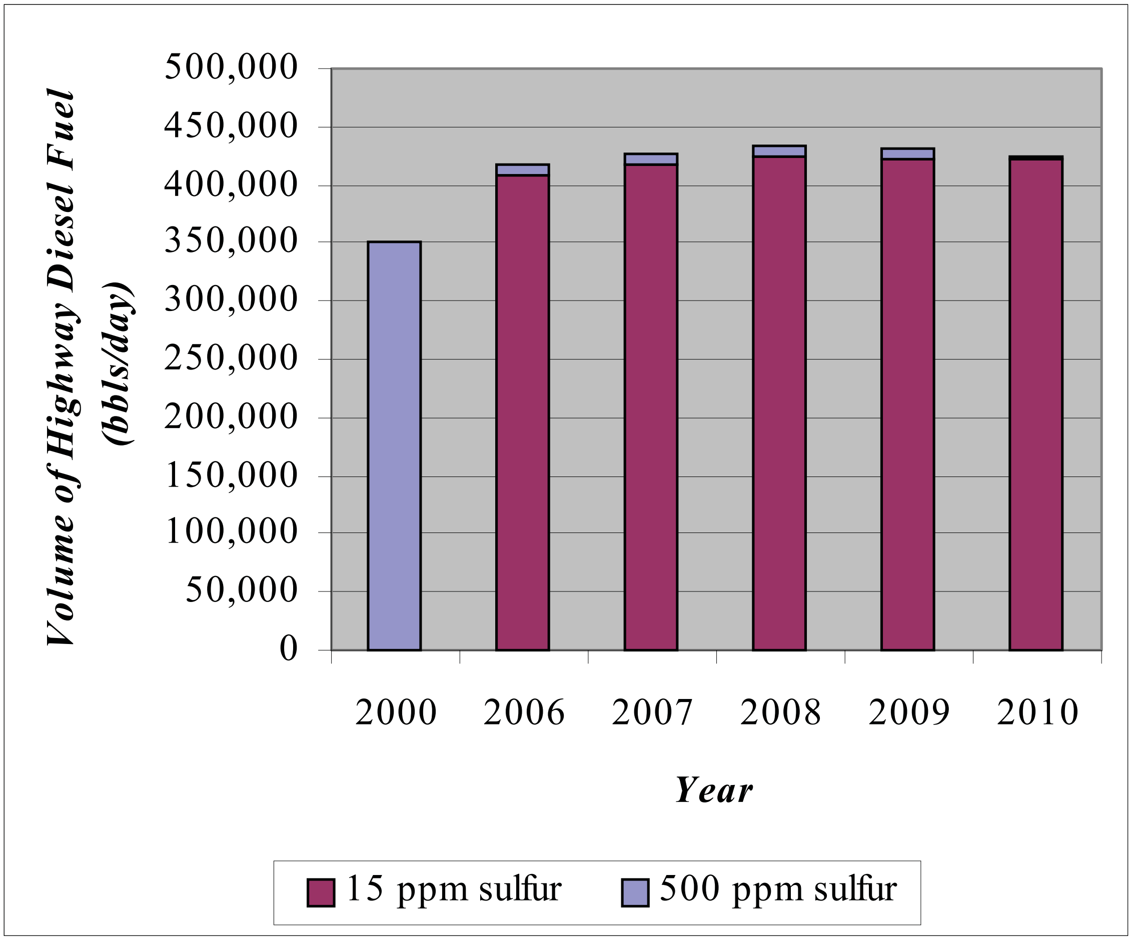

Figure 18. PADD 5 Projected Highway Diesel Fuel Production, 2006-2010

Appendix: List of Acronyms

AEO	*Annual Energy Outlook*
bbls/day	*barrels per day*
bpcd	*barrels per calendar day*
EIA	*Energy Information Administration*
EPA (or, "the Agency")	*U.S. Environmental Protection Agency*
FR	*Federal Register*
GPA	*Geographic Phase-in Area*
PADD	*Petroleum Administrative Districts for Defense*
ppm	*parts-per-million*
TCO	*Temporary Compliance Option*

Summary and Analysis of the Highway Diesel Fuel 2004 Pre-compliance Reports – September 2004

References

1. Summary and Analysis of the Highway Diesel Fuel 2003 Pre-compliance Reports, U.S. Environmental Protection Agency, EPA420-R-03-013, October 2003, http://www.epa.gov/otaq/regs/hd2007/420r03013.pdf.

2. Shell Bakersfield Refinery Closure Public Information Center http://www.shellbakersfieldrefinery.com/

3. Energy Information Administration, *Annual Energy Outlook 2003*, DOE/EIA-0383(2003), January 2003.

4. U.S. Department of Energy, *Transportation Energy Data Book*, 2002.

From: DiCicco, Dominic (D.M.)

Sent: Monday, February 23, 2009 8:54 AM

To: Misangyi, Pete (P.W.); Raney-Pablo, Beth (H.E.); Richardson, Charles (C.E.); Fulton, Brien (B.L.); Armesto, Carlos (.); Torres, Sean (S.J.)

Subject: fyi...FW: Draft Final Report for AVFL-17- for review in preparation for project meeting

Attachments: CRC_Final_Report_2-9-09-vh missing some refs.pdf

All,

Here is a summary report for biodiesel; this is a draft report so do not quote or cite.

If you have comments, please forward - I have not reviewed yet.

Best Regards,

Dominic DiCicco
Vehicle Energy Planning and Compliance
Vehicle Environmental Engineering
P: (313) 594-2916 F: (313) 594-0338
Office: 0229-E4 WHQ
ddicicco@ford.com

From: Chris Tennant [mailto:CTennant@crcao.org]
Sent: Tuesday, February 10, 2009 9:14 AM
To: Beard, Loren K.; Cannella, Bill; DiCicco, Dominic (D.M.); Eng, King ; Foster, Mike; Frusti, Jim; Jetter, Jeff; Johnson, Stuart; Jorgensen, Scott; Natarajan, Mani; Patterson, David ; Rakicki, Dennis ; Schleyer, Charles H. ; Valentine, Marie; Webster, Leah; Wright, Ken ; Clark, Wendy; Graves, Ronald L. ; Knoll, Keith; Kubsh, Joe; Lax, David ; McCormick, Robert ; Smith, Dennis A.; Stork, Kevin ; Thornton, Matthew ; Torres, Sean (S.J.); Zigler, Brad
Cc: Jane Beck; Brent Bailey
Subject: FW: Draft Final Report for AVFL-17- for review in preparation for project meeting

Dear members of the AVFL Committee and Working Group,

Please see the attached draft final report for the AVFL-17 project, with the introductory message below. Please remember that draft reports and other committee correspondence are not for distribution outside of this group.

The project leadership asks for your review of this first draft, and to come prepared with comments to the upcoming project meeting at DRI, where a presentation from the authors on the report content and any issues they saw in putting this together is anticipated. An agenda for the project meeting is in development, and will be distributed along with the call-in number for phone attendees.

Best regards,
- Chris

Dr. Christopher J. Tennant - Deputy Director
CRC Correspondence (not for public distribution)
COORDINATING RESEARCH COUNCIL, INC.
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WWW.CRCAO.ORG

From: Kent Hoekman [mailto:kent.hoekman@dri.edu]
Sent: Monday, February 09, 2009 9:12 PM
To: Chris Tennant; Natarajan, Mani
Cc: Amber Broch; Alan Gertler; crobbins; Vicki Hall
Subject: Draft Final Report for AVFL-17

Chris and Mani:

Please find attached our Draft Final Report for AVFL-17. There are still a number of formatting and referencing issues we need to address, but the main content is virtually complete and ready for your review.

Also, we have just discovered one mistake in our tabulation of NOx emissions from HD engines. Correcting this mistake will take a couple days, since it also affects a number of tables, figures, and sections of text. I thought it better to get you this draft now, and fix the NOx problem later. We'll discuss this (and many other points) with you and the AVFL-17 group when you visit on Feb. 25-26.

Have you given some thought to a meeting agenda for Feb. 25-26? Also, would you like us to put together a formal presentation?

S. Kent Hoekman
Research Professor
Division of Atmospheric Sciences
Desert Research Institute
Phone: (775) 674-7065
Fax: (775) 674-7016

Draft Final Report

CRC AVFL-17

Investigation of Plant-Derived Biofuels as Potential Blendstocks for Transportation Fuels

Prepared by:

S. Kent Hoekman
Alan Gertler
Amber Broch
Curt Robbins

Desert Research Institute
Reno, NV 89512

DRAFT

February 9, 2009

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Executive Summary

Production and use of biofuels are increasing dramatically, both in the U.S. and globally. While most interest has been focused on ethanol and its use in light-duty gasoline vehicles (LDGV), considerable growth in biofuels for diesel applications is also occurring. Drivers for this growth include the following:

- National energy security
- Diversity of energy sources
- Concerns over greenhouse gases (GHGs) and global climate change
- Desire for sustainable energy sources
- Rural economic development
- Improved balance of trade

The main purpose of this study is to assess the state-of-knowledge regarding plant-derived biofuels as blending materials for ultra-low sulfur diesel (ULSD) fuel in transportation applications. Topics of interest include policy drivers, biofuels feedstocks, fuel production technologies, fuel properties and specifications, in-use handling and performance, exhaust emissions effects, and life-cycle impacts. Data gaps were identified and areas for further work have been recommended.

The comprehensive term, biodistillate, is used to include all plant-derived fuels intended for diesel engines, regardless of the production technology used to manufacture the fuel. This includes both biodiesel (produced via transesterification of animal fats and vegetable oils) and renewable diesel (produced via hydrotreatment of the same feedstocks). Additionally, distillate fuels produced from lignocellulosic feedstocks are considered biodistillates, though such fuels are not in use today.

The term "1st Generation" refers to biofuels produced from commonly available, edible feedstocks using well-established conversion technologies. Most biofuels in use today are classified as 1st Generation. This includes ethanol produced via fermentation of sugars (from corn, sugar cane, sorghum, etc.) and biodiesel produced via transesterification of triglycerides (from vegetable oils and animal fats).

The term "2nd Generation" can refer to biofuels produced from either advanced, non-food feedstocks, or produced via advanced processing technology (or both). Examples of advanced feedstocks include lignocellulose and non-edible triglycerides, such as jatropha and algae. Examples of advanced processing technology include catalytic hydroprocessing of triglycerides and thermal conversion (gasification and pyrolysis) of lignocellulose.

In this report, the term "1st Generation" is used to refer to biodiesel produced via transesterification of edible triglycerides (including waste cooking fats and oils). The term 2nd Generation is used to refer to Renewable Diesel, Green Diesel, and biodiesel produced via transesterification of non-edible triglycerides. This report summarizes the state of knowledge for both 1st Generation and 2nd Generation biodistillates.

1. Policy Drivers for Biodistillate Fuels

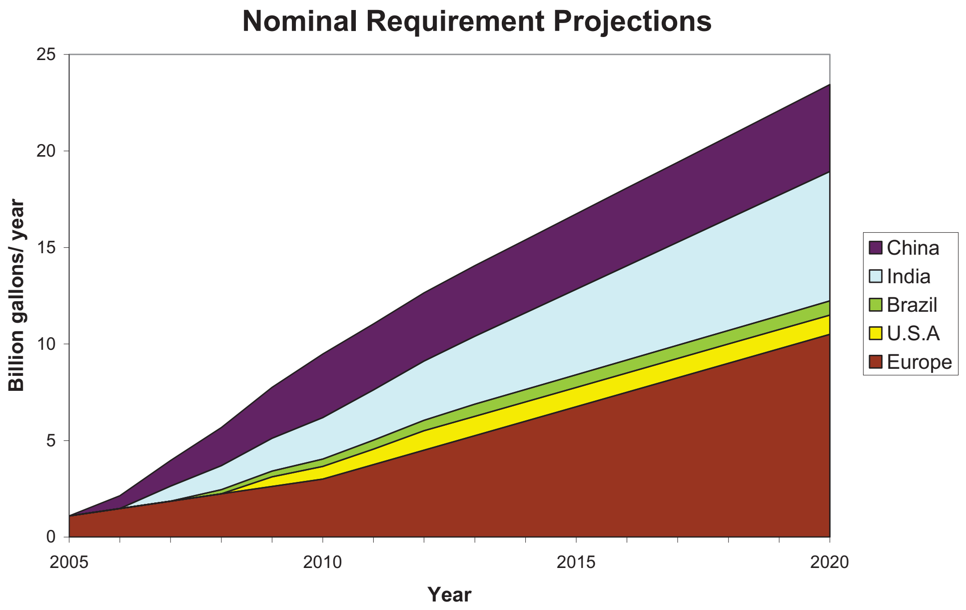
In the U.S., the current dominant policy driver for biodistillate fuels is the recently enacted Energy Independence and Security Act of 2007 (EISA). Through EISA, for the first time, Congress has established specific, volumetric requirements for biodiesel of 500 million gallons/year (mg/y) by 2009, ramping up to 1 billion gallons/year (bg/y) by 2012. (Current on-road diesel fuel usage in the U.S. is approximately 40 bg/y; the maximum EISA biodiesel requirement represents 2.5% of this total.) EISA also establishes a total renewable fuel standard (RFS) requirement of 36 bg/y, to be met by 2022, with 21 bg/y of this coming from “advanced biofuels,” meaning fuels derived from renewable biomass (excluding ethanol derived from corn) that achieve at least a 50% reduction in greenhouse gas (GHG) emissions, on a life-cycle basis.

Several U.S. States are actively pursuing policies to promote greater use of biofuels. California is developing a Low Carbon Fuels Standard (LCFS) and has recently passed legislation (AB-32) to address global warming concerns. AB-32 goals require statewide reduction of GHGs to achieve the 2000 level by 2010, the 1990 level by 2020, and 80% below the 1990 level by 2050. These reductions will be based upon “life-cycle values” by a mechanism that is still being defined. Meeting California’s LCFS and GHG reduction goals will require extensive use of biofuels, including biodistillates.

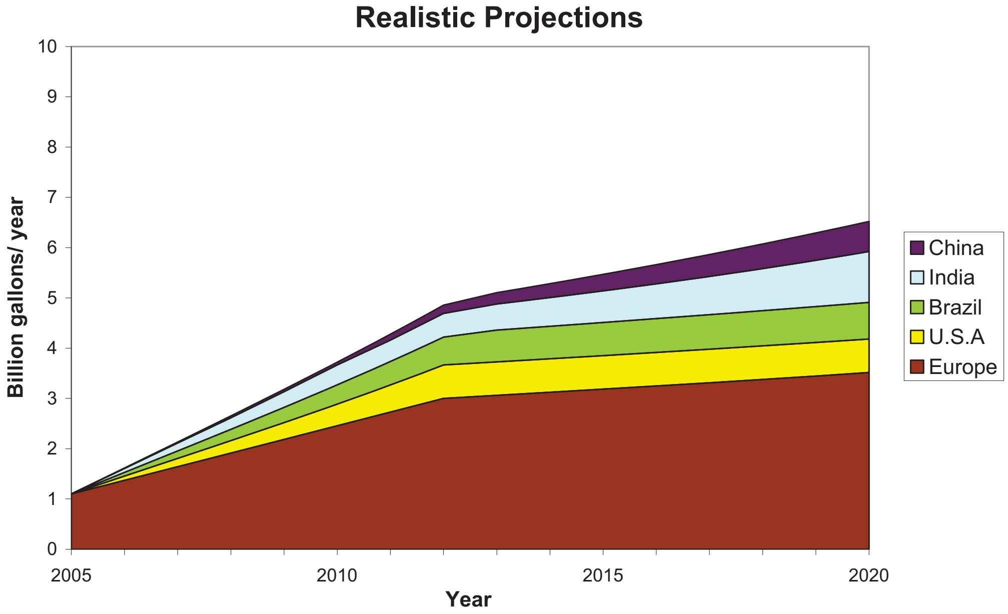
In Europe, EU Directive 2003-30-EC established targets for biofuels content of transportation fuels. According to this directive, biofuels must constitute 2% of transport fuels by 2005, and grow by 0.75% absolute per year until reaching 5.75% in 2010. These requirements apply to all transportation fuels, not just diesel fuel, though 75-80% of the requirement is being met by use of biodiesel. The EU has also defined a “benchmark” of achieving 20% biofuels content by 2020, though there is no legally binding requirement for this. At present, this 20% benchmark seems unattainable, and is not being vigorously pursued by the EU.

Many other countries are also beginning to develop policies to promote greater use of biodistillate fuels. Three of the most important are: (1) Brazil, which enacted a National Biodiesel Production Program in 2004, (2) China, which established a Renewable Energy Law in 2005, and (3) India, which developed a National Mission on Biodiesel in 2003.

All these national and regional policies include volumetric targets for biodistillate production that increase with time. Some targets are legally binding, while others are not. Combining the targets from all 5 regions (U.S., Europe, Brazil, China, and India) gives a projected biodistillate production volume of 23 bg/y by 2020. However, many of these targets are extremely optimistic, and not likely to be met. Based upon our assessment of each situation, we estimate the total biodistillate production from these 5 regions to be under 7 bg/y in 2020. Both the nominal volumetric requirements and our more conservative estimates are shown in Fig. ES-1.



(a)



(b)

Figure ES-1. Policy-Driven Volumetric Biodiesel Requirements

2. Biodiesel Volumes and Feedstocks

As shown below in Fig. ES-2, global biodiesel production has increased substantially in recent years. Europe has been – and continues to be – the dominant region for biodiesel. However, feedstock supply is expected to limit Europe's biodiesel production to well below the 5.75% goal by 2010. Growth of biodiesel in the U.S. is also limited by feedstock supply and cost.

Approximately 80% of total biodiesel cost is attributed to feedstock. While biodiesel production has grown significantly in both Europe and the U.S., plant capacity growth has been even more dramatic. Consequently, capacity utilization is declining. Utilization in the U.S. was 42% of capacity in 2006, but was estimated to be below 20% in 2008.

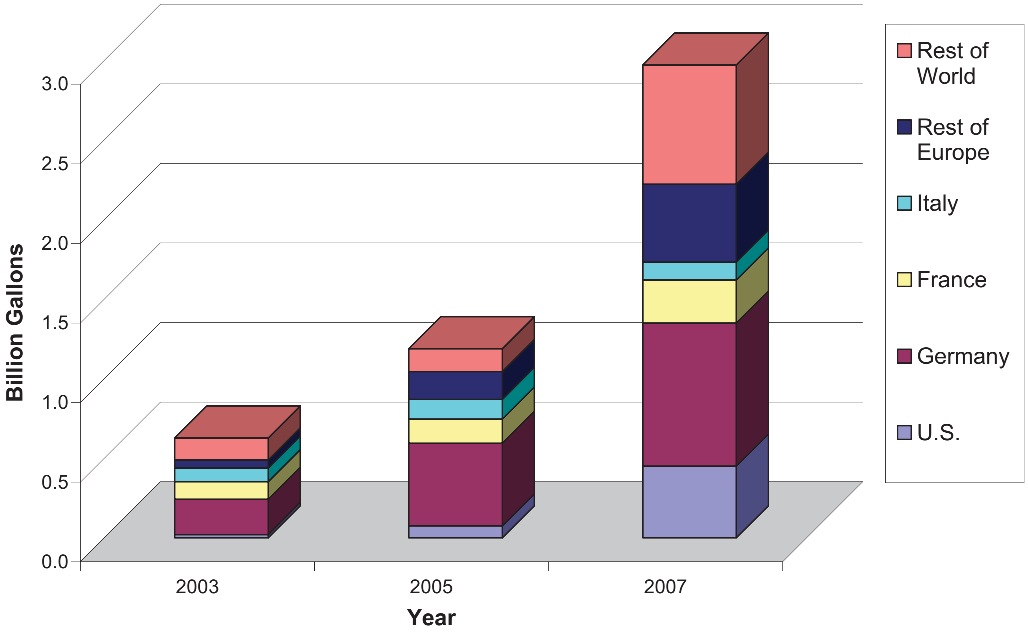


Figure ES-2. Global Growth in Biodiesel Production

While numerous alternative feedstocks are now beginning to receive attention, the only biodistillate feedstocks used commercially to-date have been triglycerides from animal fats and seed oils. As shown in Fig. ES-3, the dominant biodiesel feedstock in the U.S. (and Brazil) is soybean oil, although a number of other materials are also used. This is in contrast to the European countries, where rapeseed oil dominates. Waste cooking oil, canola oil, animal fats, and other triglycerides are finding increased usage in the U.S. as soybean oil supplies are becoming more limited and costly.

In the U.S., approximately 70 million acres of U.S. farmland are used for soybean cultivation. The fraction of the soybean crop used for biodiesel production is small, but increasing. Accurate determinations are difficult to make, since only a part of the soybean is used for fuel production, while other parts are used for animal feed and other purposes. However, it is estimated that the fraction of the total soybean crop devoted to biodiesel was 6% in 2005-2006, 8% in 2006-2007, and could reach 20% in 2008. A recent DOE study has concluded that a 3 bg/y U.S. biodiesel industry would require 30 million acres of cropland to be dedicated to seed oil production. Achieving this level will also require substantial increases in seed oil yield per acre. Numerous R&D efforts are underway to genetically modify soybeans (and other crops) to enhance yields and improve fuel properties.

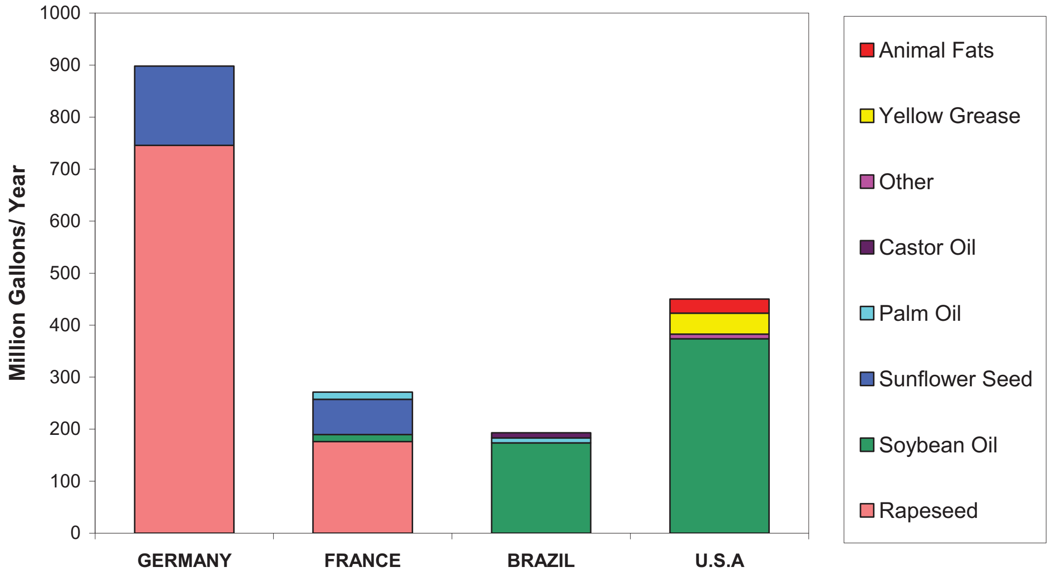


Figure ES-3. Biodiesel Feedstocks by Country – 2007

At the present time, China has approximately 4 million hectares of land area for growing oil-bearing trees, with an increasing fraction being devoted to jatropha. The first sizeable harvest of jatropha trees (also called "diesel trees" in China) is expected in 2008. By 2010, China anticipates having 13 million hectares planted in jatropha – a size approximately equal to the landmass of England. Once fully productive, this could provide 2-4 bg/y of biodiesel.

Current feedstocks for biodiesel production in India are quite varied, including waste vegetable oil, animal fats, rubberseed oil, rice bran, karanja, pongamia, and especially jatropha. Due to high edible oil prices, it is not economically feasible to produce biodiesel from vegetable oils in India. While still in its infancy, India intends to greatly expand its use of jatropha. To meet the 5% biodiesel goal by 2010 will require approximately 2.5 million hectares of jatropha and karanja. Meeting the 20% goal by 2020 would require about 20 million hectares. Significant advantages of jatropha (and some other native plants) include its ability to grow on marginal land with modest requirements for water and fertilizer. In India (and elsewhere) developing a jatropha industry is also seen as a powerful driver for rural economic development.

Many varieties of microalgae are known to produce large quantities of lipids, containing triglyceride oils, which are potential feedstocks for biodistillate fuels. Of all photosynthetic organisms, microalgae are the most productive users of CO_2, and can fix larger amounts of CO_2 per land area than other plants. Various investigations have been conducted to determine suitable algal strains for maximum growth and oil production under specific conditions. The most comprehensive investigation of algae as a potential fuel feedstock was undertaken by the National Renewable Energy Lab, who maintained an active Aquatic Species Program (ASP) from 1978 to 1996. The ASP final closeout report was issued in 1998, and remains an excellent source of information about growth conditions and productivities of various algal strains.
Due to numerous technical and economic factors, the ASP was discontinued. Now, however, DOE and NREL have renewed interest in promoting algae as a commercial energy source. In fact, DOE recently sponsored an "Algal Fuels Roadmapping" meeting, and plans to issue a roadmap document in mid-2009. Reasons cited for this renewed interest include the following:

- High costs of petroleum and other energy sources
- Increased emphasis on energy security
- Concern about CO_2 and climate change
- Advances in biotechnology and photobioreactor designs
- Petroleum refiners' interest in processing lipids

Major barriers to commercial scale implementation of algal systems include numerous technical challenges (maintaining healthy algal growth, avoiding invasive native algae, temperature control, effective light dispersion, reliable harvesting methods, etc.) as well as economics.

3. Biodistillate Production Technologies

Although straight vegetable oils (SVOs) have been used as fuels in compression-ignition engines, they are generally regarded as unsuitable for use in modern diesel engines. The most unacceptable attribute of SVO is high viscosity, that causes poor fuel atomization and combustion, injector coking, deposit formation, and other problems. The most common method for overcoming the viscosity problems of SVO involves the chemical process called transesterification, by which triglycerides are reacted with alcohols to produce fatty acid alkyl esters and glycerol. These fatty acid esters [usually fatty acid methyl esters (FAME) or fatty acid ethyl esters (FAEE)] are commonly known as biodiesel.

Considerable work has been conducted to determine optimum reaction conditions for producing biodiesel. To some degree, different conditions are required for each triglyceride feedstock. For a given feedstock, numerous factors have been found to have significant impacts on process efficiency and purity of final product. The most important parameters influencing the production and quality of biodiesel are the following:

- Ratio of alcohol to triglyceride
- Type of alcohol
- Purity of triglyceride feedstock
- Amount and type of catalyst
- Reaction time and temperature

Improving the efficiency of biodiesel production and purification remains an active area of R&D. Of particular interest is development of heterogeneous catalysts to replace the homogeneous hydroxide (or alkoxide) catalysts that are commonly used today, but which present challenges with respect to product quality. Other improvements being investigated include transesterification under supercritical alcohol conditions, use of co-solvents, and use of ultrasonic or microwave radiation to accelerate the rate of reaction.

A significant problem with the transesterification process is co-production of glycerol. In rough terms, 1 lb. of glycerol is produced for every 10 lbs of biodiesel. Complete removal of glycerol from biodiesel is difficult, but critical to meeting fuel specifications. While high purity glycerol has many commercial outlets, the increasing production of biodiesel has led to a glut of low quality glycerol, which requires extensive treatment to increase its value. The purity of glycerol at a typical biodiesel production plant is only 80-85%, even after water washing and further clean-up. Further purification involving distillation is generally performed off-site at a glycerol refinery.

As an alternative to transesterification, triglyceride feedstocks can be hydroprocessed to produce biodistillates generally known as renewable diesel. One of the first commercial processes was reported in 2005, by Neste Oil Corporation. The product, called NExBTL, is a paraffinic hydrocarbon material suitable for blending into conventional diesel fuel. UOP, in conjunction with Eni, has developed a similar process called Ecofining™. More recently, ConocoPhillips has developed a related process in which triglycerides are co-fed with petroleum feedstocks into a conventional diesel hydrotreater unit used for desulfurization.

In all of these hydroprocessing cases several reactions occur, including hydrogenation of the olefinic groups within the triglyceride, decarbonylation (loss of CO), decarboxylation (loss of CO_2) and hydrodeoxygenation (loss of H_2O). The glycerol component in the original triglyceride is converted to propane, while most of the carboxyl carbons are converted to CO or CO_2. Since triglyceride compositions are dominated by even-numbered fatty acid components, removal of the carboxyl group results in biodistillates consisting mainly of odd-numbered paraffins.

These hydroprocessed biodistillates all share several advantages over biodiesel – including higher energy content, better low-temperature flow characteristics, improved oxidative stability, complete absence of sulfur and nitrogen, and blending behavior that is completely compatible with petroleum diesel blendstocks. Additionally, production of these hydroprocessed biodistillates at a refinery allows for better integration with other refinery operations, and provides access to product testing laboratories. Finally, hydroprocessed biodistillates appear to offer NOx emissions benefits over biodiesel. One disadvantage of hydroprocessed biodistillates is their relatively poor lubricity characteristics. In this regard, they are similar to ULSD, and require additive treatment or mixing with higher lubricity blendstocks to achieve satisfactory performance.

The literature contains several reports of pyrolysis (or thermal cracking) of triglycerides to produce biodistillates. This option may be advantageous when dealing with low-quality triglyceride feedstocks, which are difficult to treat via transesterification. Pyrolysis of lignocellulosic material to produce liquid transportation fuels is an extremely active area of research. However, significant problems with these pyrolysis approaches remain to be overcome – particularly effective means of avoiding char formation, and stabilizing the pyrolysis oils that are produced. Pyrolysis oils produced from lignocellulosic feedstocks require considerable upgrading to be used as transportation fuels.

4. Fuel Properties and Specification

Biodiesel fuel consists of mono-alkyl esters of long-chain fatty acids derived from vegetable oils or animal fats. Since these oils and fats are quite varied in their composition, biodiesel (and renewable diesel) prepared from them also have variable composition. Having considerable oxygen content, biodiesel has lower carbon and hydrogen contents compared to diesel fuel, resulting in about a 10% lower mass energy content. However, because of slightly higher fuel density, the volumetric energy content of biodiesel is only about 5-6% lower than petroleum diesel. Typically, biodiesel has somewhat higher molecular weight than petroleum diesel, which is reflected in slightly higher distillation temperatures (as measured by T_{90}). Being largely straight chain esters, most biodiesel fuels have excellent cetane numbers – typically higher than No. 2 diesel fuel. The viscosity of most biodiesel fuels is significantly higher than petroleum diesel, often by a factor of 2.

Renewable diesel consists primarily of straight chain, saturated hydrocarbons having 15 or 17 carbon atoms. Structurally, renewable diesel molecules resemble cetane (n-hexadecane). Consequently, renewable diesel has excellent combustion properties, as indicated by its high cetane numbers. On a mass basis, the energy content of renewable diesel is very high, slightly exceeding that of typical No. 2 diesel fuel. However, due to its relatively low density, the volumetric energy content of renewable diesel is significantly lower than that of No. 2 diesel, but is very similar to a typical biodiesel. Typical properties of biodiesel and renewable diesel are provided below in Table ES-1, along with typical properties of conventional No. 2 diesel fuel.

Table ES-1. Typical Properties of Petroleum Diesel and Biodistillate Fuels

Property	No. 2 Petroleum ULSD	Biodiesel (FAME)	Renewable Diesel
Carbon, wt%	86.8	76.2	84.9
Hydrogen, wt%	13.2	12.6	15.1
Oxygen, wt%	0.0	11.2	0.0
Specific Gravity	0.85	0.88	0.78
Cetane No.	40-45	45-50	70-90
T_{90}, °C	300-330	330-360	290-300
Viscosity, mm^2/sec. @ 40°C	2-3	4-5	3-4
Energy Content (LHV)			
Mass basis, MJ/kg	43	39	44
Mass basis, BTU/lb.	18,500	16,750	18,900
Vol. basis, BTU/gal	130,000	122,000	122,000

In large part, the physical properties, performance attributes, and overall suitability of biodiesel are determined by the fuel's chemical composition. The two most important compositional factors are fatty acid chain length and the degree of unsaturation in the fatty acid chain. Unlike petroleum diesel, biodiesel contains virtually no branched chain paraffinic structures, naphthenes, or aromatics. All common triglycerides are dominated by even-numbered carbon chains, with C_{16} and C_{18} being the largest components. Some oils are dominated by saturated carbon chains, while others are dominated by unsaturated chains. Examples of this extreme diversity are provided by coconut oil (which is about 90% saturated) and safflower seed oil (which is about 90% unsaturated). Compositional profiles of the most common biodiesel feedstocks, (soybean oil in the U.S.; rapeseed oil in Europe) are depicted below in Fig. ES-4. This figure shows significant differences between the two feedstocks, with soybean being dominated by linoleic acid (18:2) and rapeseed being dominated by oleic acid (18:1).

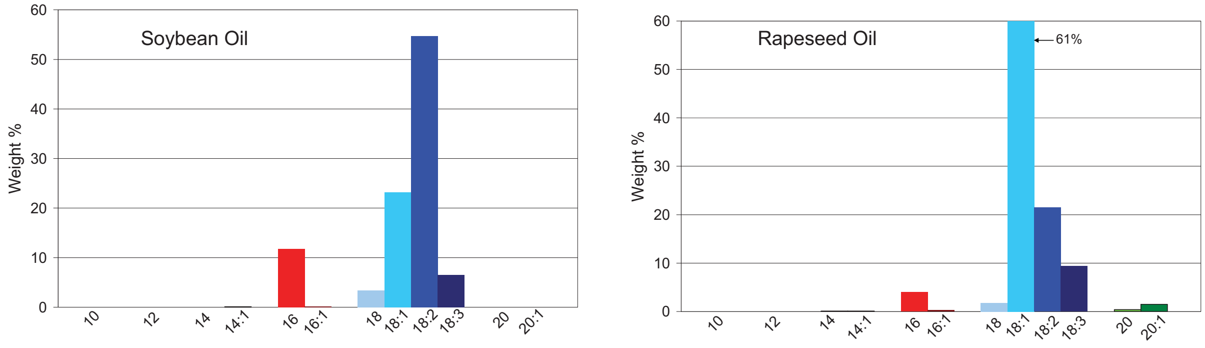


Figure ES-4. Compositional Profiles of Soybean Oil and Rapeseed Oil

Several standard-setting organizations have developed sets of standards to define acceptable quality of biodistillate fuels. The two most widely accepted organizations are ASTM (in the U.S.) and the European Commission (in Europe). ASTM has established standard specifications for biodiesel fuel blendstocks (B100) for middle distillate fuels, called ASTM D 6751. The European Commission's standard specifications for B100 are called EN 14214. At the present time, only the U.S. has established a separate standard for biodiesel blends – ASTM D 7467 is applicable to blends of B6 to B20. In all other locations, low level biodiesel blends (B20 and below) are acceptable if both the biodiesel component and petroleum diesel component meet their respective standards. No special standards have been established for renewable diesel, but finished diesel fuel that contains renewable diesel must comply with the appropriate standards for No. 2 diesel fuel (ASTM D 975 in the U.S.; EN 590 in Europe).

A major reason for many of the specifications in the B100 standards is to ensure high purity FAME, free of contaminants and unreacted starting materials that could otherwise lead to poor performance with respect to storage stability, injection quality, corrosion, deposit formation, emissions, or other problems. A fuel testing laboratory is necessary to determine compliance with established specifications. Most small producers (<1 mg/y) are unlikely to have the equipment or expertise to conduct the full range of tests specified in ASTM D 6751 for B100. Nevertheless, it is strongly recommended that even in such cases, a subset of the most critical specification tests be conducted on every batch, with other tests being conducted periodically using outside laboratories. Table ES-2 provides recommendations of quality control tests that should be performed on every batch of biodiesel, as well as other tests that should be performed periodically.

To help promote satisfactory biodiesel product quality in the U.S., the National Biodiesel Board has established a National Biodiesel Accreditation Commission to oversee the BQ-9000 Quality Management System. This Commission has recently issued two sets of requirements: one for B100 producers; the other for B100 marketers. The BQ-9000 Producers Requirements define acceptable documentation practices, management responsibilities, laboratory operations, sampling and testing methods, fuel blending and loading requirements, and other aspects of a Quality Management System. The BQ-9000 Marketers Requirements include many of the same elements with respect to documentation, management responsibilities, and laboratory procedures, but also address issues of fuel storage, blending, and distribution.

Table ES-2. QC Laboratory Testing Recommendations for B100

QC Tests Conducted on Every Batch		QC Tests Conducted Periodically	
Property	Test Method	Property	Test Method
Water and Sediment	D 2709	Cetane Number	D 613
Viscosity	D 445	Methanol	EN 14110
Flash Point	D 93	Metals (Na, K, Ca, Mg)	EN 14538
Cloud Point	D 2500	Total Sulfur	D 5453
Sulfated Ash	D 874	Phosphorous	D 4951
Acid Number	D 664	Carbon Residue	D 4530
Free and Total Glycerin	D 6584	T_{90}	D 1160
Copper Strip Corrosion	D 130	Ester Content*	EN 14103
Oxidative Stability	EN 14112	Iodine Number*	EN 14111

Because some properties of biodiesel differ from those of conventional diesel fuel, extra precautions must be taken to ensure that proper handling practices are followed, so that products having acceptable quality are delivered to the end customer. Under special circumstances, B100 may be utilized. However, for use as a transportation fuel, only blends of biodiesel with conventional diesel are generally recommended. The literature is replete with studies where various blend ratios of biodiesel have been used. For research and development purposes, investigations of wide blending ranges are valuable, since this provides a better understanding of fuel effects on injection behavior, engine performance, emissions, materials compatibility, and other factors. For commercial use, however, a much narrower range of biodiesel blend ratios is desirable. In the U.S. today, two biodiesel blend levels are most common; B2 and B20. B2 is frequently used to provide sufficient lubricity for ULSD to meet ASTM D 975 requirements. B20 is the highest blend level specified by ASTM and permitted by many engine and vehicle manufacturers.

One of the biggest concerns of the biodiesel industry is the quality of finished fuels being used in the marketplace. The use of poor quality fuels can lead (and has led) to field problems and customer complaints, which reduce public confidence and jeopardize the future of the industry. Steps to address these concerns have been taken in recent years by adoption (or modification) of ASTM Standards D 6751 (for B100) and D 7467 (for B6-B20), and by development of the BQ-9000 Quality Management System. Fuel quality surveys have indicated that problems with blending control and off-spec products are common. However, it appears that with more stringent fuel specifications and increasing producer experience, the overall quality of biodiesel in the marketplace is improving.

Ensuring satisfactory oxidation stability of biodiesel in the market place is one of the biggest product quality concerns. Due to the complex degradation pathways involved, no single test method is fully able to assess fuel stability in all circumstances. One of the most widely utilized test methods is the Rancimat oxidative stability test (EN 14112), which is based upon detection of volatile, secondary oxidation products that result from reaction of biodiesel with oxygen at elevated temperature. The Rancimat test was only recently (2007) incorporated in the ASTM standard specifications for B100. Although considered a good indicator of biodiesel's oxidative stability, the Rancimat test is not necessarily a good indicator of long-term storage stability. However, recent work has shown that storage stability of biodiesel blends (B5 and B20) can be predicted based on the Rancimat test result of the B100 used to make these blends.

For many users, low temperature operability is the greatest biodiesel concern, particularly during cold seasons of the year. Just as with conventional diesel fuel, precautions must be taken to ensure satisfactory low temperature operability of biodiesel and its blends. Poor low temperature operability may be exhibited in several ways, but principally by filter plugging due to wax formation, and engine starving due to reduced fuel flow.

As with fuel stability, there is no single best test to assess low temperature operability. U.S. fuel standards do not include explicit specifications for low temperature operability – either for conventional diesel or biodiesel (or blends of the two). However, the fuel seller is generally required to give an indication of low temperature operability by reporting the cloud point (CP) of the fuel. Poor low temperature operability is caused by long-chain paraffinic hydrocarbon groups present in biodiesel. In general, the longer the carbon chain, the higher the melting point, and poorer the low temperature operability. The presence of carbon–carbon double bonds significantly lowers the melting point of a molecule (hydrocarbon or fatty acid alkyl ester). Therefore, to a certain degree, a trade-off exists between fuel stability and low temperature operability. With increasing extent of unsaturation, stability decreases but low temperature operability improves.

In large part, the fatty acid composition of the fats and oil precursors to biodiesel dictate the low temperature operability of the final fuels. Feedstocks with highly saturated fatty acid structures (such as palm oil and tallow) produce biodiesels with poor operability; whereas feedstocks with highly unsaturated fatty acid structures (such as rapeseed and safflower oil) have better operability. Proper choice of feedstocks is critical to providing a finished biodiesel fuel having acceptable low temperature operability. Other approaches that are helpful in particular circumstances include the following:

- Blending with petroleum diesel
- Use of commercial petroleum diesel additives
- Use of new cold flow improver (CFI) additives for biodiesel
- Use of higher alcohols for transesterification
- Crystallization fractionation

Although the viscosity of a biodiesel is much lower than that of its triglyceride feedstock, it is typically higher than that of petroleum diesel – often by a factor of two. Viscosity can have significant effects on the injection quality of distillate fuels. In general, higher viscosity leads to poorer fuel injection and atomization. Biodiesel users have very few options to improve the viscosity of the fuel. The only practical approach is to dilute with petroleum diesel (or renewable diesel). Low concentration blends of biodiesel (B20 and below) generally have acceptable viscosity, and do not cause significant field problems.

In the U.S., lubricity specifications apply to both conventional diesel and B6-B20 blends of biodiesel. B100 does not have a lubricity specification. In fact, the natural lubricity of neat B100 is so high that a 1-2% blend of it with ULSD is generally sufficient to meet the lubricity specification of D 975. In part, biodiesel's good lubricity can be attributed to the ester group within the FAME molecules, but a higher degree of lubricity is due to trace impurities in the biodiesel. In particular, free fatty acids and monoglycerides are highly effective lubricants. It has been noted that purification of biodiesel by means of distillation reduces its lubricity because these high-lubricity impurities are removed. The effect of unsaturation upon lubricity is unclear, with some researchers reporting positive effects of carbon-carbon double bonds while others report no effect.

Due to its different physical and chemical properties, introducing biodiesel into systems designed for petroleum diesel raises questions about materials compatibility and other potentially adverse impacts on fuel or engine systems. Materials compatibility pertains to the impacts of biodiesel upon seals, gaskets, hoses, metal surfaces, and other materials that the fuels contact. It is well known from laboratory studies and in-use experience that changes in fuel composition can affect the integrity of elastomeric materials. In particular, changes in swelling, shrinkage, embrittlement, and tensile strength are of concern, as extreme changes in these properties can lead to seal failures, leaks, and subsequent problems. Materials compatibility issues are of greatest concern with use of B100. Limiting biodiesel blends to B20 and below, and ensuring that only on-spec fuel is used, greatly reduces these concerns.

Water solubility and water contamination are other issues of concern. At room temperature, water is very slightly soluble in conventional diesel fuel (<100 ppm), but has significant solubility in B100 (up to 1200 ppm). Water solubility in B20 is intermediate between these two extremes. The generally higher water levels in biodiesel can exacerbate problems with corrosion, wear, suspension of solids, and microbial growth. When dealing with biodiesel, extra "housekeeping" precautions may be necessary to remove excess water and sediment. In particular, this is required when first introducing biodiesel into tanks previously used for conventional diesel, as accumulated water and sediment may become dispersed and plug filters under these conditions.

5. Exhaust Emissions Impacts

Diesel vehicles are a significant source of both NO_x and PM emissions and, to a lesser extent, CO, HC, and other toxic species. Since NO_x is a precursor to ozone (O_3) formation, it is also a key variable in the development of control strategies to reduce this secondary pollutant. The impacts of biodiesel upon exhaust emissions have been a topic of interest for many researchers. A thorough review of B20 emissions impacts in HD engines was conducted by EPA and documented in a 2002 report. In 2006, another review of this topic was conducted by McCormick et al.

In this current study, emissions results published in 94 literature references were examined. These reports include HD, LD, and single-cylinder test engines (TE) utilizing both engine and chassis dynamometers, operating under a wide variety of transient and steady-state conditions.

Many different biodiesel blend levels have been investigated, using fuels produced from numerous different feedstocks.

Considering this wide variety of engine configurations, fuels, and testing conditions, it is very difficult to compare directly the measured emissions levels from different studies. To overcome this problem, we expressed all results as the percent change in emissions levels between a test biodistillate fuel and a reference fuel used in the same study. If a particular publication did not include a reference diesel fuel for comparison, the biodistillate results were not used to evaluate a percent change in emissions.

Using this approach, the impacts of specific biodistillate blends on emissions could be discerned more clearly. Graphical displays were developed to illustrate the variation in results across different studies, and to show emissions trends as a function of biodistillate blend level. Examples of these graphs for HD engines are shown in Figure ES-5. The top panel in this figure shows single data points representing averages of each reported test (i.e., studies generally reported a range of emission rates for a given engine and fuel) at a given biodistillate level and is color coded by pollutant type (NO_x, CO, PM and HC). To display the full range of observations, the y-axis spans a percent change of +/- 100%. A linear trend line for each of the species is included, which provides an assessment of the overall change in emissions with increasing levels of biodistillate. The middle panel collapses the data from the top panel by displaying the average of all test results at a given blend level vs. blend level. Error bars represent the minimum and maximum percent change from a reference diesel fuel for all test results within at a specific biodistillate blend level. The bottom panel uses the same dataset as the middle panel, but displays a logarithmic trend line based on the average of all emissions for a given biodistillate level. This is the simplest way of showing the trend in emissions for each pollutant as a function of biodistillate level.

To compare the results of this analysis with findings of other studies, the regression equations derived from the logarithmic trendlines were used to predict the percent change in emissions of a given pollutant for a specified biodiesel blend level. The blend levels of greatest interest are B20 and B100. Regression fits at these levels give the emissions changes shown below in Table ES-3.

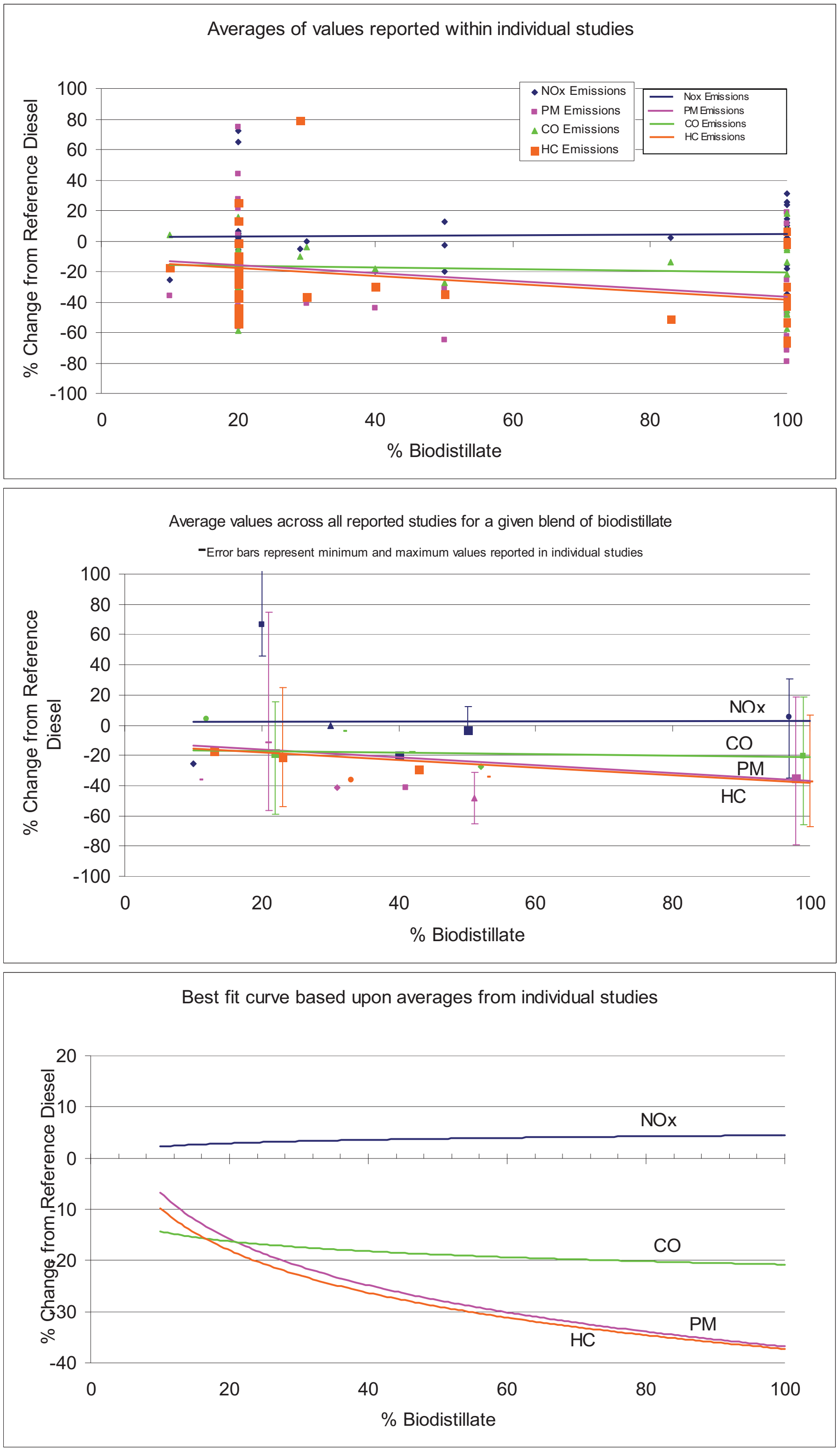


Figure ES-5. Effects of Biodistillate Blends on Exhaust Emissions from HD Engines

Table ES-3. Predicted Changes in Emissions using B20 and B100

	Pollutant	HD	LD	TE
B20	NO_x	+2.9	+10.8	-8.1
	CO	-15.7	-10.1	-13.4
	HC	-18.0	-16.6	-15.4
	PM	-15.8	-36.0	-12.9
B100	NO_x	+4.5	+15.3	-1.7
	CO	-20.8	-12.3	-16.2
	HC	-37.3	-22.9	-16.3
	PM	-36.8	-33.1	-26.8

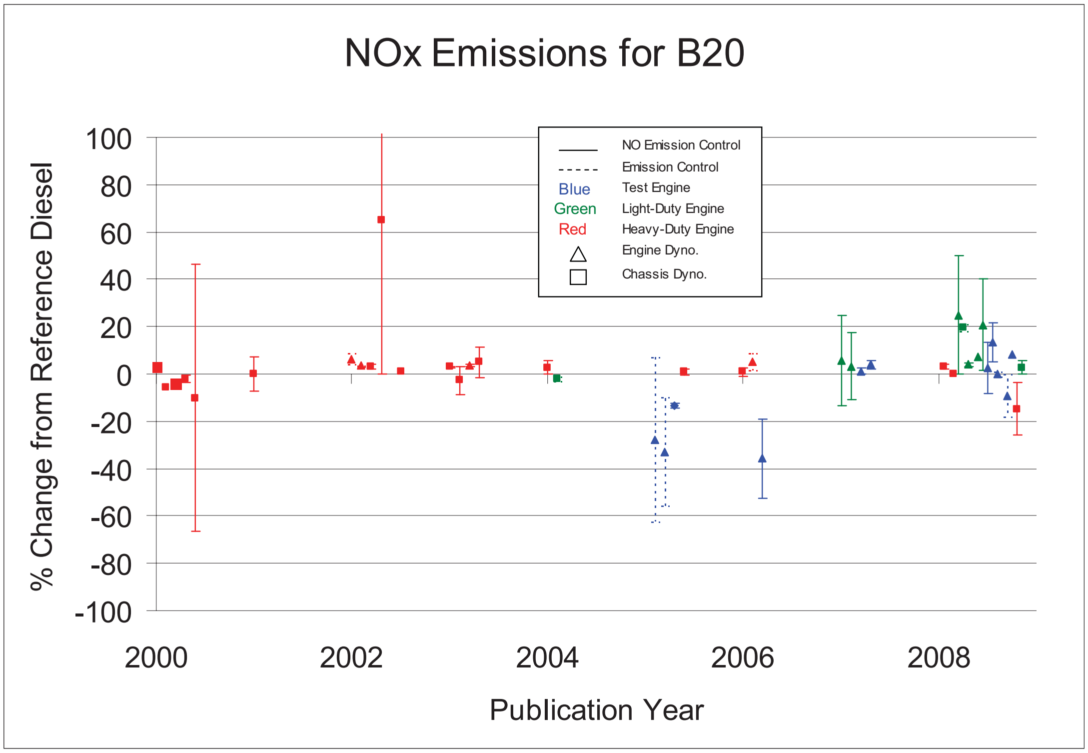
The B20 results for HD engines are further compared with those reported by EPA (2002) and McCormick et al. (2006) in Table ES-4. In large part, our results are consistent with those reported in these earlier reviews. For CO, HC, and PM, all three reviews show substantial emissions reductions from use of B20 (generally 10-20% reduction) with this study's results falling between the other two. NOx emissions results are less clear. EPA reported a 2.0% NOx increase with B20, while McCormick et al. reported a 0.6% increase (which was determined to not be statistically significant). In this study, the logarithmic data fit predicts a 2.9% NOx increase with B20.

Table ES-4. Comparison of the Average Change in Emissions from HD Dynamometer Tests using B20

Pollutant	EPA, 2002	McCormick et al., 2006	This Study
NO_x	+2.0	+0.6*	+2.9
CO	-11.0	-17.1	-15.7
HC	-21.1	-11.6	-18.0
PM	-10.1	-16.4**	-15.8

*Reported as statistically insignificant.
**Excludes engines equipped with DPF.

While the emissions reduction benefits of biodistillates for CO, HC, and PM seem quite clear, the NOx impacts remain small and uncertain. Some have suggested that the NOx effects may be sensitive to engine technology and operating condition. To explore this, the biodistillate emissions results reported in the literature were plotted vs. publication year, as a rough surrogate for engine technology. (Most publications do not clearly describe the engines with respect to model year, technology type, or certification level.) The NOx results for both B20 and B100 blends are shown in Figure ES-6. Given the limited results for each year, coupled with large error bars associated with most data points, it is difficult to draw quantitative conclusions. However, qualitatively it appears that the percent change in emissions (for both B20 and B100) is largely unchanged with model year/technology.



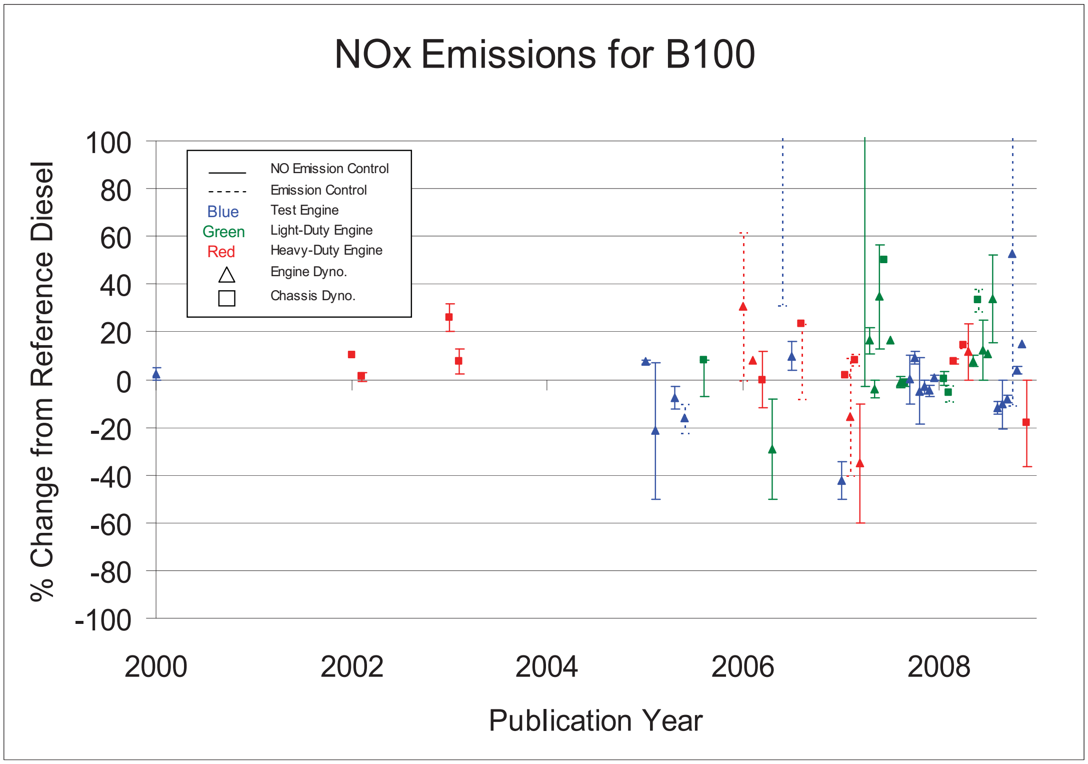


Figure ES-6. NO_x Emissions for Biodistillate Fuels Compared to Reference Diesel Fuel

The potential impact of biodistillate blends on emissions of toxic species was also investigated. The findings were limited, with most observations being for carbonyls -- particularly formaldehyde and acetaldehyde. Results for these species and total carbonyls are shown in Figure ES-7. Overall, the results imply there is a decrease in emissions with increasing blend level; although a number of studies reported increasing emissions for B20. This trend is somewhat surprising since biodiesel, which consists of oxygenated species (FAME), might be expected to increase aldehyde emissions.

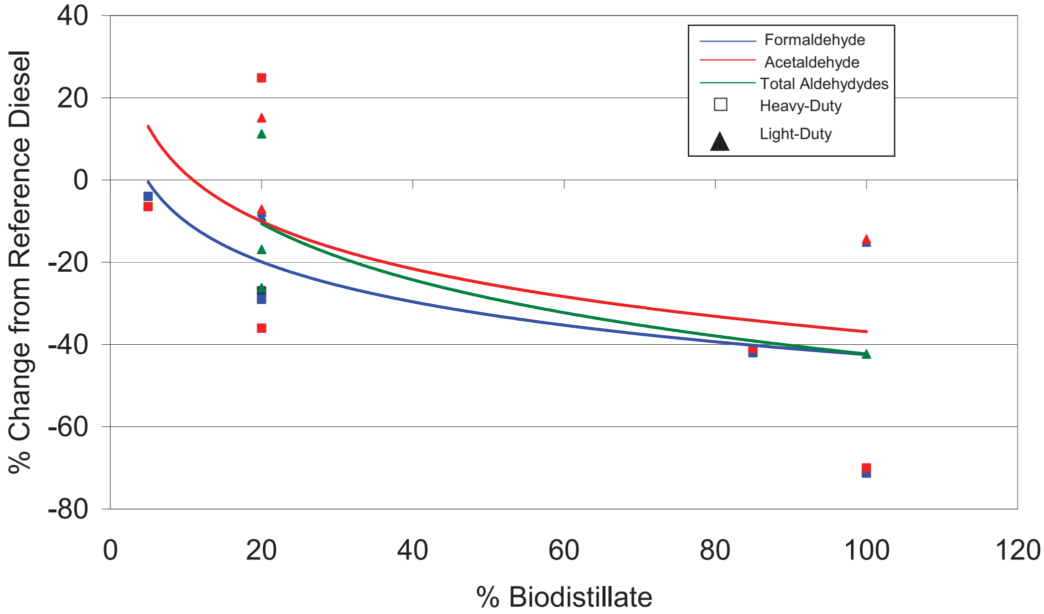


Figure ES-7. Effects of biodistillate Blends on Carbonyl Exhaust Emissions from HD and LD Engines

6. Life-Cycle Analysis and Land Use Impacts

In comparing energy and environmental impacts of different fuels, it is increasingly recognized that the entire life-cycle of the fuel must be considered. In fact, life-cycle models have become a common aid for policy regarding the use of alternative fuels. Life-cycle assessments (LCA) provide a tool to evaluate the energy and environmental impacts that result from all stages of a product's life, from manufacturing through disposal. Full fuel LCAs are commonly broken into two parts: (1) well-to-tank (WTT) and (2) tank-to-wheels (TTW). The combination of the two parts represents the complete well-to wheels (WTW), or "cradle-to-grave," life-cycle for a transportation fuel.

The WTT pathway for a biodistillate fuel commonly includes growth of the crop which may involve land-use change (LUC) and farming inputs like fertilizers, harvesting of the crop, processing or crushing to extract the oil, production (via transesterification or some other method), and distribution to the fuel-pump. The TTW analysis includes combustion of the fuel in a vehicle, and depends on the type of vehicle, its efficiencies and type of driving. However, common practice for biofuels is to assume a carbon-neutral principle in which the amount of CO_2 emitted by the fuel during combustion is the same as that taken up by the plant during its growth through photosynthesis. With this assumption, the WTT results for GHG emissions of biofuels are similar to the complete WTW results.

Although established databases and modeling tools exist, differences in LCA modeling approaches are still common. Two models can be run with the same types of assumptions, yet produce different results. Standards have been developed to maintain some consistency in data. For example, ISO 14044:2006 provides requirements and guidelines, and ISO 14048:2002 outlines standards for data documentation and format within the model. However, the standards do not specify methodologies that should be used, so results of different assessments can be highly varied. Therefore, fuel LCA models are typically used to determine the relative benefits of different scenarios in which conventional petroleum fuels are displaced with alternative fuels.

Differences in methodologies arise from variations in defining fuel pathways, scenario boundaries, input assumptions, and dealing with co-products. Most LCA data inputs are specific to the process, fuel type, or region that is being evaluated. For example, crop yields can vary dramatically based upon type of crop or growing location; also, energy use for a 2nd Generation production process may not be well established and must be estimated from scant data.

The use of crops to support a biofuel industry would require some existing crop lands to be converted to biofuel crops, as well as conversion of other arable lands to crop-land. This topic of land use change (LUC) and the way that it is considered (or not considered) in LCA modeling have drawn considerable attention recently. Both direct and indirect LUC may have significant impacts on the overall life-cycle results for a particular fuel. Direct impacts are those that are associated directly with the cultivation of feedstocks used to produce a biofuel in the region where it is used. Indirect effects are those that could potentially arise when a crop is produced in one region of the world in response to fuel demand changes in another region.

Many LCA models include some type of direct LUC assessment to address changes in GHG emissions resulting from modifications to soil carbon, or variations in above ground biomass from preparation of existing crop-lands or conversion to new crop-land. Methods of including direct LUC are somewhat controversial, specifically with respect to N_2O, a potent GHG produced by biological processes. Because small changes in N_2O can result in significant differences in GWP, it is crucial to account for all nitrogen inputs and outputs associated with cultivation -- including crop residues, fertilizers, nitrogen fixation, manure usage, deposition, gaseous losses, crop output, runoff, nitrogen transfer between co-rotated crops, and others. Variations in assumptions about N_2O can swing the final GWP results of a particular biofuel scenario from positive to negative, compared to a conventional baseline fuel.

Indirect LUC has been a topic of recent publicity and concern as having potentially serious adverse GHG impacts. As crops are diverted to fuels in one geographic location, increased crop production will be required elsewhere to compensate. This increased production could occur through displacement of existing crops, expansion of croplands, or intensification of existing production. Expansion of croplands may require reducing forest lands or other fallow lands elsewhere, which could result in an extremely large release of CO_2 previously sequestered by roots and soil. Intensification of production may require more fertilizer usage. Both could have a net-negative GHG effect for a particular biofuel. Most LCA models do not include the effects of indirect LUC because these effects are much more difficult to analyze and require subjective assumptions that contain substantial uncertainty. However, policy is trending toward including indirect LUC into already required LCA models. To do this, some type of economic model is required to estimate the economic supply and demand of developing new crop lands.

Another major source of variation among LCA results is the method by which co-products are treated. Several by-products are produced during the manufacturing of biodiesel; for example, animal feed meal is produced during the oil extraction process, and glycerol is produced during transesterification. (Co-products such as naphtha or propane may be produced in 2nd Generation biodiesel manufacturing involving hydroprocessing.) Common practice in LCA modeling is to allocate some of the energy and emissions produced during the fuel life-cycle to these co-products since they can replace other similar products in the market. At least four different allocation methods are commonly used:

- Physical allocation
- Economic allocation
- Expanded allocation
- No co-product allocation

The choice of allocation method is controversial and not clearly defined. As with LUC, variations in co-product allocation can also swing the final LCA results of a particular biofuel scenario from positive to negative, compared to a conventional baseline fuel.

The life-cycle energy use required to produce and/or use a unit of fuel is one of the impacts most frequently assessed in an LCA. The overall energy benefit or energy return (ER) of the entire process is determined by dividing the energy out of the process (the heating value of the fuel) by the total life-cycle energy inputs. A net energy benefit results when the ER is greater than one; an ER less than one indicates more energy is required to produce the fuel than is contained in the final product. [This value of ER is sometimes called Energy Return on Investment (EROI).] Common practice in biofuel LCA is to report only the required fossil energy inputs in the EROI, but not any renewable energy inputs, such as the energy content of the plant itself. This typically results in an ER greater than one for biodistillates. In contrast, the energy requirements to make conventional diesel are almost entirely fossil energy, (including the energy content of petroleum itself) which typically results in a life-cycle ER of less than one.

ER results for 17 literature reports are depicted below in Fig. ES-8. Very large ranges of results are shown for some studies which included several scenarios or sets of assumptions. In most cases, biodistillates showed a significant increase in ER compared to conventional diesel fuel. This is true for both biodiesel and renewable diesel scenarios. An overall average ER value from all the studies is approximately 3.1. Information such as this is the basis of claims that biodistillates offer a 3-fold improvement in energy return compared to petroleum diesel.

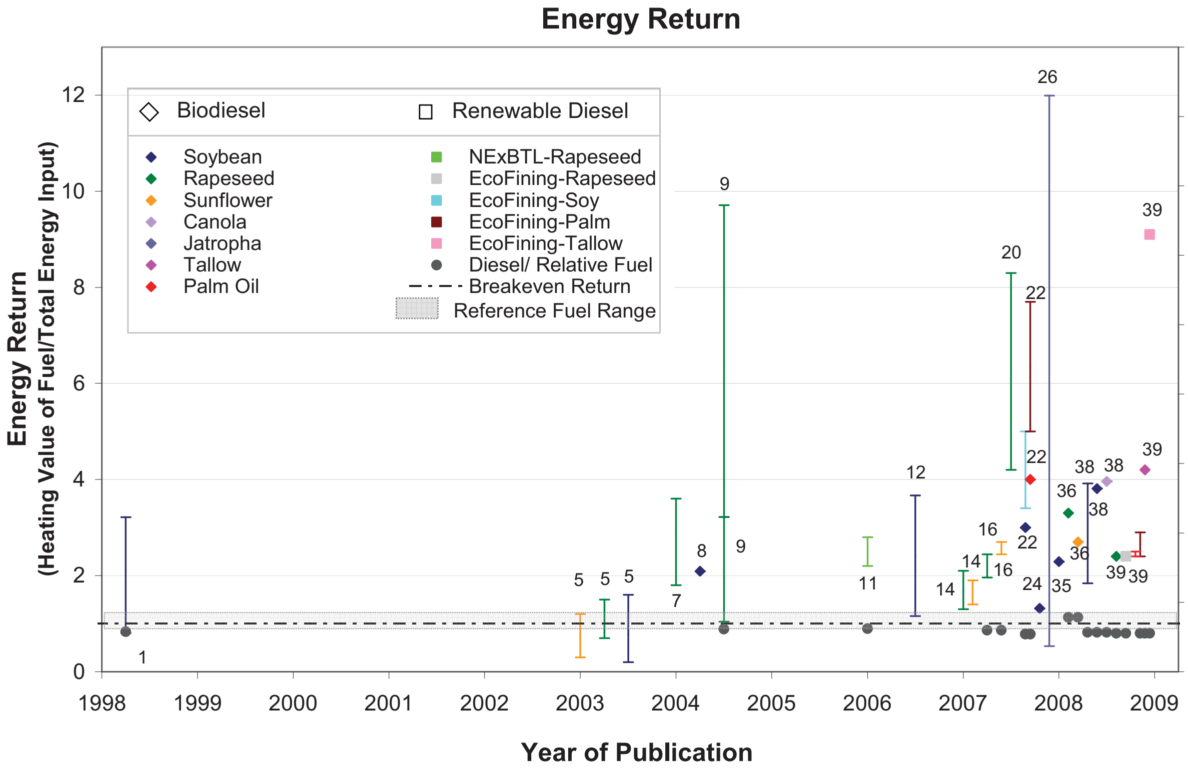


Figure ES-8. Energy Return for 17 LCA Models
Study No's identified in Appendix VI

In LCA analyses of transportation fuels, GHG results are generally aggregated and reported on the basis of total global warming potential (GWP). To do this, emissions of all GHGs are converted to a CO_2-equivalent basis using factors recommended by the IPCC or some other organization. Typically, the final GWP results are reported as grams of CO_2-equivalent GHG emissions per MJ of fuel. Direct comparison of results among different studies should be done with extreme care, since different studies vary significantly in their assumptions and pathways. Of the 16 literature studies that reported life-cycle GHG impacts, most computed final GWP results in the range of 10-60 grams of CO_2-equivalent emissions per MJ of fuel produced. The range of conventional diesel GWP values reported in these studies was from 22 to 240 grams of CO_2-equivalent emissions per MJ of fuel.

A more instructive way to compare results among different LCA studies is to evaluate differences between the biodistillate and conventional fuel scenarios within each study. On this relative basis, most LCA studies report that biodistillate scenarios result in 10-90% lower GWP compared to a conventional diesel baseline. Similar benefits are seen for both biodiesel and renewable diesel cases, from a variety of feedstocks. However, as shown in Fig. ES-9, many of these studies include wide ranges of results, resulting from different assumptions and approaches. Study No. 32, which showed a significant dis-benefit for biodiesel, utilized much higher N_2O emissions than most other studies. This clearly illustrates the sensitivity of LCA results to input assumptions.

In addition to GWP and energy requirements, other ecological or resource impacts are often assessed using LCA methodologies. Some of the most important impact categories pertain to water resources, eutrophication, acidification, and photochemical ozone creation potential. However, compared to CWP and energy impacts, assessments of these other life-cycle impacts are still in their infancy.

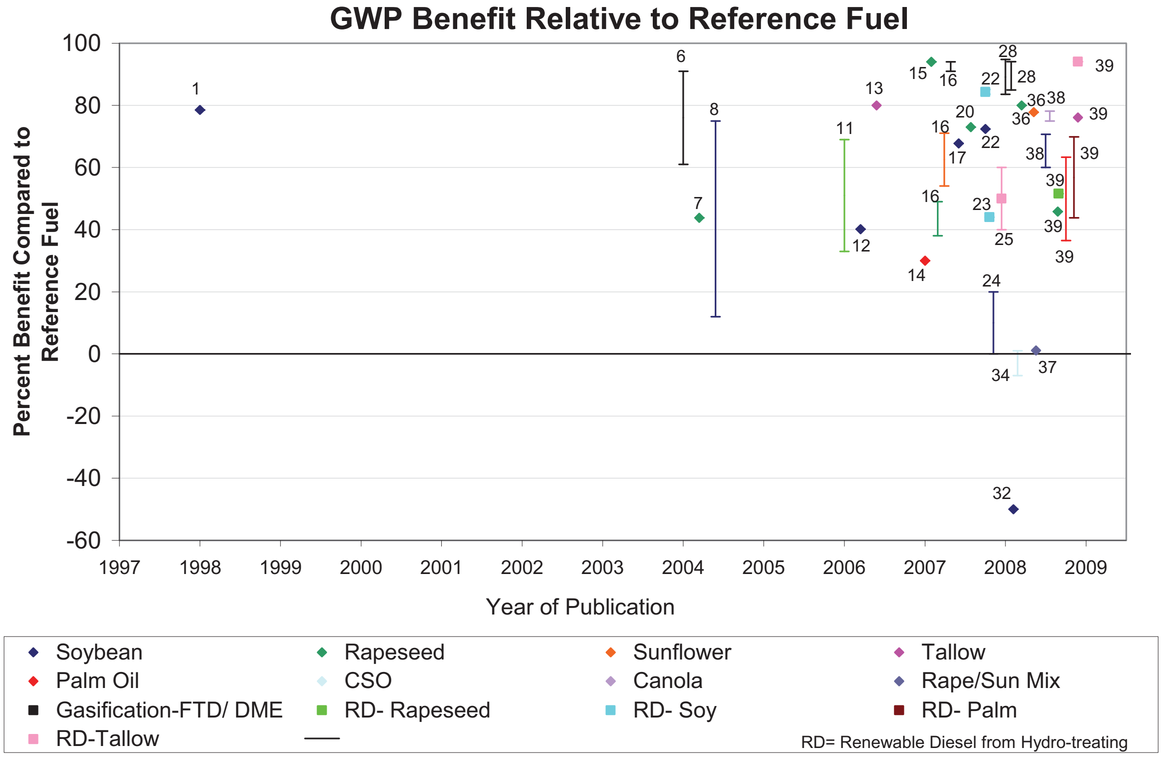


Figure ES-9. Relative GWP for 20 Biodiesel LCA Studies
Study No's identified in Appendix VI

7. Summary and Conclusions

The major results and conclusion from this review of biodistillate topics are summarized below:

- Many countries have developed policies to promote greater production and use of biodistillate fuels. The U.S. Energy Independence and Security Act (EISA) of 2007 requires 0.5 bg/y of biodiesel by 2009, and 1.0 bg/y by 2012. Even more aggressive targets are set by Europe and several other countries. Taken together, the policy-driven volumetric requirements of the U.S., Europe, China, India, and Brazil total 23 bg/y by 2020. Based upon our assessment of the situation, we forecast a much lower usage of about 7 bg/y in 2020.

- While numerous triglyceride feedstocks have been investigated as potential feedstocks for biodiesel production, only a few are in widespread commercial use. The dominant feedstock in the U.S. is soybean oil, with far lesser amounts of other seed oils, used cooking oils, and animal fats being used. In Europe, the dominant feedstock is rapeseed oil.

- Biodiesel production capacity has grown much faster than actual production volumes, and excess capacity has become a serious problem within the biodiesel industry. This is driven by limited availability and high costs of current feedstocks. Consequently, there is great interest in developing alternative feedstocks, particularly those that do not have concurrent uses as food. Two of these so-called, 2nd generation feedstocks receiving considerable attention are jatropha and microalgae. It is likely that commercially produced biodistillates from these feedstocks will begin to appear in the marketplace within the next 5 years.

- In most locations, the predominant use of biodiesel is as a low-concentration blend with petroleum diesel. Concentrations of 2% (B2), 5% (B5) and 20% (B20) are most common. Only in Germany and Austria is use of neat biodiesel (B100) commonly employed as a transportation fuel.

- The dominant biodiesel production technology in commercial use involves transesterification of triglyceride feedstocks (from fats and oils) with methanol to produce fatty acid methyl esters (FAME). This process also results in production of low-purity glycerol, which must be upgraded or otherwise disposed. Process improvements involving co-solvents, better catalysts, and alternative heating methods are being actively investigated.

- Hydroprocessing of triglycerides is an alternative route to biodistillates that does not involve alcohols or glycerol production. The product of this process is commonly known as renewable diesel, as opposed to biodiesel. Renewable diesel consists of hydrocarbons that are virtually identical to those found in petroleum diesel. Production of renewable diesel is most conveniently accomplished within an integrated petroleum refinery.

- The properties of biodiesel are largely dictated by the chemical composition of the fatty acid methyl esters comprising the fuel. Two of the most important chemical parameters affecting the overall fuel properties are carbon chain length and degree of unsaturation (carbon-carbon double bonds) within the FAME molecules.

- Biodiesel typically contains about 11% oxygen, in the form of methyl esters. As a consequence, it has lower mass energy content than petroleum diesel – by about 10%. Renewable diesel, containing no oxygen, has a mass energy content very similar to petroleum diesel.

- Standard specifications for biodiesel fuel have been developed, and are continuing to evolve. In the U.S., biodiesel (B100) specifications are defined by ASTM D 6751-08; European specifications are defined by EN 14214. At present, the U.S. is the only country having specifications for biodiesel blends: ASTM D 7467-08 applies to B6-B20 blends.

- Biodiesel fuel standards include numerous specifications and test methods to ensure acceptable product quality and performance. Attaining full compliance with biodiesel standard specifications requires extensive and regular laboratory testing.

- Adhering to established quality control/quality assurance (QC/QA) measures is critical to ensuring satisfactory biodiesel quality in the marketplace. In the U.S., the BQ-9000 Quality

Management System was recently developed to define acceptable QC/QA measures. BQ-9000 includes separate sets of requirements for B100 producers and B100 marketers.

- U.S. fuel quality surveys have shown significant inaccuracies of blending, with some reported B20 blends actually containing much more or much less than 20% biodiesel. These surveys also reveal problems with off-spec biodiesel in the marketplace, with poor oxidative stability being the greatest concern. More recent surveys indicate that overall, product quality in the marketplace is improving.

- In general, biodiesel has somewhat poorer low temperature operability than petroleum diesel, though the extent of the difference varies substantially based upon the unique chemical composition of the biodiesel in question. Low temperature operability can be improved by greater dilution with petroleum diesel, use of cold flow improver additives, and use of ethanol rather than methanol in the transesterification process.

- While exceptions are possible, acceptable in-use handling and performance of biodiesel is best achieved by strict adherence to established fuel specifications and implementation of good fuel housekeeping practices. Additionally, to minimize concerns regarding fuel stability, viscosity, materials compatibility, and others, it is prudent to limit the biodiesel composition to B20 and below.

- Our review of the emissions literature indicated that in most cases, use of biodistillates substantially decreases emissions of CO, HC, and PM – generally by 10-20%. Although results vary considerably from one study to the next, these emissions benefits are typically seen in both LD and HD engines, regardless of engine technology or test cycle. Although data are much more limited for renewable diesel cases, it appears that similar benefits in reduction of CO, HC, and PM are observed with these hydroprocessed fuels.

- NOx emissions impacts are much smaller, and difficult to discern. Though highly variable, most studies indicate a slight NOx increase when using biodiesel fuel. For HD engines, our best estimates are that NOx emissions increase 2.9% with B20, and 4.5% with B100. These results are largely consistent with previous reviews by EPA. There is limited data to suggest that use of renewable diesel provides a NOx emissions benefit compared to biodiesel. Further testing is necessary to confirm this finding.

- Much less information is available regarding non-criteria pollutant emissions from use of biodistillate fuels. The pollutants most frequently reported are formaldehyde and acetaldehyde. Somewhat surprisingly, the majority of published reports indicate a slight decrease in aldehyde emissions when using B20, and a larger decrease when using B100. A more substantial body of emissions data is necessary to confirm (or refute) these observations.

- Life-cycle assessments (LCA) of “well-to-wheels” energy inputs and GHG emissions are now recognized as important tools for understanding the relative benefits of biodistillate fuels compared to conventional fuels. However, LCA models are very data intensive, and require numerous inputs having high uncertainty. Some of the most critical inputs are in areas in areas that are most uncertain – such as assumed agricultural practices and their emissions, impacts attributed to co-products, and land use changes (LUC).

- Variations in LCA model assumptions have drastic effects on the final results. Consequently, it is difficult to compare directly LCA results from different studies. Comparison of relative effects between biofuel and conventional fuel scenarios conducted within the same study is often more informative.

- Life-cycle energy results are typically reported as energy return on investment (EROI, or more simply, ER), meaning the heating value of the final biofuel divided by the total fossil energy inputs involved in producing, distributing, and using the fuel. Typically, ER values for conventional diesel fuel are slightly under 1.0. Our analysis of 17 LCA studies gave an overall average ER value of about 3.1 for biodistillates, indicating substantial benefits for these fuels (both biodiesel and renewable diesel) in terms of life-cycle energy.

- LCA results for GHG emissions are usually expressed in terms of relative global warming potential (GWP). In almost every published LCA study, biodistillate scenarios resulted in lower GWP compared to conventional diesel. In the 20 studies we investigated, the GWP benefits of the biodistillate fuels ranged from 10% to 90%, with an overall average value of about 60%. However, there are a few exceptions, mainly due to assumptions of high N_2O emissions, where biodiesel scenarios showed overall GWP dis-benefits compared to conventional diesel.

1. Introduction and Background

In recent years, the production and use of biofuels have increased dramatically, both in the U.S. and around the world. This growth is driven by somewhat different factors from one country to the next, but the strongest factors generally include the following:

- National energy security
- Diversity of energy sources
- Concerns over greenhouse gases (GHGs) and global climate change
- Desire for sustainable energy sources
- Rural economic development
- Improved balance of trade

Over the past 10-20 years, most of the interest and activity regarding biofuels was focused on ethanol, and its use in light-duty gasoline vehicles (LDGV). While ethanol remains a topic of considerable interest and debate, recent years have seen rapid growth in activities pertaining to biofuels meant for blending with diesel fuel and used in vehicles with compression ignition (CI) engines.

Numerous aspects of biofuels are of interest and importance – including feedstocks, production technologies, fuel properties and standards, vehicle emissions, fuel performance and handling, and life-cycle impacts. Due to the evolving nature and rapid growth of information in these areas, CRC wished to conduct a study to assess the state-of-knowledge regarding plant-derived biofuels as blending materials for ultra-low sulfur diesel (ULSD) fuel in transportation applications. This report documents our efforts to meet these objectives, and provides a summary of the information we believe to be most pertinent to CRC's interests.

1.1 Limits of Study

Although CRC's primary interest relates to plant-derived biofuels used in ULSD, we believe it useful to expand the scope of the study somewhat, to provide greater context for this particular area of focus. For example, ULSD is a fuel designation exclusive to the U.S., and has been in common usage only since 2006. Thus, while our study does emphasize recent information pertaining to ULSD blend applications in the U.S., we also consider use of neat biofuels (B100), biofuel blends in non-ULSD diesel fuels, and use of biofuels and blends in other countries.

In addition, besides "plant-derived" biofuels, we have included biofuels produced from animal fats – another common feedstock for biodiesel. There is also considerable interest in converting lignocellulosic feedstocks into biofuels. For production of mid-distillates, thermal processes involving gasification and pyrolysis are being developed.(1,2) However, as these areas of development are evolving rapidly – and largely involve proprietary information – this report will not emphasize the production of mid-distillate biofuels from lignocellulosic feedstocks.

It is also important to point out what biofuels topic areas will not be covered in this report. With the emphasis on diesel applications and ULSD blends, we do not consider ethanol (or other alcohols) intended for use in spark-ignition (SI) engines. Other topics excluded from this study include the following:

- Mid-distillate fuels used in non-transportation applications (turbines, boilers, other stationary sources)
- Theoretical or fundamental studies of combustion chemistry, kinetics, and modeling
- Analytical methodologies for detecting and characterizing biodistillates
- Toxicity and health impacts of emissions
- Social, political, or economic studies
- Agriculture, agronomy, and food science studies

1.2 Definitions

Before proceeding, it is important to define fuel-related terminology that is commonly used within the fuels and automotive industries, and is incorporated into this report. A detailed list of common abbreviations and acronyms was provided at the beginning of this report. Some of the most frequently used transportation fuel terms are shown below in Table I. A more complete glossary of fuel terms is provided in Appendix I.

Certain biofuel terminology requires explanation. In this report, we use the term “Biodistillate” to designate all common distillate fuels (diesel, kerosene, jet fuel, and heating oil) that are produced from biological feedstocks – including animal fats, vegetable oils, and lignocellulose. Thus, “biodiesel” and “renewable diesel” will generally be described together, except when distinctions are made regarding production technologies, fuel properties, or performance.

Terminology regarding “1st Generation” and “2nd Generation” biofuels also requires clarification. Generally, the term “1st Generation” refers to biofuels produced from commonly available, edible feedstocks using well-established conversion technologies. Most biofuels in use today are classified as 1st Generation. This includes ethanol produced via fermentation of sugars (from corn, sugar cane, sorghum, etc.) and biodiesel produced via transesterification of triglycerides (from vegetable oils and animal fats).

The term “2nd Generation” can refer to biofuels produced from either advanced, non-food feedstocks, or produced via advanced processing technology (or both). Examples of advanced feedstocks include lignocellulose and non-edible triglycerides (such as jatropha and algae). Examples of advanced processing technology include catalytic hydroprocessing of triglycerides and thermal conversion (gasification and pyrolysis) of lignocellulose.

In this report, which is focused on biodistillate fuels, we use the term 1st Generation to refer to biodiesel produced via transesterification of edible triglycerides (including waste cooking fats and oils). The term 2nd Generation is used to refer to Renewable Diesel, Green Diesel, and biodiesel produced via transesterification of non-edible triglycerides.

Table I. Definitions of Common of Transportation Fuel Terms

1st Generation Biofuels	Fuels produced from commonly available, edible food feedstocks via fermentation (such as grain to ethanol) or transesterification (vegetable oil to biodiesel).
2nd Generation Biofuels	Biofuels produced from non-food feedstocks (such as jatropha, algae, and lignocellulose) by any processing technology, or from edible feedstocks using advanced conversion processes (such as catalytic hydroprocessing).
Alternative Fuel	Any fuel produced from non-petroleum sources. Includes biofuels as well as liquid fuels produced from coal and natural gas.
Biodiesel	Fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oil or animal fats.
Biodistillate	Any mid-distillate fuel (diesel fuel, kerosene, jet fuel, or heating oil) produced from recently living plant or animal materials by a variety of processing technologies.
Biofuel	Fuel produced from recently living plants or animals. This includes gases, liquids, and solids produced via fermentation, digestion, enzymatic hydrolysis, thermal conversion, and other processes.
Cellulosic Fuel	Subset of biofuel, produced from lignocellulosic feedstocks.
Clean Fuel	Ill-defined, colloquial term having variable meanings. Often used in regulatory language.
Conventional Fuels	Any fuel produced from petroleum sources.
Fossil Fuel	Fuel produced from fossil resources – including coal, petroleum, and natural gas.
Green Diesel	Non-fossil hydrocarbon fuel produced by catalytic hydroprocessing of triglycerides from vegetable oils or animal fats. Synonymous with Renewable Diesel.
Renewable Diesel	Non-fossil hydrocarbon fuel produced by catalytic hydroprocessing of triglycerides from vegetable oils or animal fats. Synonymous with Green Diesel.
Renewable Fuel	Gas, liquid, or solid fuel produced from modern biologic feedstocks (plants and animals) that can be replenished.
Synthetic Fuel	Liquid fuel, produced from non-petroleum resources, generally via gasification and subsequent reaction of the synthesis gas.

Note: For a more complete glossary of fuel terms, see Appendix I.

1.3 Information Sources

Much of the effort in this study consisted of a thorough review of the technical literature regarding the feedstocks, production technologies, properties, characterization, testing, performance, and environmental impacts of biodistillate fuels. An excellent starting point for information on all these topics is *The Biodiesel Handbook*,(3) published in 2005. This handbook consists of numerous chapters on these individual topics, written by experts in each area.

With the field of biodistillates being fairly young, our literature search focused on recent years (2000 to the present) though selected older items of interest were also reviewed. The principal sources used to locate the relevant literature are the following five:

1. Web of Science: Used to search peer-reviewed publications in over 6000 scientific journals/periodicals.
2. SAE literature search engine: Used to search literature published by the Society of Automotive Engineers, International (SAE).
3. ASME literature search engine: Used to search literature published by the American Society of Mechanical Engineers (ASME).
4. DOE citation database: Used to search DOE reports and other DOE-sponsored work reported in conference presentations and technical reports.
5. Trade literature, patents, and other sources: Web sites of trade organizations, fuel producers and marketers, governmental agencies, and other relevant entities were searched to obtain additional information of interest. Also, a few patents of particular interest were reviewed.

The general approach was to begin with broad search terms such as “renewable diesel” and “biodiesel,” then use an iterative process to exclude those items of little or no interest. For example, most pamphlets and presentations were excluded, as well as most foreign-language items. Further screening and elimination was done based upon a review of titles and abstracts. Through this process, we reduced the items of interest to less than 1000.

The first step in organizing the literature was to compile all relevant citations using a Thomson ResearchSoft computer program called Reference Manager. Literature sources identified by the Web of Knowledge search tool were directly downloaded into Reference Manager. However, sources identified through the SAE, ASME, or DOE databases required manual entry into Reference Manager.

Based primarily upon review of abstracts, we constructed a reasonably comprehensive bibliography of literature that is relevant for this study. In the process, we identified specific biodiesel/renewable topics that were discussed in each literature report. The topic categories were selected to correspond to the organizational structure of this final report, including the following 6 areas:

1. Feedstocks
2. Fuel production technology
3. Fuel properties and specifications
4. Vehicle emissions
5. Fuel handling and performance
6. Life-cycle analysis

The final bibliography was constructed as an Excel Worksheet, and included here as Appendix II. This spreadsheet approach enables the reader to sort the information by author, date, or topic area. Many of the over 900 items in this bibliography are of minimal relevance to CRC's interests, but are included for the sake of completeness.

The reader will note that in addition to the 6 topic areas mentioned above, some of the literature reports listed in Appendix II include discussions of economics and fuel policy. In this project, no deliberate effort was made to search the literature for these additional topics; rather a few literature sources identified in our search for the main 6 topic areas also contained ancillary information about economics and policy. We merely include this information here as an additional item of interest. This report should not be considered to provide a thorough review on the topics of economics and fuel policy of biodistillates.

Perhaps more useful to the reader is the much smaller bibliography subset indicated by the shaded entries in Appendix II. This subset contains about 50 items that we have judged to be the most important for gaining a thorough understanding of the biodistillate technical topics of greatest interest to the automobile and fuels industries.

It should be emphasized that the subject areas related to biodistillate fuels are currently very active, with about 15-20 new items of interest appearing in the literature each month. Because of this rapid expansion of information, we updated our search several times throughout the course of this study. Our final complete literature search update was conducted on September 30, 2008. The reader should be aware that additional, relevant publications have appeared since that time.

As shown below in Fig. 1, most literature of interest is very recent. Over 75% of relevant journal papers -- and 75% of SAE papers -- have appeared within the past 3 years. In this figure, the category called "Papers" consists mainly of SAE and ASME papers. The category called "Reports" consists mainly of governmental reports (especially from DOE) and company publications. The largest category, called "Journals," consists of peer-reviewed papers appearing in dozens of different science and engineering periodicals.

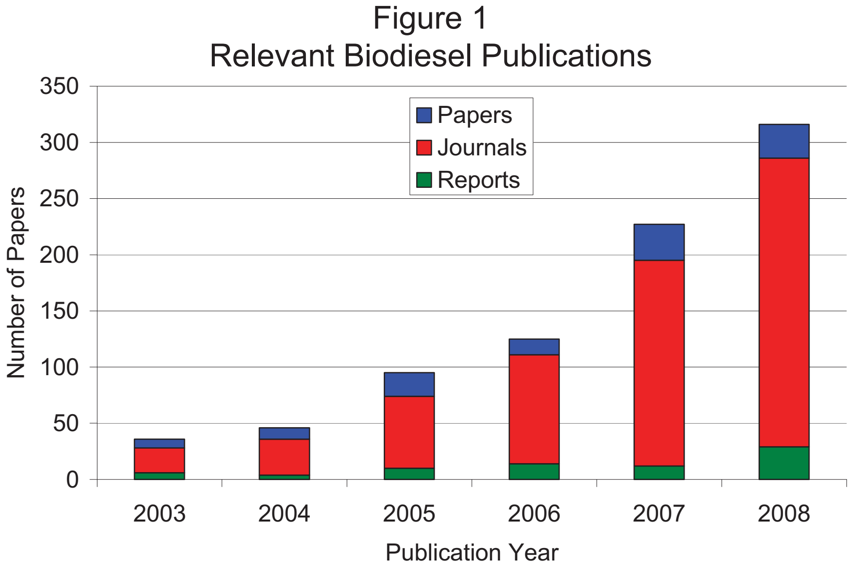


Figure 1. Biodistillate Fuel Publications by Year

2. Policy Drivers for Biodistillate Fuels

2.1 U.S. Federal

In the U.S., the current dominant policy driver for biodistillate fuels is the recently enacted Energy Independence and Security Act of 2007 (EISA).(4) Through EISA, for the first time, Congress has established specific, volumetric requirements for biodiesel of 500 million gallons/year (mg/y) by 2009, ramping up to 1 billion gallons/year (bg/y) by 2012. (Current on-road diesel fuel usage in the U.S. is approximately 40 bg/y; the maximum EISA biodiesel requirement represents 2.5% of this total.)

Though still not implemented, it is expected that EPA will adopt an “energy content multiplier” for biodiesel, whereby each physical gallon is credited as 1.5 gallons in meeting the renewable fuel standard (RFS) within EISA. If this multiplier approach is used, the 1 bg/y biodiesel mandate will only require 0.67 bg/y of actual use.

EISA also establishes a total RFS requirement of 36 bg/y, to be met by 2022, with 21 bg/y of this coming from “advanced biofuels,” meaning fuels derived from renewable biomass (excluding ethanol derived from corn) that achieve at least a 50% reduction in GHG emissions, on a life-cycle basis. Biodiesel and renewable diesel may both qualify as “advanced biofuels,” though this determination has not yet been made.

Numerous other federal incentive programs exist to promote greater use of biodiesel. Many of these are voluntary, with relatively little participation. Some of the better known programs include the following:

- Clean School Bus USA
- Clean Construction USA
- Clean Agriculture USA
- Clean Fuels Grant Program
- Clean Cities Program
- Biobased Products and Bioenergy Program

These and many other federal initiative programs are summarized by the Alternative Fuels and Advanced Vehicle Data Center, and posted on their website.(5)

2.2 U.S. States

Several U.S. States have also established policies to promote greater use of biodiesel. One of the most aggressive states is Minnesota, which established a statewide B2 requirement in 2005.(6) More recently, Minnesota has adopted a measure that will require increasing from B2 to B20 by 2015.(7) Due to difficulties experienced in meeting the earlier B2 requirement, the current B20 plan incorporates several safeguards and checkpoints. It remains to be seen whether the B20 standard is achievable within the designated timeframe.

California is also actively promoting increased use of biofuels. As early as 2000, California passed legislation requiring investigation of ways to reduce the State's petroleum dependence.(8) In response to this, the California Energy Commission (CEC) and the California Air Resources Board (CARB) prepared a joint agency report that recommended increasing alternative fuel usage to constitute 20% of total on-road transportation fuels by 2020, and 30% by 2030.(9)

Subsequently, California Bill AB-1007 required CEC and CARB to "develop and adopt a State Alternative Fuels Plan (AFP) to increase the use of alternative fuels" in California.(10) This AFP must establish specific goals for alternative fuel usage in 2012, 2017, and 2022. Furthermore, CEC and CARB are required to conduct Full Fuel-Cycle Analyses (FFCA) of the alternative fuels proposed in this plan, and ensure "no net material increase in air pollution, water pollution, or other substances known to damage human health." The California AFP has now been developed, and calls for the total alternative fuel volumes shown below in Table II.(11) Biodiesel and renewable diesel are two of the specific biofuels included in this AFP, though there are no specific volumetric requirements for them.

Table II. Goals Included in California's Alternative Fuels Plan

Year	Alternative Fuel Volume, bg/y	Reduction of Conventional Fuels, %
2012	2.4	9
2017	3.7	11
2022	5.3	26
2030		30
2050		50

Currently, CARB is conducting an experimental program with biodiesel and renewable diesel to ensure compliance with the AB-1007 requirement of no harm.(12) This program includes detailed engine laboratory work to investigate the emissions impacts of using blends of biodiesel and renewable diesel in petroleum diesel. NOx emissions are of particular interest. This CARB study will also investigate several strategies for mitigating the NOx increase that is anticipated from use of biodiesel.

California is also developing a Low Carbon Fuels Standard (LCFS)(13) and has recently passed legislation (AB-32) to address global warming concerns.(14) AB-32 goals require statewide reduction of GHGs to achieve the 2000 level by 2010, the 1990 level by 2020, and 80% below the 1990 level by 2050. These reductions will be based upon "life-cycle values" by a mechanism that is yet to be fully defined. Meeting California's LCFS and GHG reduction goals will require various aggressive measures, including extensive use of biofuels.

Very recently, Massachusetts adopted legislation, the Clean Energy Biofuels Act, that mandates inclusion of biodiesel in all diesel fuel and heating oil.(15) The biodiesel fraction begins at 2% in 2010, then increases by an additional 1% absolute per year until reaching 5% in 2013. In addition, this legislation requires Massachusetts to develop a LCFS (similar to California's) that would reduce GHG emissions from the transport sector by 10%.

2.3 Europe

Biodiesel has been produced and used in Europe to a much larger extent than in any other location – particularly in Germany, France, and Italy.(16,17) While each country has its own policies and incentives, broad European Union (EU) policies have also been established. In 2003, EU Directive 2003-30-EC established targets for biofuels content of transportation fuels.(18) According to this directive, biofuels must constitute 2% of transport fuels by 2005, and grow by 0.75% absolute per year until reaching 5.75% in 2010. These requirements apply to all transportation fuels, not just diesel fuel, though 75-80% of the requirement is being met by use of biodiesel. Approximately 20% of the EU biofuels requirement is currently being met with bioethanol, and the small remainder is being met with straight vegetable oil (SVO).(19)

The EU has also defined a "benchmark" of achieving 20% biofuels by 2020, though there is no legally binding requirement for this. At present, this 20% benchmark seems unattainable, and is not being vigorously pursued by the EU. A reduced target of 10% biodiesel by 2020 has been proposed and is now being discussed within the EU, though at present, there is no legally binding requirement to meet this target either.

2.4 Other Countries

Many other countries around the world are beginning to develop policies to promote greater use of biodiesel.(20) Those of particular note are Brazil, China, and India.(21) In 2004, Brazil enacted a National Biodiesel Production Program (PNPB) which established a mandate for all petroleum diesel fuel to contain biodiesel by 2008.(22) Later legislation in 2005 (Federal Law 11.097 and Decree 5448) defined the requirement of 2% biodiesel by 2008 (estimated to be 222 mg/y) and 5% biodiesel by 2013 (estimated to be 634 mg/y).

China established a Renewable Energy Law in 2005, which calls for biodiesel consumption of 2 million tons/year (mt/y; approx. 600 mg/y) by 2020.[*] An interim goal of 0.2 mt/y (approx. 60 mg/y) by 2010 is also in place. These current goals are much less aggressive (by an order of magnitude) compared to the biofuels targets that China had announced previously. A major reason for this less aggressive stance is China's concern about food security, and the potential competition between food and fuel uses of vegetable oil feedstocks.

In India, the Central Government developed a "National Mission on Biodiesel" in 2003. Subsequently, a detailed project report was developed to lay out a national plan for promoting increased production and use of biodiesel. This plan emphasizes greatly increased cultivation of jatropha curcas, and use of its seed oil as a biodiesel feedstock. The government also established a target of 5% biodiesel by 2007 (estimated to be 0.78 bg/y), with a longer term goal of 20% by 2020 (estimated to be 6.71 bg/y).

The nominal sum of these policy-driven biodistillate volumetric requirements is shown in Fig. 2a. However, for several reasons, we believe these values greatly overestimate the actual

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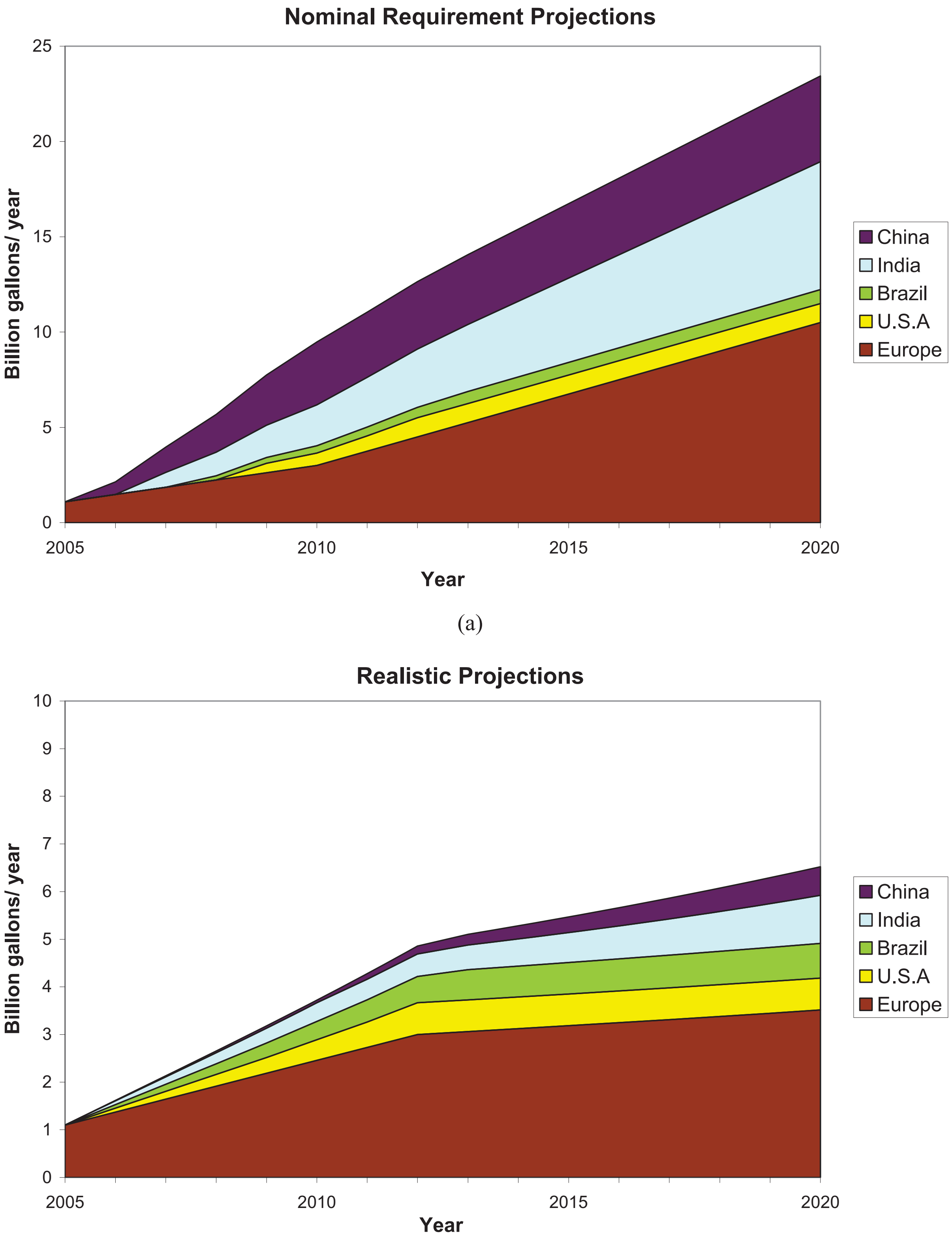
[*] In most countries outside the U.S., biodiesel production and usage requirements are expressed as million metric tonnes per year (mmt/y). In this report, we have converted all mmt/y values to U.S. volumetric values of mg/y. Assuming a specific gravity of 0.88 for biodiesel, 1 metric tonne equals 300 U.S. gallons.

amounts of biodistillates that will exist in the marketplace over this period of time. Our best estimates are shown in Fig. 2b. Our estimates – and rationale for them – are explained below for each of the major geographic regions discussed above:

- Europe: Europe is currently satisfying its 2005 biofuels requirement content of 2%. However, due to severe feedstock shortages and high prices (described in the next section) we do not expect Europe to meet the 5.75% biofuels requirement until 2012 (rather than 2010). After that, we anticipate slow growth of 2% per annum (resulting mainly from increased imports of biodistillates) reaching a level of 3.51 bg/y in 2020. We do not think attainment of Europe's 2020 goal of 20% biofuels is possible. Even the reduced target of 10% by 2020 seems unlikely to be met. The growth estimates we have used in developing Fig. 2b lead to a total biofuel contribution of 6-7% in 2020.
- U.S.: We expect the U.S. to achieve the 1.0 bg/y biodiesel requirement included in the 2007 EISA. However, we believe that an energy content adjustment will be applied, effectively reducing the 2012 requirement to 0.67 bg/y. Lacking any additional legislative action, we expect that this level will remain flat through 2020, with any additional production being exported to help satisfy other countries' requirements.
- Brazil: We believe that Brazil will meet its goals of 2% biodiesel by 2008 and 5% biodiesel by 2013. Beyond this, we anticipate a 2% per annum growth rate in biodiesel volume used in Brazil. From this, we project a 2020 level of 0.73 bg/y.
- China: In developing Fig. 2b, we have assumed that China will meet its new (less aggressive) biodiesel goals of 60 mg/y by 2010 and 600 mg/y by 2020. While much easier than its previous goals, achieving this projected increase from 2010 to 2020 requires a growth rate of 25% per annum, which may be very difficult to maintain.
- India: India's currently stated biodiesel goals appear to be unattainable. Reliable figures are very difficult to obtain, but it is clear that India is not close to meeting its 2007 goal of 5% biodiesel. We expect that India will follow the same path as China, and will announce dramatically reduced biodiesel goals in the future. In Fig. 2b, we have assumed that India will achieve 2% biodiesel in 2010, and will then maintain a growth rate of 10% per annum through 2020. From this, we project a 2020 level of 1.01 bg/y.

The sum of these five regional projections shown in Fig. 2b is 6.51 bg/y of biodistillate by 2020. This is far less than the nominal regulatory requirement of 23.4 bg/y shown in Fig. 2a, but still represents a 2.5-fold increase from today's actual production level. Achieving this projected 2020 level of 6.51 bg/y will require an annual growth of about 8%.



(a)

(b)

Figure 2. Policy-Driven Volumetric Biodiesel Requirements

3. Biodiesel Volumes and Feedstocks

In recent years, the growth of biodiesel production and use around the world has been dramatic, though exact figures are somewhat difficult to obtain and confirm. In this section, we summarize information gleaned from global market surveys (especially Biodiesel 2020 (21)), industry web sites (especially NBB(23) and EBB(24)), and other published sources to present a picture of current and future fuel volumes and feedstocks.

3.1 Current/Conventional Feedstocks

While alternative feedstocks are now beginning to receive some attention, the only feedstocks used commercially to-date have been triglycerides from animal fats and seed oils. Thus, this report will emphasize these conventional biodiesel feedstocks, while including some discussion of alternative feedstocks.

Figure 3 presents an overall summary of biodiesel production around the world. Clearly, Europe has been – and continues to be – the dominant region for biodiesel. This is also evident by comparing the number of biodiesel plants in Europe and the U.S., as shown in Fig. 4.

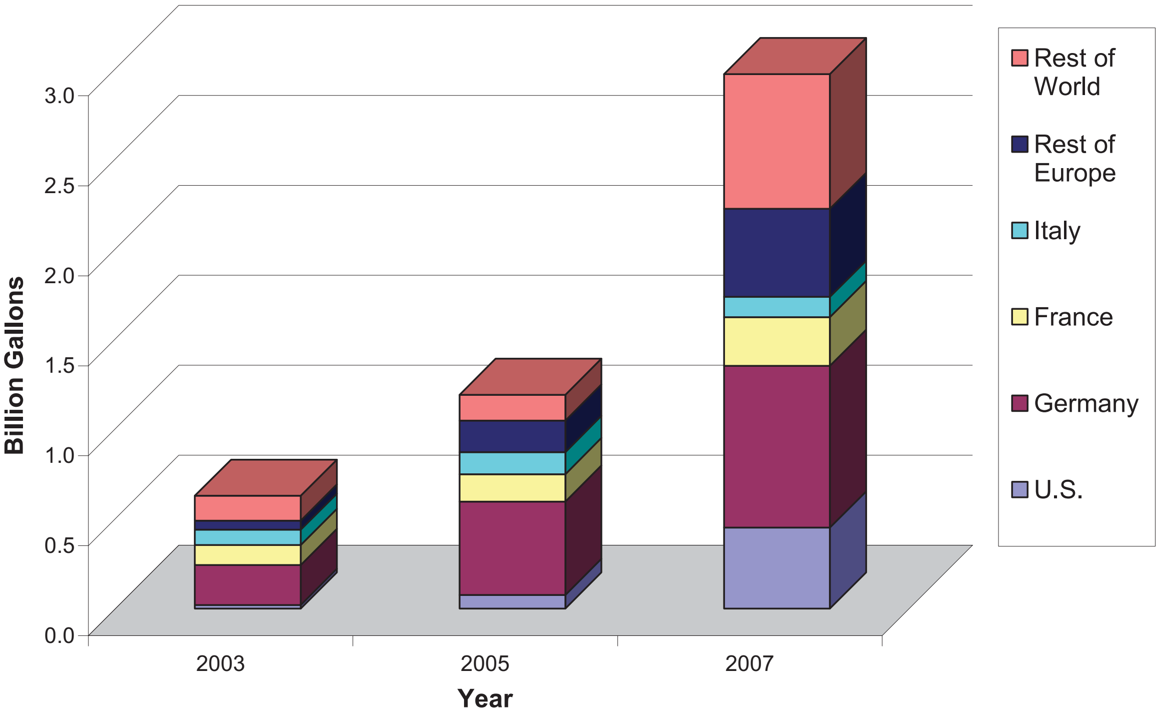


Figure 3. Global Growth in Biodiesel Production

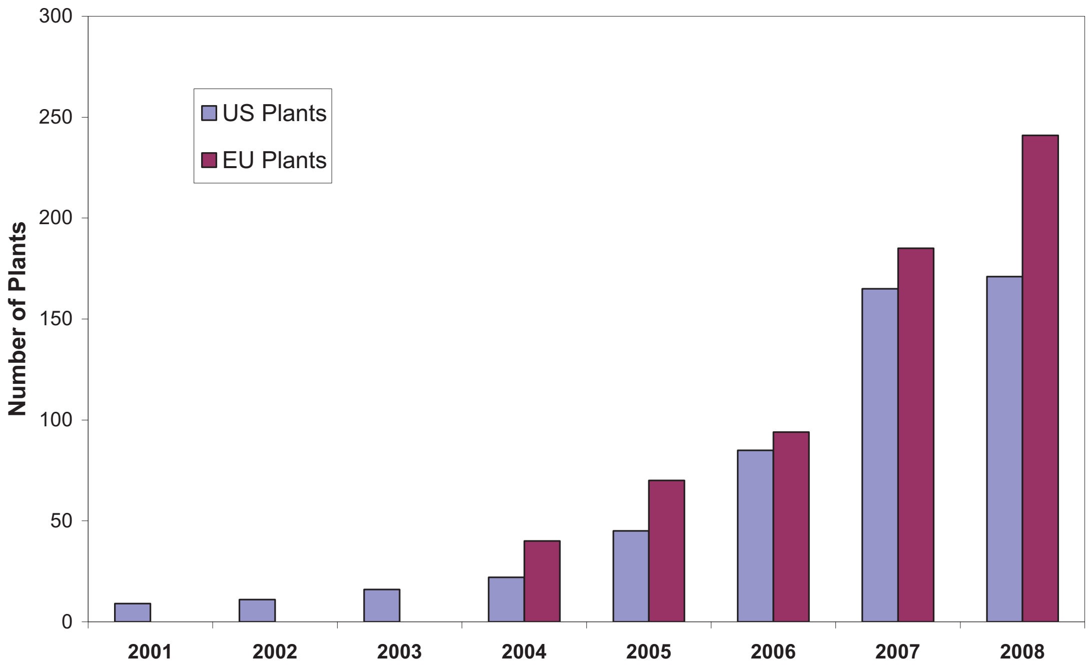


Figure 4. Growth in Number of Biodiesel Plants

In Europe, the dominant biodiesel feedstock is rapeseed oil, while soybean oil dominates in the U.S. However, increasing diversity in feedstocks is occurring globally, as the demand for conventional feedstocks is beginning to exceed supply, and producers are seeking alternative, less expensive feedstocks. In addition, many other oil-bearing plants are now being investigated commercially (or semi-commercially), with several offering the possibility of greater yields than the conventional rapeseed or soybean. This is illustrated below in Table III.

Table III. Potential Biodistillate Output

Source	Potential Yield, gallons/acre	Source of Info (Reference Nos.)
Corn	18	(25,26,27)
Soybean	40-55	(21,25,26,28,27)
Canola (Rapeseed)	110-145	(21,25,26,27)
Sunflower	102	(26)
Safflower	83	(25)
Cotton	35	(26)
Mustard	60-140	(21)
Jatropha	175-200	(21,26,27)
Coconut	290	(27)
Palm Oil	600-650	(21,25,26,27)
Algae	>5000	(21,25,27)

3.1.1 Europe

According to the European Biodiesel Board (EBB), there are currently 185 fully operational biodiesel plants in the EU, with another 58 under construction. Europe has dominated the global biodiesel industry to-date, with approximately 80% of global production. Currently, the overall share of biodiesel in the European diesel pool is between 2 and 3%, though the EU goal is to reach a level of 5.75% by 2010. (The 5.75% biofuels goal applies to all transportation fuels – including gasoline – though 75-80% of European biofuels today is in the form of biodiesel.) The top three European producers of biodiesel are Germany, France, and Italy, though nearly every EU country has some production, as shown in Fig. 5. (21,17)

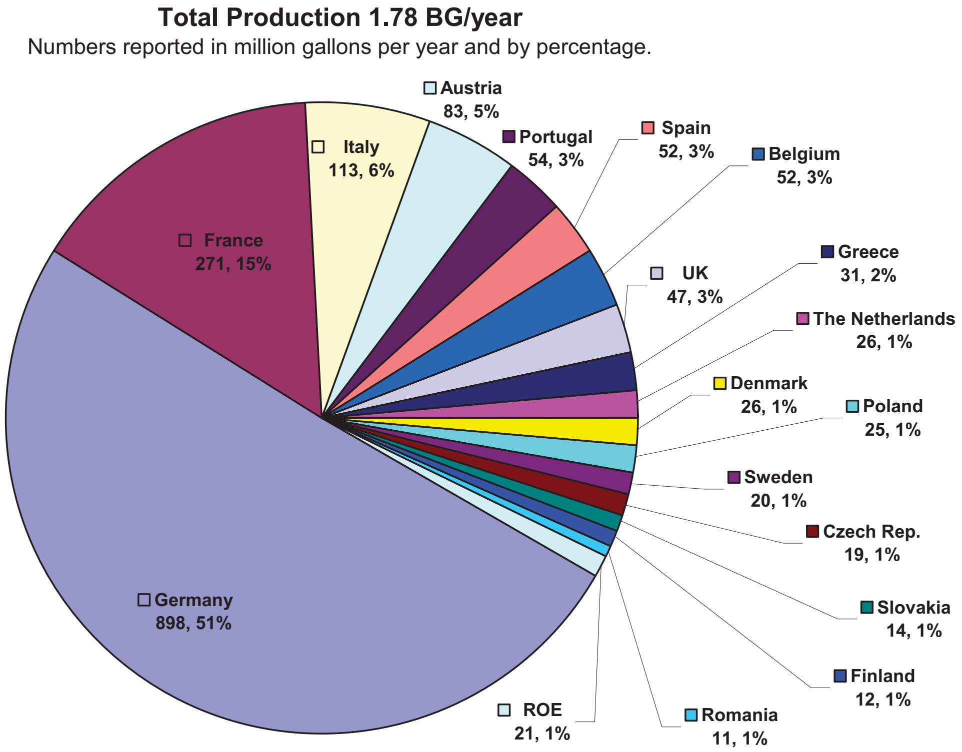


Figure 5. European Biodiesel Production by Country - 2007

While European biodiesel production has been growing, production capacity has grown even faster. This is illustrated in Fig. 6, which shows that in 2007, capacity was twice as large as production. This underutilization of capacity has become even more severe in 2008, as difficulties with feedstock supply and cost have occurred, and biodiesel tax incentives have diminished.

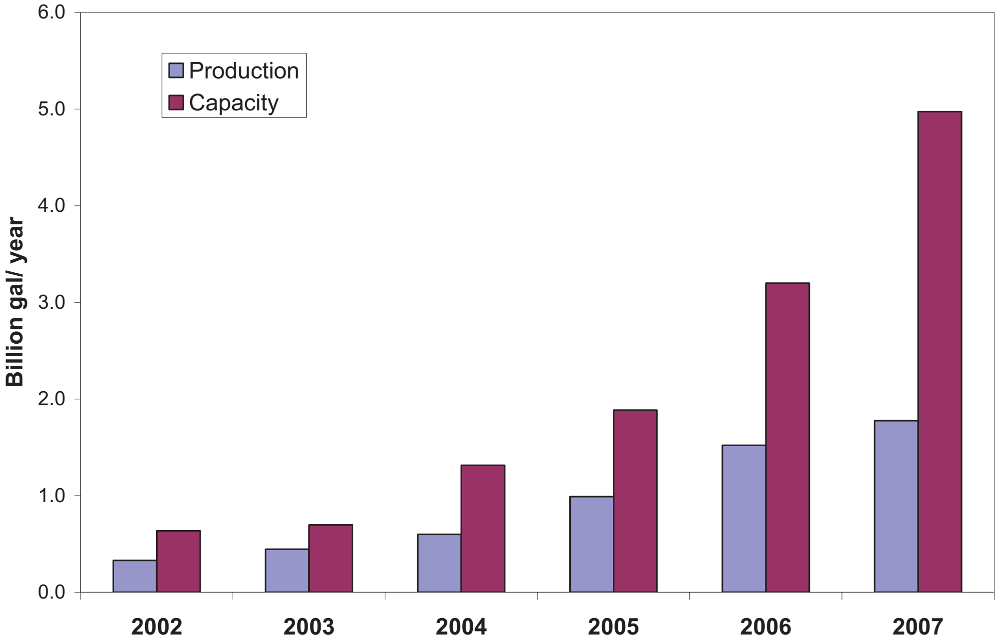


Figure 6. European Biodiesel Capacity and Production

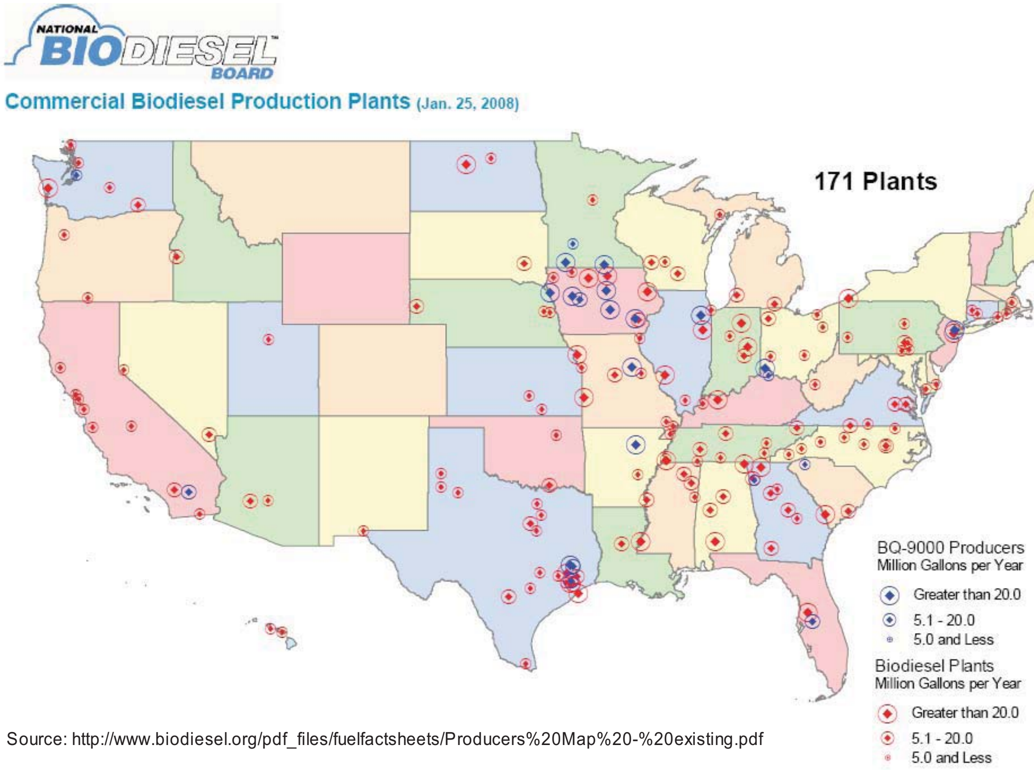
These problems are most severe in Germany, where current capacity utilization is reported to be below 25%. Until 2006, B100 was sold "tax free" in Germany. With the phase-out of this and other financial incentives, the cost of biodiesel has risen dramatically and the demand has dropped. Also, of all the EU countries, Germany and Austria are the only ones where B100 is in widespread use. In all other countries, lower level blends (B2, B5, and B20) are much more common.(29)

The dominant feedstock for European biodiesel is rapeseed -- a close relative of canola, which is used in the U.S. -- with sunflower seed being a distant second. Despite agricultural incentives and use of set-aside lands for rapeseed cultivation, the amount grown is insufficient to satisfy the goal of 5.75% biofuel by 2010. To help meet this policy-driven mandate, Europe has imported significant volumes of biodiesel in recent years – both from the U.S. (soybean-based) and from Southeast Asia (palm-based). However, due to concerns about sustainability, biodiversity, and GHG emissions, the EU's Environmental Committee amended their fuel quality directive in late 2007 to ensure that biofuels must meet strict environmental goals.(19) In effect, this will restrict the importation of palm oil from Southeast Asia.

Feedstock supply is expected to limit Europe's biodiesel production to well below the 5.75% goal by 2010.(30) The reliance upon rapeseed as feedstock has now become very restrictive, as the supply is far less than the demand, leading to very high feedstock costs. (80% of total biodiesel cost is attributed to feedstock.) Even in Germany, which is the European leader in biofuel production, it is clear that not enough rapeseed can be grown to meet its needs. Other, lower-cost feedstocks (such as yellow grease and tallow) are beginning to be used, but their availability is also very limited. For continued growth of the European biodiesel industry, significant new feedstocks are required, such as algal oils and biomass-to-liquids (BTL) products.

3.1.2 U.S.

According to the National Biodiesel Board (NBB), at the end of 2007 there were 165 fully operational plants in the U.S., with another 80 under construction. The locations of these plants are shown on the map in Fig. 7.



Source: http://www.biodiesel.org/pdf_files/fuelfactsheets/Producers%20Map%20-%20existing.pdf

Figure 7. Location of U.S. Biodiesel Plants – 2008

Total U.S. diesel fuel consumption is currently approximately 60 bg/y, with 40 bg/y of this being used for on-road transportation applications. U.S. biodiesel production in 2007 was approximately 450 mg/y, or about 1.1% of the on-road diesel volume. However, much smaller volumes of biodiesel were actually consumed in the U.S., as at least ½ of U.S. produced biodiesel was exported to Europe.(21) With phase-in of the U.S. EISA requirement of 1 bg/y biodiesel, it is likely that a larger share of U.S. produced fuel will remain in this country.

Growth in the U.S. biodiesel industry in recent years has been very rapid. Figure 8 provides information about both biodiesel production and total plant capacity over the past several years. This illustrates that while production has grown significantly, capacity growth has been even more dramatic. Consequently, capacity utilization is declining. Utilization was 42% of capacity in 2006, but is estimated to be below 20% in 2008.(21) Similar to the European situation, this underutilization is a serious problem for the U.S. industry, caused by limited availability and high costs of feedstocks.

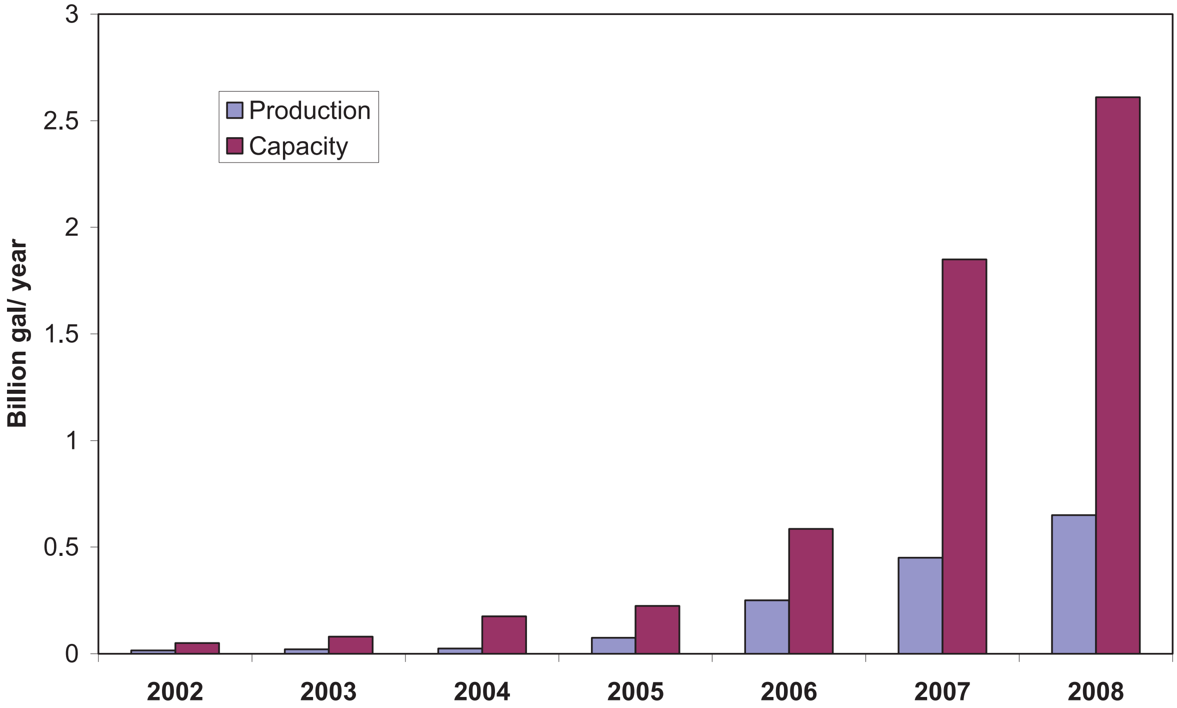


Figure 8. U.S. Biodiesel Capacity and Production

As shown in Fig. 9, the dominant biodiesel feedstock in the U.S. (and Brazil) is soybean oil, although a number of other materials are also used. This is in contrast to the European countries, where rapeseed oil dominates. Waste cooking oil, canola oil, animal fats, and other triglycerides are finding increased usage in the U.S. as soybean oil supplies are becoming more limited and costly.

In the U.S., approximately 70 million acres of U.S. farmland are used for soybean cultivation. The fraction of the soybean crop used for biodiesel production is small, but increasing. Accurate determinations are difficult to make, since only a part of the soybean is used for fuel production, while other parts are used for animal feed and other purposes. However, it is estimated that the fraction of the total soybean crop devoted to biodiesel was 6% in 2005-2006, 8% in 2006-2007, and could reach 20% in 2008.(21) A recent DOE study has concluded that a 3 bg/y U.S. biodiesel industry would require 30 million acres of cropland to be dedicated to seed oil production.(31) Achieving this level will also require substantial increases in seed oil yield per acre. Numerous R&D efforts are underway to genetically modify soybeans (and other crops) to enhance yields and improve fuel properties.(32,33)

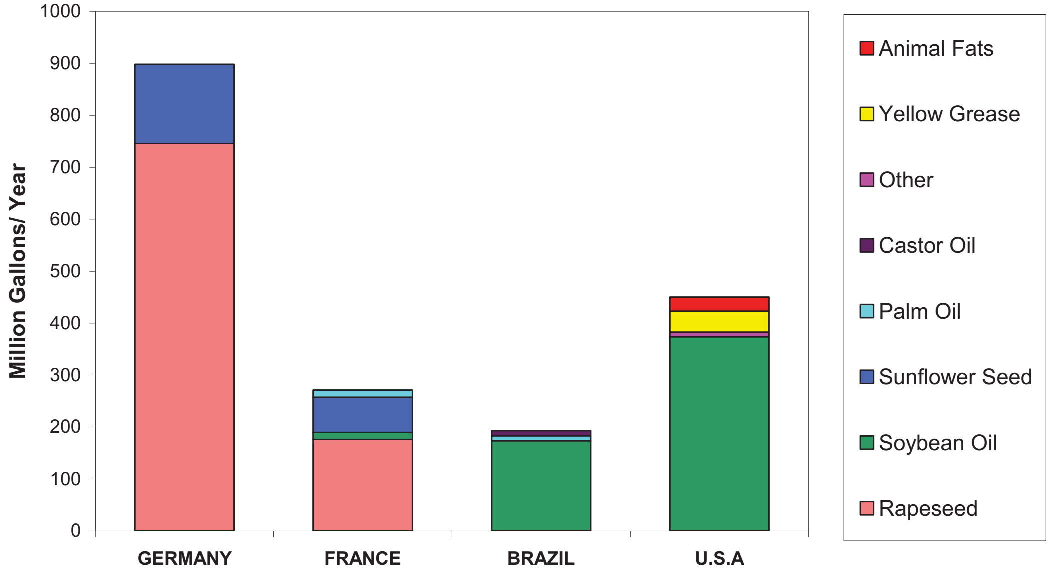


Figure 9. Biodiesel Feedstocks by Country – 2007

Growth in total biodiesel capacity in the U.S. is being driven by the introduction of several very large plants. For example, Imperium Renewable Corp. has opened a 100 mg/y plant in Grays Harbor, Washington; Green Hunter Energy has opened a 100 mg/y plant in Houston. Also, ConocoPhillips and Tyson Foods have announced plans to build the largest U.S. biodiesel plant, at 175 mg/y capacity. While the average U.S. plant size is still quite small at 12 mg/y, the trend is towards much larger plants. Figure 10 shows the extent of this growth trend in just one year, between 2006 and 2007.

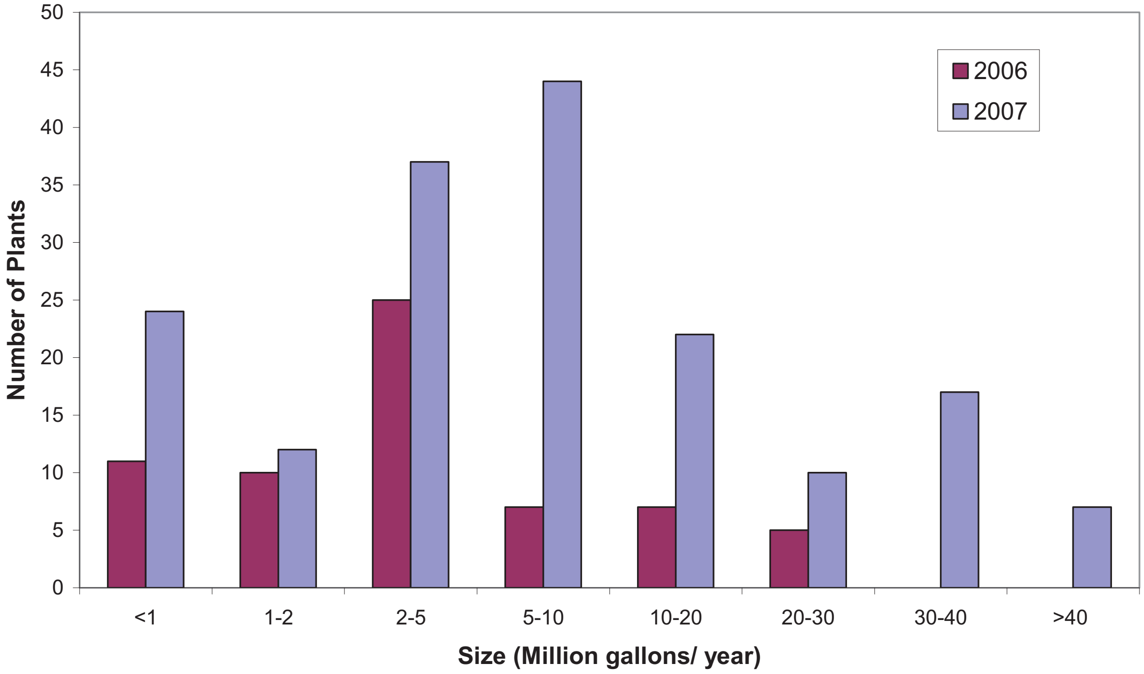


Figure 10. Growth in U.S. Biodiesel Plant Size

In addition to biodiesel plant size increasing, the locations are migrating away from the traditional farm belt regions towards international port locations (Houston, Puget Sound, Boston, etc.) The same trend is occurring globally, with very large biodiesel plants existing (or being built) near Rotterdam, Singapore, and other major port locations.) These new locations provide access to a much wider range of potential feedstocks. Thus, the historically close connection between biodiesel and local agriculture is starting to weaken.

3.1.3 Other Countries

Numerous other countries are beginning to develop biofuels in general, and biodiesel in particular.(34) In most of these locations, the biodiesel industry is still very small and poorly documented. Three countries that have advanced quite far, and have definite plans for increased development, are Brazil, China, and India. These three are also highlighted in the Biodiesel 2020 Market Survey report, which provides some documented information about their biodiesel operations.(21)

3.1.3.1 Brazil

At the end of 2007, Brazil had 42 biodiesel plants in operation, with a total production capacity of about 560 mg/y. Considerable growth is forecast in both the number of plants and actual production of biodiesel in Brazil, with the State oil company, Petrobras, playing a significant role in this development.

Currently, about 90% of Brazilian biodiesel is produced from soybean oil, with much smaller contributions from cottonseed, sunflower seed, castor seed, rapeseed, corn, palm, coconut, and other feedstocks.(22) Brazil is actively promoting the growth of agriculturally-derived feedstocks, and is opening up new (non-rainforest) areas for this.(35) Expansion of soybean cultivation is particularly preferred in the near term, due to its current high demand and favorable growing conditions. Brazil is likely to become a major exporter of both food and fuel from soybeans. Other biodiesel feedstocks that appear very promising for Brazil include castor, jatropha, palm, and cottonseed.

3.1.3.2 China

China is now the second largest energy consumer in the world (after the U.S.). Petroleum demand in China is growing very rapidly, at about 4% per annum, while production remains relatively stable near 3.5 mb/d. Currently, China imports about 40% of its petroleum, but this fraction is rising rapidly, and is expected to reach over 60% by 2020. These factors have caused China to begin aggressively promoting development of domestic biofuels.

China's biofuels industry is still in its infancy. Currently, there are approximately 35 biodiesel plants in operation, but all are quite small. Total biodiesel production is estimated to be 50-60 mg/y. In 2006, China announced very aggressive plans for growing biodiesel production to over 3 bg/y by 2010 and 5 bg/y by 2020. The main feedstocks identified to meet these goals are animal fats and waste vegetable oils by 2010, to be supplemented with new non-food crops (especially jatropha) by 2020.(36) In view of concerns about food supply, China has now greatly reduced its projected volumes of biodiesel. The current feedstock focus is on waste vegetable oil and palm oil from Malaysia. For the longer term, China is pursuing the development of jatropha and other non-food sources.

At the present time, China has approximately 4 million hectares of land area for growing oil-bearing trees, with an increasing fraction being devoted to jatropha. The first sizeable harvest of jatropha trees (also called "diesel trees" in China) is expected in 2008. By 2010, China anticipates having 13 million hectares planted in jatropha – a size approximately equal to the landmass of England. Once fully productive, this could provide 2-4 bg/y of biodiesel.

3.1.3.3 India

India is currently the sixth largest energy consumer in the world. Similar to China, India is experiencing very rapid growth in demand for petroleum. Current petroleum consumption in India is approximately 40 bg/y, while diesel fuel consumption is about 15 bg/y. Diesel fuel accounts for about 80% of all transportation fuels in India. At present, India imports 72% of its petroleum, with this fraction increasing each year. Because of the growing gap between production and consumption, India is pursuing an aggressive path towards biofuel development, as laid out in their "National Mission on Biodiesel."

Current commercial production of biodiesel in India is almost negligible.(37) Although accurate statistics are not available, it seems likely that current levels are close to 0.5 bg/y.(38) The Government of India has established a 5% biodiesel blend requirement beginning in 2010, which translates to a volume of about 1 bg/y. Achieving a 10% goal by 2020 would require about 3.5 bg/y of biodiesel. (The stated goal for 2020 is still 20%, but presently, this does not seem achievable.) The largest users of biodiesel include Indian Railways and other state-owned transport companies that have established experimental trial projects for biodiesel production.

Current feedstocks for biodiesel production in India are quite varied, including waste vegetable oil, animal fats, rubberseed oil, rice bran, karanja, pongamia, and especially jatropha.(39) Due to high edible oil prices, it is not economically feasible to produce biodiesel from vegetable oils. While still in its infancy, India intends to greatly expand its use of jatropha. To meet the 5% biodiesel goal by 2010 will require approximately 2.5 million hectares of jatropha and karanja. Meeting the 20% goal by 2020 would require about 20 million hectares. The Government of India has identified sufficient space for such plantations, mostly involving land that is not used productively at present. Significant advantages of jatropha (and some other native plants) include its ability to grow on marginal land with modest requirements for water and fertilizer. In India (and elsewhere) developing a jatropha industry is also seen as a powerful driver for rural economic development.

3.2 Algal Feedstocks

Many varieties of microalgae are known to produce large quantities of lipids, containing triglyceride oils, which are potential feedstocks for biodistillate fuels. Of all photosynthetic organisms, microalgae are the most productive users of CO_2, and can fix larger amounts of CO_2

per land area than other plants (see Table 3).(40) Some of the most commonly cited factors for favoring algae as a biofuel feedstock include the following:

- Rapid growth
- High oil content
- Tolerance for poor quality water
- Use of relatively little land space
- Use of non-productive land
- Mitigation of fossil CO_2 emissions
- Use of wastewater treatment effluents for nutrients
- Production of valuable co-products

Various investigations have been conducted to determine suitable algal strains for maximum growth and oil production under specific conditions. The most comprehensive investigation of algae as a potential fuel feedstock was undertaken by the National Renewable Energy Lab, who maintained an active Aquatic Species Program (ASP) from 1978 to 1996. The ASP final closeout report was issued in 1998, and remains an excellent source of information about growth conditions and productivities of various algal strains.(41)

Due to numerous technical and economic factors, the ASP was discontinued. Now, however, DOE and NREL have renewed interest in promoting algae as a commercial energy source. In fact, DOE recently sponsored an "Algal Fuels Roadmapping" meeting, and plans to issue a roadmap document in mid-2009. (42) Reasons cited for this renewed interest include the following:

- High costs of petroleum and other energy sources
- Increased emphasis on energy security
- Concern about CO_2 and climate change
- Advances in biotechnology and photobioreactor designs
- Petroleum refiners' interest in processing lipids

Major barriers to commercial scale implementation of algal systems include numerous technical challenges (maintaining healthy algal growth, avoiding invasive native algae, temperature control, effective light dispersion, reliable harvesting methods, etc.) as well as economics.(43,44,45) The standard operations currently in use for microalgae biomass production (mainly for producing high-value food supplements) involve open "raceway ponds," with sparging of CO_2-containing gases into the ponds. There is also considerable interest in closed, photobioreactor designs, which help maintain purity of the desired algal strains being used and offer better control of operating controls (nutrient levels, irradiation, flow rates, etc.), but with much higher capital and operating costs.(27) The economics of algal fuel systems may be improved by combining them with waste water treatment operations that can provide much of the nutrients needed for algal growth.

In addition to lipids, many algal strains produce large amounts of carbohydrates and protein. The proteins are useful as food/feed supplements, while the carbohydrates are potential feedstocks for fuels via thermal processing approaches, such as gasification and pyrolysis.

Current interest in developing algae-to-biofuels systems and technologies is extremely high. This is evident from the extensive list of companies and organizations shown in Appendix IV who are presently working in this area. Despite this tremendous interest, there currently are no functioning, commercial-scale operations producing biodistillate fuels from algae. However, this situation may change soon, as substantial investments by major technology developers and fuel producers are being made. As one example, the Defense Advanced Research Projects Agency (DARPA) is planning to support several development and demonstration projects to produce military jet fuel (JP-8) from algae.(46)

3.3 Other Triglyceride Feedstocks

It has been reported that over 350 oil-bearing crops exist in the world.(28) The literature is replete with reports of biodiesel produced from diverse feedstocks around the world. Many of these reports describe use of seed oils from rather obscure, local plants. Table IV provides a listing of many (but certainly not all) such reports.

Perhaps the greatest interest in seed oil feedstocks for biodiesel is in India. As described above, India has very aggressive plans for large-scale commercialization of Jatropha plantations. Other India feedstocks of significant interest include pongaia,(47,48,49,50) karanja,(51,52,53) soapnut(54), bran(55,56), and rubber seed.(57) Other feedstocks of interest in South America (especially Brazil and Argentina) include tucum,(58) babassu,(59,60) and castor oil.(61) Other potential European feedstocks of interest include cottonseed,(62) carinata(63,64,65) and cynara.(66,67,68) Potential seed oil feedstocks that have been investigated in the U.S. include milkweed,(69) mustard,(70) tobacco seed,(71) and camelina.(72,73)

Besides seed oils, a wide variety of animal fats have been used as biodiesel feedstocks – especially from beef, hogs, sheep, and poultry. Other significant feedstocks are fats and oils recovered from restaurant cooking activities. These are commonly referred to as yellow grease (used cooking oil) and brown grease (recovered from grease traps). In the U.S., total annual production of animal fats and used vegetable oils is estimated at 1.6 bg/y.(28) Other, minor non-food related feedstocks include tall oil from paper/pulp manufacturing,(74) fleshing wastes from leather production,(75) sewage sludge,(76) and waste from fish oil.(77)

Table IV. Vegetable Oils used for Biodiesel Production

NORTH AMERICA	
Reported Feedstock	**Edible**
Algae	No
Beech	No
Camelina	Yes
Corn Oil	Yes
Cottonseed Oil	Yes
Jatropha	No
Lesquerella	No
Linseed	Yes
Rape Seed	Yes
Safflower	Yes
Soapnut Oil	No
Soybean	Yes
Spruce	No
Sunflower Oil	Yes
Walnut	Yes

EUROPE	
Reported Feedstock	**Edible**
Algae	No
Beech	No
Camelina	Yes
Cottonseed Oil	Yes
Hazelnut	Yes
Jatropha	No
Linseed	Yes
Poppy Seed	Yes
Rape Seed	Yes
Safflower	Yes
Soapnut Oil	No
Spring Mustard	Yes
Spruce	No
Walnut	Yes

SOUTH/CENTRAL AMERICA	
Reported Feedstock	**Edible**
Algae	No
Andiroba	Yes
Babassu	Yes
Castor Oil	No
Coconut Oil	Yes
Cottonseed Oil	Yes
Cumaru	
Jatropha	No
Lesquerella	No
Linseed	Yes
Palm Oil	Yes
Peanut	Yes
Rubber Seed Oil	No
Safflower	Yes
Soapnut Oil	No
Tucum oil	Yes

AFRICA	
Reported Feedstock	**Edible**
Algae	No
Castor Oil	No
Cottonseed Oil	Yes
Crambe	No
Cynara	
Jatropha	No
Linseed	Yes
Olive	Yes
Palm Oil	Yes
Polanga	No
Safflower	Yes
Sesame	Yes
Soapnut Oil	No

ASIA	
Reported Feedstock	**Edible**
Ailanthus	No
Algae	No
Camelina	Yes
Castor Oil	No
Cottonseed Oil	Yes
Hazelnut	Yes
Jatropha	No
Linseed	Yes
Mahua	Yes
Neem	
Olive	Yes
Palm Oil	Yes
Polanga	No
Pongamia	No
Poppy Seed	Yes
Rice Bran	Yes
Safflower	Yes
Sesame	Yes
Soapnut Oil	No
Spring Mustard	Yes
Spruce	No
Vann	Yes
Walnut	Yes

3.4 Lignocellulosic Feedstocks

If plant-derived biofuels are to play a significant role in satisfying transportation fuel demands in the U.S. and elsewhere, it is necessary to consider feedstocks that are more diverse and abundant than triglycerides – such as lignocellulosic biomass. The term "lignocellulose" is used when referring to a combination of the three primary polymers that make up plant cell wall: cellulose, hemicellulose, and lignin. Depending upon plant species and cell type, the dry weight of a cell wall typically contains about 35-50% cellulose, 20-35% hemicellulose, and 10-25% lignin.(78)

These biomass resources are commonly categorized as deriving from forest resources or agricultural resources. More detailed examples of subcategories within these resources are shown below in Table V.

Table V. Biomass Resource Classification

	Forest Resources	Agricultural Resources
Primary	• Logging residues • Forest fuel treatment • Fuel wood	• Crop residues • Grain • Perennial grasses • Woody crops
Secondary	• Mill residues • Pulping liquors • Wood processing residues	• Animal manures • Food/feed processing residues
Tertiary	• Construction debris • Demolition debris • Urban tree trimmings • Packaging waste	• Municipal solid waste (MSW) • Landfill gases

Recently, the USDA and DOE collaborated on a study to assess the biomass resource base within the U.S., both currently and in the future.(79) A particular objective was to determine whether the land resources of the U.S. are capable of producing a supply of biomass sufficient to displace 30% or more of the country's present petroleum consumption. Achieving this goal was estimated to require a continuous supply of 1 billion dry tons per year (bdt/y) of biomass feedstock.

This so-called "Billion Ton Study" considered several modeling scenarios which included numerous sets of assumptions. In the case of forest biomass resources, the study concluded that today's level of 142 mdt/y could be increased to 368 mdt/y, mainly by: (1) greater use of urban waste residues, (2) use of forest thinnings removed by fire prevention treatments, and (3) greater use of logging residues. These projections are illustrated below in Fig. 11.

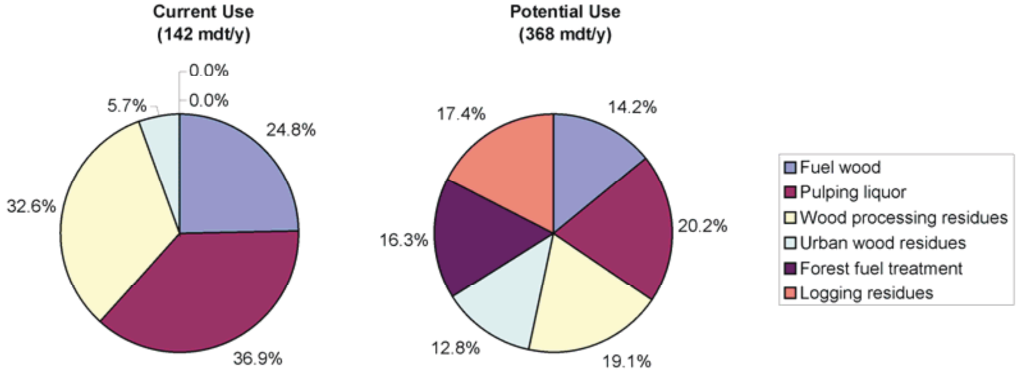


Figure 11. U.S. Forest Biomass Resources – Current and Potential Future Amounts
(Taken from Reference No. 1)

Even greater potential biomass amounts are available from agricultural resources. In this area, the Billion Ton Study developed various scenarios having different assumptions regarding crop yields, land use changes, harvesting efficiency, tillage practices, and introduction of perennial crops for biomass. The main results from these scenarios are presented graphically in Fig. 12.

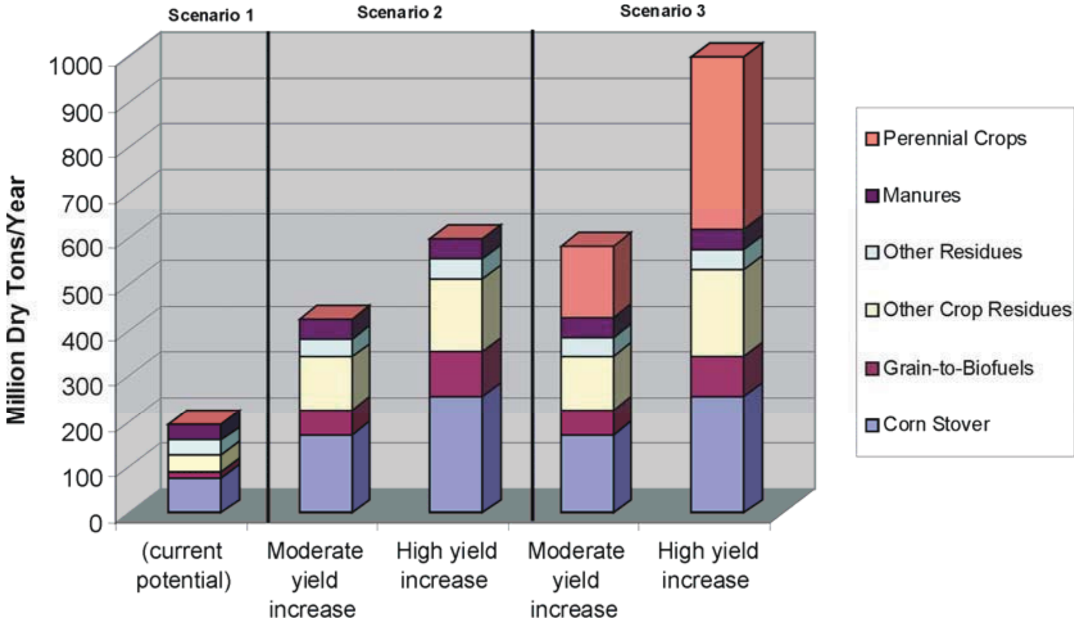


Figure 12. U.S. Agricultural Biomass Resources – Current and Potential Future Amounts
(taken from Reference No. 1)

In this figure, Scenario 1 represents the current U.S. agricultural situation, where the total amount of biomass available for energy conversion is estimated to be 194 mdt/y (although most of this is not used today). Scenario 2 assumes continued use of conventional agricultural lands and crops, but with increased crop yields representing what could reasonably be expected in 2020 (424 mdt/y) and 2040 (597 mdt/y). No land use changes are assumed in Scenario 2.

Scenario 3 assumes introduction of new, perennial crops (grasses and trees) grown for energy uses, as well some land use changes. As in Scenario 2, moderate and high yield increases are used to represent biomass amounts that could be expected in 2020 (581 mdt/y) and 2040 (998 mdt/y). The principal land use changes in Scenario 3 are modest reductions in the amounts of active cropland and idle land, to allow for introduction of perennial crops. It is important to note, however, that in this Billion Ton Study, no changes in total acreage were assumed. Further details of the land allocation assumptions used in this study are given below in Table VI.

Table VI. U.S. Land Allocations used in USDA/DOE Billion Ton Study, million acres

	Scenario 1 (current allocation)	**Scenario 2 (moderate and high yield increases)**	**Scenario 3 (moderate yield increase)**	**Scenario 3 (high yield increase)**
Active cropland	344	344	339	319
Idle land	37	37	27	27
Pasture	68	68	43	43
Perennial crop	0	0	40	60
Total	449	449	449	449

Numerous other assessments of lignocellulosic feedstock availability, logistics, economics, and growth potential have been conducted in recent years. On a national level, these efforts have been driven mainly by DOE and USDA. Relevant documents to consult include the Biomass Multi-Year Program Plan,(80) the Roadmap for Agricultural Biomass Feedstock Supply,(81) the Genomics: GTL Roadmap,(82) and the Roadmap for Bioenergy and Biobased Products in the U.S.(83)

In addition, several states have been actively investigating their biomass resources as potential feedstocks for fuels. Of particular note is California, where the California Energy Commission (CEC) has recently conducted a Biomass Resource Assessment for the State,(84) and has issued a Preliminary Roadmap for the Development of Biomass in California.(85)

3.5 Near-Term Biodiesel Market Trends

The global biodiesel/renewable diesel industries are rapidly evolving – driven by both regulatory requirements and business economics. In this section, we briefly mention a few of the most significant current market trends, and those expected in the near future (approximate 5-year time horizon). This relatively short time period precludes significant introduction of lignocellulosic feedstocks for production of plant-derived biofuels. Thus, our discussion here focuses on the traditional triglyceride feedstocks. Five main points are summarized below:

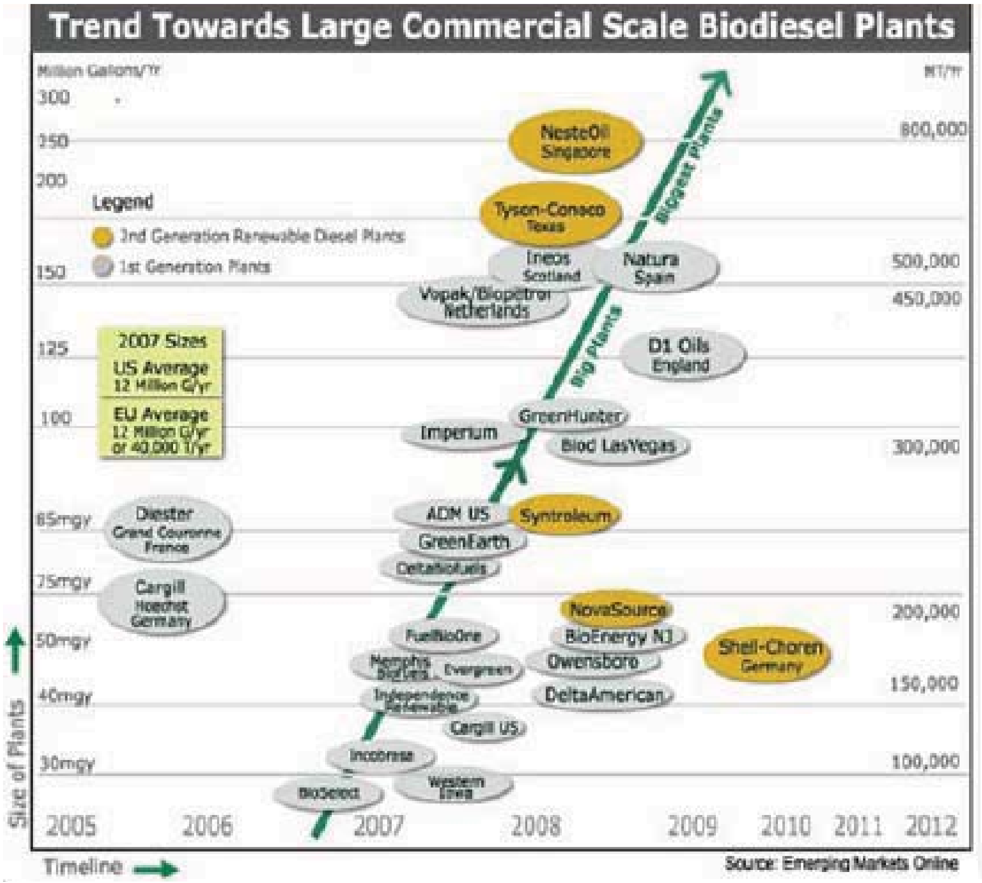
- Enormous over-capacity at present: Current biodiesel production in the U.S. and Europe is well below 40% of capacity. Plant capacity has grown dramatically over the past few years, while feedstock supplies have not. This has resulted in high feedstock costs, increased interest in feedstock diversity, shut-down of some plants, and uncertain near-term economic outlook for many other existing plants.

- Scramble for currently available feedstocks: While soybeans (U.S.) and rapeseed (Europe) continue to dominate, many more feedstocks are being investigated, and are likely to find increased commercial use in the near future. Waste cooking oils and animal fats – while always used to some extent – are likely to become more important globally.

- Search for non-food feedstocks: Concerns about food vs. fuel are driving many countries to search for non-food biofuel feedstocks. Two receiving the greatest attention at present are jatropha and algae. Several countries (especially India, China, and some African countries) have aggressive plans to develop millions of hectares in jatropha plantations within the next 5-10 years. Commercial scale algae production will likely lag behind jatropha by a few years. However, interest and investment in algae-to-fuels processes are growing, and we expect that some commercial operations will be realized within 5-10 years.

- Biodiesel is becoming mainstream, big business: While most biodiesel plants in operation today are very small (<25 mg/y) the recent trend is clearly towards larger and more flexible operations. Large plants are generally more sophisticated, allowing for wider diversity of feedstocks, greater quality control, and economics of scale. The location of large, new plants is being dictated more by access to international shipping of feedstocks than by proximity to locally-grown agricultural feedstocks. This trend towards larger, more complex biodiesel plants is illustrated in Fig. 13.

- Involvement by Major Energy Companies: In recent years, large international oil companies have become active participants is the biodiesel/renewable diesel industries. Significant operations are underway (or announced) by British Petroleum, Chevron, Marathon, ConocoPhillips, and Shell. The distinctions between petroleum diesel and biodiesel are likely to become blurred in the future, as triglyceride feedstocks are increasingly used in conventional refinery processes, such as with UOP's Ecofining™ process and Neste Oil's NExBTL process.



Source: Emerging Markets Online

Figure 13. Trend Towards Large Commercial-Scale Biodiesel Plants

4. Biodistillate Production Technologies

There is a long record of using straight vegetable oil (SVO) as fuel for compression ignition engines, going back to Rudolph Diesel (1853-1913) himself. The literature contains many references to the early use of SVO as a "diesel fuel," and cites numerous advantages of such usage.(86,87,88,89) Among these advantages are the following:

- SVO is a high energy, easily transported liquid fuel (about 90% the heat content of petroleum diesel)
- Vegetable oils are ubiquitous around the world, making local fuel supply possible
- Some vegetable oils crops can be grown on marginal lands, promoting rural economic development
- Refining SVO involves relatively simple (and inexpensive) processes
- SVO has low sulfur and aromatic levels
- SVO is renewable and biodegradable

On the other hand, SVO has some major disadvantages, which make it unacceptable as a diesel fuel in nearly all situations. Vegetable oils are composed of 90-98% triacylglycerides, commonly referred to as triglycerides, along with small amounts of mono- and di-glycerides, free fatty acids, phospholipids, and other trace constituents.(88) The molecular weight (MW) range for most triglycerides is 700-950, much higher than typical petroleum diesel which has MW range of 200-350. This results in triglycerides having much higher viscosities than petroleum diesel. Typical viscosities of vegetable oils are 35-60 cSt at 40°C, compared to about 4 cSt for petroleum diesel. Figure 14, taken from a DOE Fact Sheet, compares the viscosity of sunflower oil and conventional diesel fuel over a range of temperatures.(90)

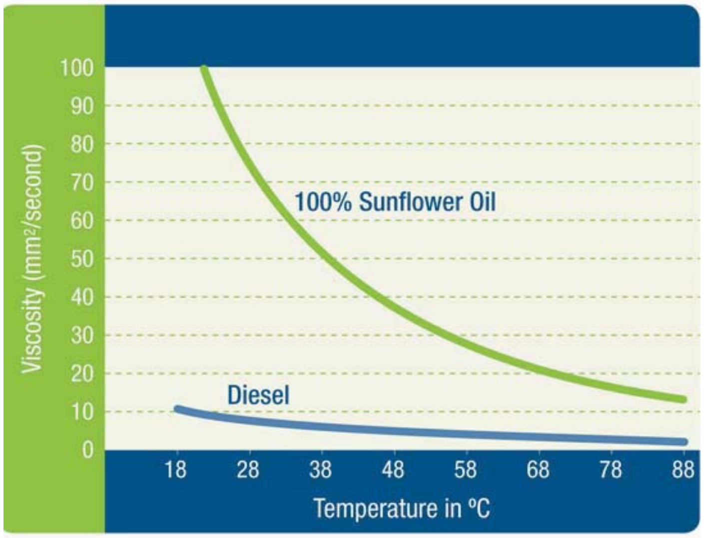


Figure 14. Viscosity of Sunflower Oil and Petroleum Diesel

The high viscosity of SVO is a major cause of poor fuel atomization that can lead to operational problems of poor combustion, injector coking, deposit formation, and others.(91,92) Several approaches have been taken to overcome the problem of SVO's high viscosity, and allow vegetable oil-based materials to be used in diesel engines. In general, these approaches can be classified into four groups:

1. Dilution with conventional diesel fuel
2. Microemulsification
3. Transesterification
4. Thermal conversion

Of these four approaches, the first two do not change the chemical structure of the triglyceride molecules, while the second two do. Simple dilution of vegetable oils with petroleum diesel has been widely used, but with mixed success.(89,93,94) Lower blend levels of SVO (<20%) are generally more acceptable than high blend levels, but long term concerns still remain due to high viscosity, free fatty acid content, storage stability, lube oil thickening, and other problems.(91,95)

Microemulsions of SVO with alcohols have also been used to reduce viscosity.(93,94) Often, a surfactant is necessary to maintain stability of the microemulsion. Many different formulations of SVOs, alcohols, and surfactants have been investigated – with somewhat mixed results. Due to difficulties in preparing these microemulsions, maintaining their stability in real-world applications, and gaining consumer acceptance, the use of such fuels has not been widespread.

By far the most common method for overcoming the viscosity problem of SVO is transesterification, though recently there has been growing interest in hydroprocessing and other thermal methods of treating SVO. The remainder of this section deals with these processes.

4.1 Transesterification

Transesterification is the chemical process by which triglycerides are reacted with alcohols to produce fatty acid alkyl esters and glycerol. These fatty acid esters [usually fatty acid methyl esters (FAME) or fatty acid ethyl esters (FAEE)] are commonly known as biodiesel. In the past few years, several excellent reviews on the topic of biodiesel manufacturing have appeared in the literature.(96,97,98,89) Given below is a discussion of some important aspects of biodiesel production.

4.1.1 Biodiesel Production Chemistry

The basic chemical reactions involved in the production of biodiesel are shown below in Fig. 15. One mole of a triglyceride is reacted with three moles of alcohol (usually methanol) in the presence of an alkaline catalyst to produce three moles of biodiesel and one mole of glycerol. For simplicity, the chemical structures in Fig. 15 only show fully saturated molecules. In reality, triglycerides in fats and oils have varying degrees of unsaturation (carbon-carbon double bonds) which is retained in the biodiesel product. Also, the carbon chain length in triglycerides typically varies from C_{12} to C_{20}. (More discussion of composition is provided later in this report.)

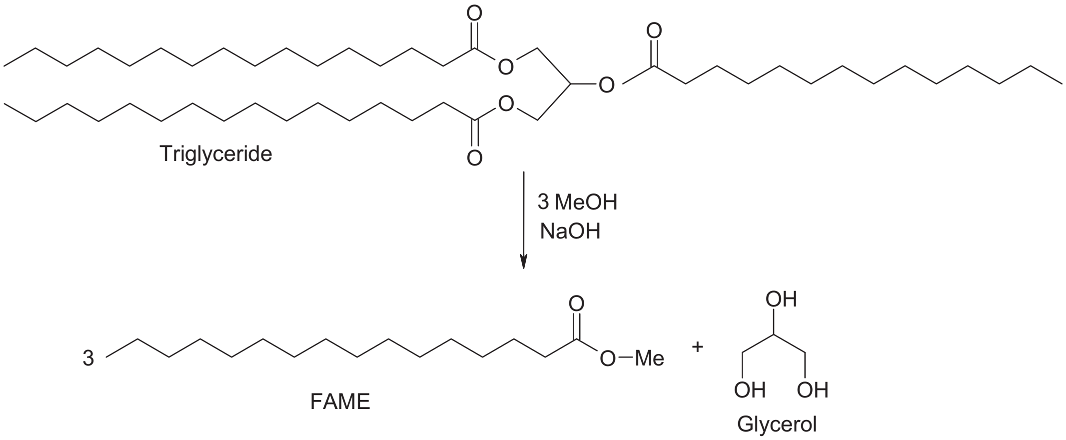


Figure 15. Transesterification Chemistry of Biodiesel Formation
(For simplicity, only saturated fatty acid structures are shown)

For reasons of cost and ease of reaction, the most common alcohol used in the transesterification process is methanol, leading to the production of FAME, as shown in Fig. 15. However, there are also numerous reports of using ethanol in place of methanol, leading to formation of FAEE.(99,100,101) The use of ethanol offers the possibility of total renewable feedstocks, whereas methanol is generally produced from fossil sources (natural gas). Additionally, some locations, such as Brazil, have an abundance of locally-produced, low-cost ethanol.

4.1.2 Commercial Biodiesel Reaction Conditions

A simplified process flow diagram for producing biodiesel from vegetable oils is shown below in Fig. 16. This depicts a common, small operation (< 1 mg/y) utilizing a batch process. Most large biodiesel plants use continuous processes, which generally include multiple reactors in series, with settling vessels located between the reactors. Several thorough descriptions of common biodiesel production technology are available in the literature.(98,102)

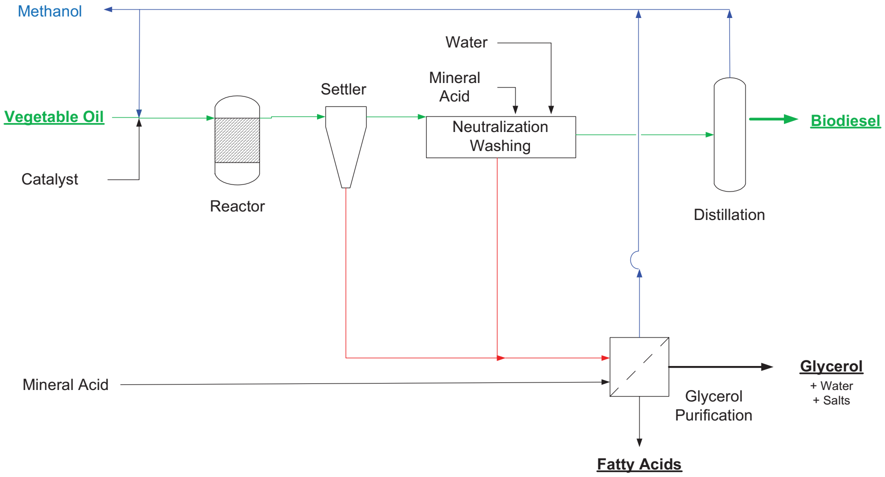


Figure 16. Process Flow Diagram for Typical, Batch-Mode Biodiesel Production

Considerable work has been conducted to determine optimum reaction conditions for producing biodiesel. To some degree, different conditions are required for each triglyceride feedstock. For a given feedstock, numerous factors have been found to have significant impacts on process efficiency and purity of final product.(89,98,103) Several of the most important factors are discussed below in more detail:

4.1.2.1 Ratio of Alcohol to Triglyceride

According to the stoichiometry shown in Fig. 15, the theoretical molar ratio of alcohol to triglyceride is 3/1. However, in most commercial operations, a much higher ratio of alcohol/triglyceride is used – typically around 6/1. The main reason for using excess alcohol is to drive the transesterification reaction to completion. As shown in Fig. 17, transesterification of triglycerides actually proceeds through a stepwise process involving intermediate production of a diglyceride, and a monoglyceride, before the final glycerol product is released. At each of these three steps, a molecule of FAME is produced. To ensure acceptable biodiesel product quality (further discussed in the next section) it is critical for these reactions to proceed to completion, so that concentrations of the intermediate diclycerides and monoglycerides in the finished fuel are kept very low. Other reasons for using excess alcohol are to provide some solvency for the reactants, and to assist in separation of glycerol from the product FAME. However, use of an excessive amount of alcohol is avoided, since considerable energy is required to distill the unreacted alcohol from the final FAME product.

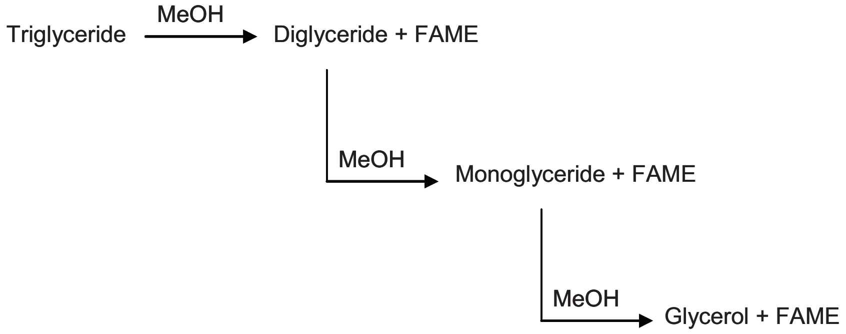


Figure 17. Step-Wise Process of Biodiesel Formation

4.1.2.2 Type of alcohol

Although nearly any alcohol could be used in the transesterification process, in most cases, methanol is the alcohol of choice. This is not only an economic decision; several technical factors are also involved. First, the transesterification reaction rate is significantly faster with methanol than with higher alcohols.(104,105,106) Also, higher alcohols are better solvents for glycerol and other impurities, making it more difficult to separate from the desired biodiesel product. Finally, higher alcohols (especially ethanol) are harder (and more expensive) to dry. As discussed below, the presence of water is very problematic in biodiesel production processes.

4.1.2.3 Purity of Triglyceride Feedstock

The amount and type of impurities present in triglyceride feedstocks are critical factors dictating optimum conditions for transesterification. Perhaps most important is the free fatty acid (FFA) content of the starting feedstock. As shown in the reactions of Fig. 18, FFA will react with the alkali catalyst to produce salts. This is very detrimental. Not only does salt formation "waste" the energy-rich FFA by eliminating its contribution to the final fuel, it also causes severe foaming and separation problems. To overcome this, it is generally recommended that feedstocks containing over 1% FFA first undergo a preliminary acid-catalyzed esterification process.(96) This pretreatment produces FAME and water, while the triglyceride remains largely unreacted. Following neutralization and drying, the conventional alkali-catalyzed transesterification reaction is then conducted to complete formation of the biodiesel. This 2-step approach appears to be used quite widely.(107,108,109) While this 2-step process for biodiesel production adds complexity and equipment, it can be financially advantageous since it allows for use of less expensive triglyceride feedstocks, such as waste cooking oils and soapstocks.(96,107,110,111,112,113)

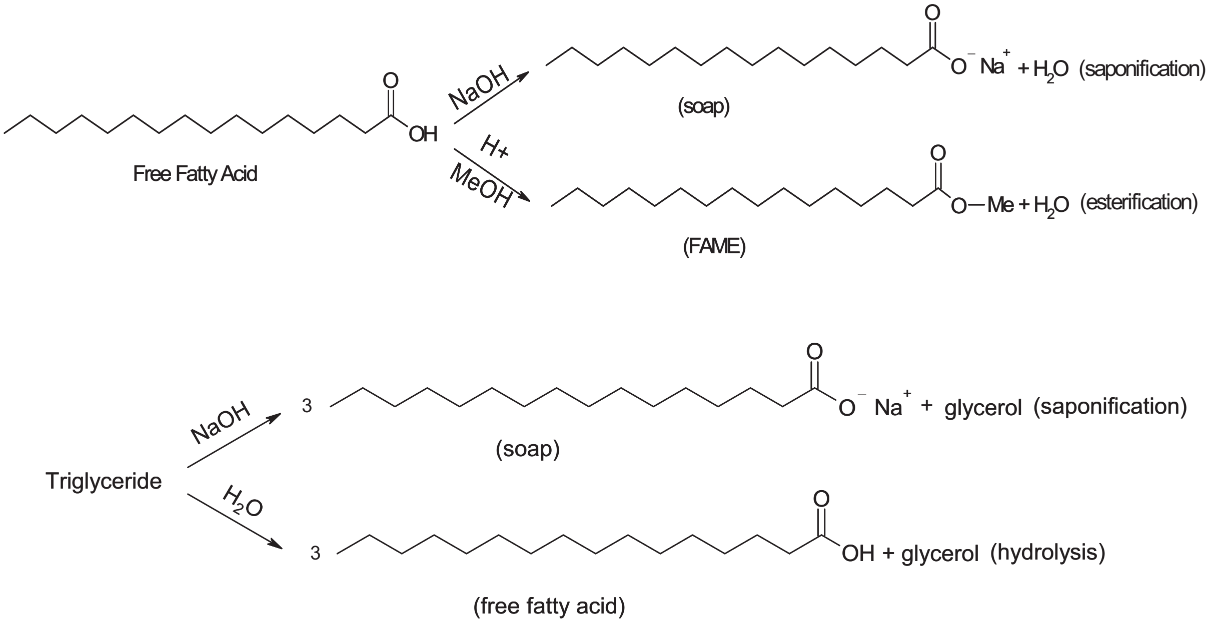


Figure 18. Other Important Reactions in Biodiesel Production Processes
(For simplicity, only saturated fatty acid structures are shown)

4.1.2.4 Amount and Type of Catalyst

There has been much research to investigate the use of different catalysts for biodiesel production, but commercially, only two general types are used in significant amounts: (1) hydroxides (NaOH and KOH) and (2) methoxides (NaOMe and KOMe). For reasons of cost and availability, NaOH is often the catalyst of choice.(96,105) However, sodium methoxide (NaOMe, also called sodium methylate), is becoming increasingly common, despite its higher cost, due to its ease of storage and handling, and the improvements in process efficiency that result.(103,114) In particular, use of sodium methoxide avoids the problem of water formation that results when hydroxide catalysts are used with alcohols (e.g. NaOH + MeOH → NaOMe + H_2O). The presence of water promotes hydrolysis of triglycerides, producing FFA with the attendant problems of soap formation (see Fig. 18 above). An additional problem with KOH (and to a lesser extent with NaOH) is that when purchased as a "pure" solid, it still contains appreciable amounts of water.

4.1.2.5 Reaction Time and Temperature

Reaction time and temperature are generally optimized for each situation. For commercial, alkali-catalyzed, batch-mode transesterification with methanol, typical reaction temperatures are in the range of 50-60°C (slightly below the boiling point of methanol), with a reaction time of about 1-hour.(102,97,115,98) With use of ethanol in place of methanol, slightly higher reaction temperatures are used.

Somewhat surprisingly, despite many years of experimentation, and the existence of a rich literature database, considerable efforts continue today in defining optimum process conditions for producing biodiesel via transesterification of triglycerides. Evidence of this is the appearance of several very recent publications which describe optimization of reaction conditions for transesterification of rapeseed oil,(116) safflower oil,(117) linseed oil,(118) and rice bran oil.(119)

4.1.3 Modifications to Typical Transesterification Conditions

The sections above were meant to present typical commercial biodiesel processes, and discuss the most important factors affecting biodiesel production. However, there are several other process issues worthy of mention, although most of them remain in the R&D arena rather than in commercial applications.

4.1.3.1 Co-Solvents

As already mentioned, triglycerides are very sparingly soluble in methanol, and only slightly more soluble in ethanol. This limits the transesterification reaction rate, and is one reason why a large excess of alcohol is generally used. To help overcome this problem, several researchers have investigated the use of co-solvents, that increase the interaction between the triglyceride and alcohol. Tetrahydrofuran (THF) is one co-solvent that has been widely used.(120) More recently, dimethylether (DME) has been reported as an attractive co-solvent.(121) DME is particularly advantageous since it can easily be flashed off and recycled at the end of the reaction. Similarly, CO_2 has been reported as a useful co-solvent, though this requires use of pressure reactor vessels.(122)

4.1.3.2 Heterogeneous Catalysts

While most commercial biodiesel production involves use of soluble, homogeneous catalysts such as hydroxides or methoxides, there has been tremendous R&D interest in development of heterogeneous catalysts.(120,123) Several dozen of the bibliography entries shown in Appendix II as dealing with biodistillate fuel production technology are focused on this topic of heterogeneous catalysis. In most cases, these catalysts consist of metal oxides(124,125,126,127) ion exchange resins,(128,105) or other materials immobilized on solid supports.(129,130,131,132)

There are several clear advantages to use of heterogeneous catalysts. Perhaps most important, avoiding soluble hydroxide catalysts eliminates the problems associated with saponification and water contamination. Consequently, there is no ester loss due to soap formation, and the by-product, glycerol, is obtained in much higher purity. Additionally, biodiesel purification is considerably easier, since there is no soluble catalyst to remove. As a downside, somewhat higher reaction temperatures are required, since the heterogeneous catalysts are generally less reactive. The only commercial application of a heterogeneous catalytic process for biodiesel production that we are aware of was developed by the French Petroleum Institute, and is being used at a plant in France.(104)

A particular topic of heterogeneous catalysis receiving considerable current interest involves enzymatic materials, such as lipases, immobilized on solid supports.(100,101,107,133,134,135,136) As with the heterogeneous catalysts mentioned above, enzymatic catalysts provide for cleaner separation of high quality biodiesel, and production of high purity glycerol. Additionally, it is reported that use of enzymatic catalysts allows for milder reaction conditions and better performance for ethanol compared to methanol.(101) However, enzymatic catalysts entail high costs and are still regarded as experimental. We are not aware of any commercial biodiesel production process that utilizes enzymatic catalysts today.

4.1.3.3 Supercritical Reaction Conditions

In recent years, there have been several reports of using supercritical conditions to enhance the transesterification reactions of triglycerides with methanol.(38,88,137,138,139,140) Methanol becomes a supercritical fluid at temperatures above 240°C and pressures above 8.1 MPa. Under these conditions, methanol and triglycerides become miscible, greatly accelerating the transesterification reaction, without the presence of added catalyst. Other advantages of supercritical conditions are elimination of salt formation, production of high purity glycerol, reaction of both free fatty acids and triglycerides, tolerance of water contamination, and easy cleanup of the desired biodiesel product. A recent publication reports greater oxidative stability of biodiesel produced via supercritical methods compared to the conventional alkali-catalyzed process.(141)

However, there are disadvantages to supercritical processes as well. Generally, a very large excess of methanol is used (40/1 ratio of methanol/triglyceride) requiring considerable energy to distill and recover the unreacted alcohol.(142,143) Also, to achieve high reaction rates requires quite high temperatures (300-350°C) and high pressures (15-20 MPa). This entails higher capital cost in equipment that can tolerate these temperature and pressure demands.

There is evidence that at temperatures above 300°C, cis-to-trans isomerization of the olefinic structures in FAME can occur, leading to a degradation in cold flow properties.(144) One suggested approach to reducing the severity of supercritical reaction conditions is to use two or more reactors in series, with glycerol removal between the reactors. In this way, temperatures as low as 275°C, pressures as low as 10 MPa, and methanol/triglyceride ratios as low as 10/1 can be used.(143)

One additional supercritical process for producing biodiesel looks promising, but has not yet been widely studied, involves use of ethanol in place of methanol. The conditions required to produce supercritical ethanol are slightly milder than for methanol – about the same temperature, but lower pressure (6.4 MPa vs. 8.1 MPa).(145,146) This may be a fruitful area for further research.

4.1.3.4 Ultrasonic and Microwave Conditions

There are a few reports in the literature of using low-frequency ultrasonication (24-40 kHz) to enhance the transesterification reaction of triglycerides with short chain alcohols.(147,148,149,150,151,152) Ultrasonication has the effect of emulsifying immiscible liquids, thus improving the contact between the reactants and enhancing the reaction rate. Although this may result in a shorter reaction time, the process still requires alkali catalysts, with attendant problems due to salt formation and clean-up of the produced biodiesel.

Another reported enhancement in the transesterification of triglycerides with methanol involves use of microwave irradiation, in either a batch or continuous process.(153,154) The benefit imparted by microwave irradiation is rapid heating of the reaction mixture, resulting in faster reaction rates. One group of researchers has reported that use of microwaves is a more energy efficient process than use of conventional heating approaches.(155) Another group has reported that use of microwaves can increase the reaction temperature to supercritical conditions, in which case no additional catalyst is necessary.(156) Another recent publication reports the use of radio frequency (RF) heating to enhance transesterification.(157) To our knowledge, there is no biodiesel production plant in commercial operation today that uses ultrasonication, microwave, or RF irradiation to enhance the transesterification process.

4.1.4 Glycerol Considerations

As already discussed, production of glycerol by-product during the transesterification of triglycerides to produce biodiesel can lead to numerous problems. While high purity glycerol has many commercial outlets,(158) the increasing production of biodiesel has led to a glut of low quality glycerol, which requires extensive treatment to increase its value.(159) In rough terms, 1 lb. of glycerol is produced for every 10 lbs of biodiesel. The purity of glycerol at a typical biodiesel production plant is only 80-85%, even after water washing and further clean-up.(96,104) Further purification involving distillation is generally performed off-site at a glycerol refinery.

Besides problems with purifying the glycerol itself, the presence of glycerol creates fuel quality problems with the biodiesel. Remaining traces of glycerol can lead to off-spec product. Water washing is typically employed to remove glycerol from biodiesel, but several washes – with intermediate separation steps – are required. In one published study, it was determined that 5-7 washes were required to give acceptable quality product.(160) Clearly, any process that avoids glycerol formation offers an advantage in this area.

Developing alternative, higher-value uses of glycerol has been identified by NREL as an important R&D area,(161) as this would improve the overall economics of biodiesel production. Currently, low-grade glycerol is used as a boiler fuel, where it can be cost competitive with natural gas.(162) With modest upgrading, glycerol can be used as an animal feed. Numerous approaches are also being investigated to use glycerol as a feedstock for the production of higher-value chemicals, including 1,3-propanediol,(76,163) epichlorohydrin,(164) propylene glycol,(165,166) and numerous other 3-carbon molecules.(162) One recent report describes use of glycerol as feedstock for a steam reforming process to produce hydrogen.(167)

One particularly interesting means of reducing glycerol involves transesterification of triglycerides with methanol in the presence of dimethylcarbonate (DMC). Under certain conditions, DMC chemically reacts with triglycerides to produce fatty acid glycerol carbonate (FAGC) along with conventional FAME.(168) (The chemical reaction is shown below in Fig. 19). By this means, the glycerol moiety is converted into a biofuel so that it does not need to be removed from the desired product.

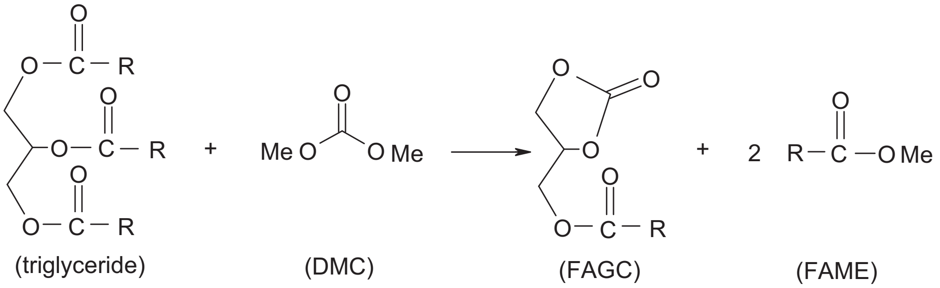


Figure 19. Reaction of Triglycerides with Dimethylcarbonate

Another example of converting glycerol into a diesel fuel component was recently reported by the French Institute of Petroleum.(169) In this case glycerol was reacted with isobutylene to produce glycerol-t-butyl ether (GTBE), which was used as a diesel fuel blendstock. Finally, a group of Spanish researchers has investigated the reaction of glycerol with acetic acid to produce mono-, di-, and tri-acetylglycerol,(170) (MAG, DAG, and TAG, respectively). These products are reported to be beneficial as octane improvers for gasoline and low-temperature flow improvers for diesel fuel. The chemical reactions for this process are shown below in Fig. 20.

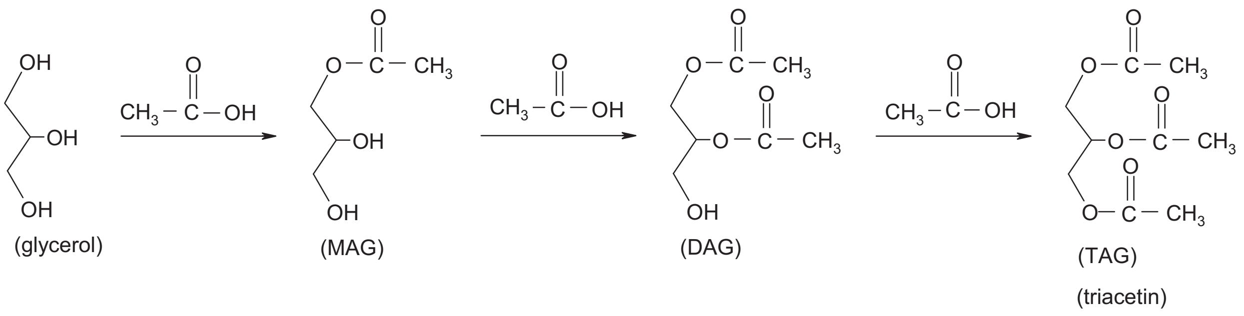


Figure 20. Reaction of Glycerol with Acetic Acid

4.2 Hydroprocessing

In recent years, several academic and industrial organizations have investigated the conversion of triglyceride feedstocks into biodistillate products via hydroprocessing. One of the first commercial processes was reported in 2005, by Neste Oil Corporation.(171,172) The product, called NExBTL, is a paraffinic hydrocarbon material (no aromatics, sulfur, oxygen, or nitrogen) suitable for blending into conventional diesel fuel. At about the same time, UOP in conjunction with Eni, reported a similar process called Ecofining™.(173,174)

In the Neste Oil and the UOP/Eni processes, triglyceride feedstocks can be hydroprocessed directly or co-blended with petroleum feedstocks priod to hydroprocessing, though separate processing is preferred. In contrast, a process recently developed by ConocoPhillips involves co-feeding triglycerides with petroleum feedstocks for hydroprocessing in a conventional diesel hydrotreater unit used for desulfurization.(175) Other companies reported to be developing commercial hydroprocessing of triglyceride feedstocks include Petrobras, BP, and Syntroleum.(176)

In all of these hydroprocessing cases several reactions occur, including hydrogenation of the olefinic groups within the triglyceride, decarbonylation (loss of CO), decarboxylation (loss of CO_2) and hydrodeoxygenation (loss of H_2O).(177,178) These reactions are depicted below in Fig. 21. In these hydroprocessing reactions, most of the glycerol component in the original triglyceride is converted to propane, while most of the carboxyl carbons are converted to CO or CO_2. Since triglyceride compositions are dominated by even-numbered fatty acid components, removal of the carboxyl group results in biodistillates consisting mainly of odd-numbered paraffins.

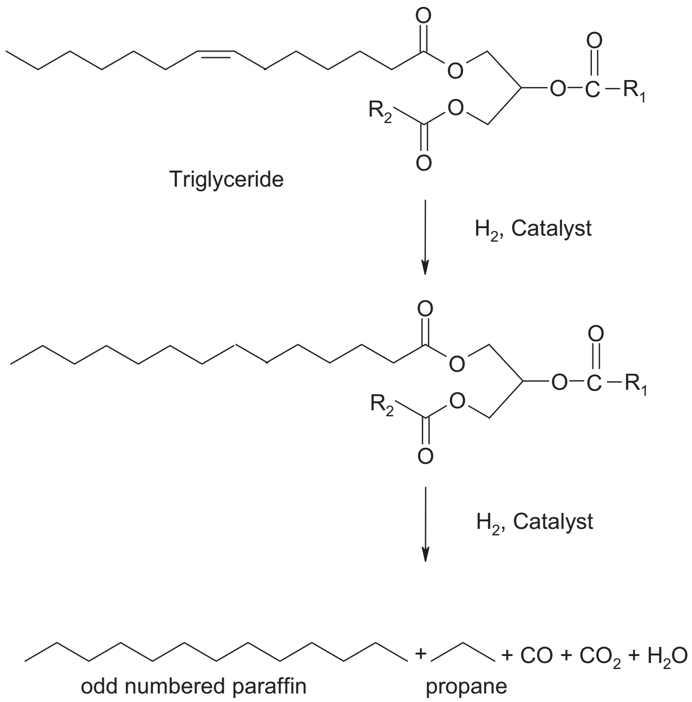


Figure 21. Hydroprocessing of Triglycerides

Various terminology is used to define the biodistillates produced via hydroprocessing. Besides "NExBTL," other common terms are "Renewable Diesel" and "Green Diesel." These products all share several important advantages over conventional biodiesel – including higher energy content, better low-temperature flow characteristics, improved oxidative stability, complete absence of sulfur and nitrogen, and blending behavior that is totally compatible with petroleum diesel blendstocks. Additionally, production of these hydroprocessed biodistillates at a refinery allows for better integration with other refinery operations, and provides access to product testing laboratories. Finally, hydroprocessed biodistillates exhibit emissions advantages over conventional biodiesel (discussed further in a later section). One disadvantage of hydroprocessed biodistillates is their relatively poor lubricity characteristics. In this regard, they are similar to ULSD, and require additive treatment or mixing with higher lubricity blendstocks to achieve satisfactory performance.

4.3 Pyrolysis

In this review, the term "pyrolysis" is used quite broadly to include a variety of processing technologies by which organic feedstocks are treated with heat to break them down to smaller molecules. In the broadest sense, this definition could also include gasification and Fischer Tropsch (FT) processes by which organic feedstocks (fossil or biomass) are converted to liquid fuels via intermediate production of synthesis gas (syngas). The topic area of gas-to-liquids is vast, and well beyond the scope of this review on biodistillates. However, several types of pyrolysis applications that are of direct relevance to our topic of interest are discussed below.

4.3.1 Pyrolysis of Triglycerides

The literature contains many reports of pyrolysis (or thermal cracking) used to treat triglycerides as an alternative to conventional transesterification.(123,89,88) This option may be advantageous when dealing with low-quality triglyceride feedstocks, which are difficult to treat via transesterification. In thermal cracking processing, the oxygen originally present in the triglyceride is largely removed in the form of CO, CO_2, and H_2O – leaving hydrocarbons, which after further upgrading may be suitable mid-distillate components.(179,180)

A recent publication has reported on the thermal cracking of triglycerides that are co-fed with conventional petroleum feedstocks used in a fluidized catalytic cracker (FCC).(181) Besides cracking the triglycerides into smaller fragments, considerable rearrangement and aromatization occurs, producing hydrocarbons suitable for both gasoline and diesel blending. While still at the R&D stage, this approach may eventually provide another means of utilizing triglyceride feedstocks within a petroleum refinery to produce conventional transportation fuels (both gasoline and diesel).

Another approach to pyrolyzing triglycerides involves treatment of the entire plant seed, not just treatment of the oil that has been extracted from the seed.(182,183) Typical oil seeds – such as rapeseed, safflower seed, and soybeans – may contain only 40% triglyceride oil, with the remainder being protein, cellulose, and other materials. It has been reported that by treating the entire seed, a pyrolysis oil yield of up to 68% was achieved.(182) However, oils produced in this way require further refining before they are suitable for blending into diesel fuel. To our knowledge, the approach of pyrolyzing whole oil seeds has only been applied to small-scale R&D applications.

4.3.2 Pyrolysis of Lignocellulose

Pyrolysis of lignocellulose to produce liquid transportation fuels is an extremely active area of research. A review of this area is outside the scope of the present study, though we refer the interested reader to two very useful sources of information on this topic.(2,184) Significant problems with these pyrolysis approaches remain to be overcome – particularly effective means of avoiding char formation, and stabilizing the pyrolysis oils that are produced. In all cases, pyrolysis oils produced from lignocellulosic feedstocks require considerable upgrading to be used as transportation fuels.

One interesting approach recently published used biodiesel fuel (FAME) to extract pyrolysis oil produced from treatment of wood chips.(185) Potentially, this approach could extend the supply of biodistillates, though the suitability of extracted pyrolysis oil components as transportation fuels has not been demonstrated.

4.3.3 Other Thermal Processes

Several other thermal processes for producing biodistillates are in existence or under development, though obtaining reliable information about most of them is quite difficult. One process, developed by Changing World Technologies, Inc. (CWT) is in commercial operation. This is called Thermal Conversion Process (TCP), though it is also known as the Thermal De-Polymerization (TDP) Process.

In the TCP process, organic materials – such as sewage sludge, offal, shredder residues, plastics, and others – are treated through a multi-stage process involving varying temperatures, pressures, and water contents. Though chemical details are not known, it is likely the TCP involves hydrolysis, decarboxylation, and de-polymerization reactions. The products produced from this process include a combustible gas (generally used within the process itself), a liquid hydrocarbon oil, and a solid residue that can be used as a fertilizer or soil amendment.

A commercial plant utilizing the TCP process is in operation in Carthage, Missouri. According to the CWT website, the feedstock being utilized consists of turkey offal and fats.(186) This plant has a capacity of 250 tpd of feedstock, which produces approximately 500 barrels/day of fuel oil. More information about CWT's TCP process is available in the patent literature.(187,188,189)

The oil produced at CWT's Carthage plant has a reported energy content of 18,800 BTU/lb, which is similar to petroleum diesel, suggesting that the oxygen content is quite low. Although this fuel is referred to as "Renewable Diesel," it is unlikely to meet all applicable ASTM specifications for ULSD. It may be more appropriate to consider this product as a diesel blendstock.

Another thermal process has been developed and is being marketed by a company called EcoKat Applied Technologies. (A predecessor company was known as Alphakat.) This technology, called catalytic pressureless deploymerization, is known by its German abbreviation, KDV. In the KDV process, various organic waste feedstocks are mixed with a catalyst (alkali-doped aluminum silicate) and heated to 300-400°C at atmospheric pressure. At these conditions, the organic feedstocks undergo de-polymerization reactions, producing a diesel-like hydrocarbon product. An innovation of this process is use of high agitation pumps and mixers to provide an internal source of frictional heat, and to minimize coking and sludge formation.

The liquid hydrocarbon product produced by EcoKat's KDV process is called Renewable Diesel, but as with the CWT product described above, it may be more appropriate to consider it a diesel blendstock. According to their website, EcoKat has small-scale plants (<100 bpd) operating in Germany, Mexico, and Canada.(190) Further information about the KDV process can be obtained from the patent literature.(191)

5. Fuel Properties and Specification

Biodiesel fuel consists of mono-alkyl esters of long-chain fatty acids derived from vegetable oils or animal fats. Since these oils and fats are quite varied in their composition, biodiesel (and renewable diesel) prepared from them also have variable composition. In this section, we define the chemical composition of typical biodistillates and their precursors, summarize important physical and chemical properties of these materials, and highlight fuel specifications that have been established by various standard-setting organizations. In addition, we describe several physical and chemical treatments of biodiesel that have been reported to improve certain fuel properties.

Consisting of oxygenated species, biodiesel differs from petroleum diesel in many respects. Some of the most important areas of difference are illustrated below in Table VII, which compares typical properties of biodiesel and petroleum-derived No. 2 ULSD. Also shown here are typical properties of renewable diesel. The property values shown in Table VII were derived by compositing information from several literature sources.(174,172,173,171,192,193)

Table VII. Typical Properties of Petroleum Diesel and Biodistillate Fuels

Property	No. 2 Petroleum ULSD	Biodiesel (FAME)	Renewable Diesel
Carbon, wt%	86.8	76.2	84.9
Hydrogen, wt%	13.2	12.6	15.1
Oxygen, wt%	0.0	11.2	0.0
Specific Gravity	0.85	0.88	0.78
Cetane No.	40-45	45-50	70-90
$T_{90,}$ °C	300-330	330-360	290-300
Viscosity, mm^2/sec. @ 40°C	2-3	4-5	3-4
Energy Content (LHV)			
Mass basis, MJ/kg	43	39	44
Mass basis, BTU/lb.	18,500	16,750	18,900
Vol. basis, BTU/gal	130,000	122,000	122,000

Having considerable oxygen content, biodiesel has lower carbon and hydrogen contents compared to diesel fuel, resulting in about a 10% lower mass energy content. However, because of slightly higher fuel density, the volumetric energy content of biodiesel is only about 5-6% lower than petroleum diesel. Typically, biodiesel has somewhat higher molecular weight than petroleum diesel, which is reflected in a slightly higher distillation temperatures (as measured by T_{90}). Being largely straight chain esters, most biodiesel fuels have excellent cetane numbers – typically higher than No. 2 diesel fuel. The viscosity of most biodiesel fuels is significantly higher than petroleum diesel, often by a factor of 2.

Renewable diesel consists primarily of straight chain, saturated hydrocarbons having 15 or 17 carbon atoms. Structurally, renewable diesel molecules resemble cetane (n-hexadecane). Consequently, renewable diesel has excellent combustion properties, as indicated by its high cetane numbers. On a mass basis, the energy content of renewable diesel is very high, slightly exceeding that of typical No. 2 diesel fuel. However, due to its relatively low density, the volumetric energy content of renewable diesel is significantly lower than that of No. 2 diesel, but is very similar to a typical biodiesel.

5.1 Chemical Composition of Biodiesel

In large part, the physical properties, performance attributes, and overall suitability of biodiesel are determined by the fuel's chemical composition. The two most important compositional factors are fatty acid chain length and the degree of unsaturation in the fatty acid chain. Unlike petroleum diesel, biodiesel contains virtually no branched chain paraffinic structures, naphthenes, or aromatics. Thus, in some respects, the composition of biodiesel is much simpler than that of petroleum diesel.

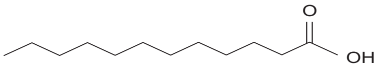
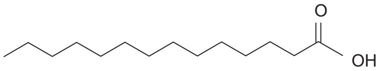
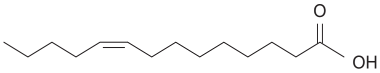
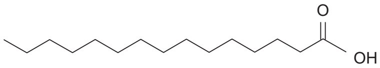
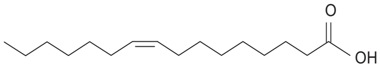
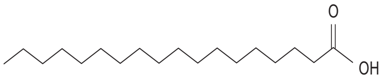
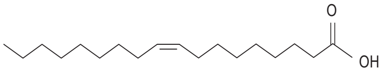
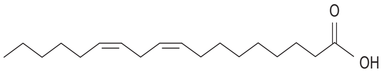
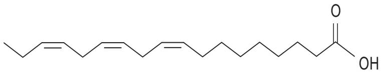
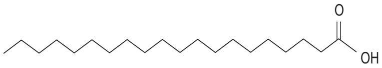
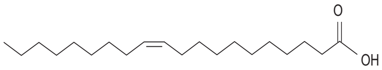
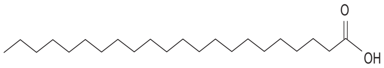
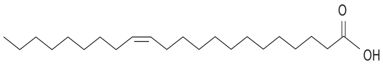
A simple naming convention has been developed and is widely used to identify these two main compositional features of fatty acids (and esters prepared from them). This convention consists of two numbers, with the first representing the number of carbon atoms in the fatty acid chain, and the second number representing the number of carbon-carbon double bonds in the fatty acid chain. Following this convention, the four most common C_{18} fatty acids (stearic, oleic, linoleic, and linolenic) are referred to as 18:0, 18:1, 18:2, and 18:3, as they contain 0, 1, 2, and 3 double bonds, respectively.

Table VIII below provides chemical information and structures for 13 of the most common fatty acid precursors to biodiesel. A more comprehensive table is included as Appendix IV-1. These common materials range from 12 to 22 carbon atoms, with varying degrees of unsaturation in the carbon chains. As illustrated in this table, the dominant double bond orientation in these fatty acids is *cis* (or "Z"). The *cis* orientation has important consequences for biodiesel properties, as the alternative *trans* orientation leads to much higher melting points and low temperature performance problems.

Vegetable oils and animal fats contain fatty acid moieties in the form of triglycerides. As mentioned previously, there are hundreds of different seed oils and fats that have been investigated as biodiesel precursors. Compositional information that we obtained from the literature is shown in Appendix IV-2 for several dozen of these triglycerides. However, several limitations of these data should be mentioned:

- First, a particular, named oil or fat may exhibit considerable compositional variability from one sample to another. A good illustration of this is soybean oil, which has reported oleic acid content (18:1) ranging from 20% to 80%.
- Second, the chemical compositional data reported in the literature were obtained from dozens of different sources, using many different analytical methods. The data shown in Appendix IV-2 simply summarize the analytical results as reported, without any attempt to harmonize or adjust them for variations in methodology.
- Third, the compositions of many of the more exotic seed oils shown in Appendix IV-2 are based on only 1 or 2 literature sources (often using questionable analytical methodologies). Thus, there may be considerable uncertainty for some of the reported compositions.

Table VIII. Common Fatty Acid Precursors to Biodistillates

Common Name	Formal Name	CAS. No.	Abbreviation	Molecular Formula	Molecular Weight	Molecular Structure
Lauric Acid	Dodecanoic acid	143-07-7	12:0	$C_{12}H_{24}O_2$	200.32	
Myristic Acid	Tetradecanoic Acid	544-63-8	14:0	$C_{14}H_{28}O_2$	228.38	
Myristoleic Acid	cis-9-Tetradecenoic Acid	544-64-9	14:1	$C_{14}H_{26}O_2$	226.26	
Palmitic Acid	Hexadecanoic Acid	57-10-3	16:0	$C_{16}H_{32}O_2$	256.43	
Palmitoleic Acid	cis-9-Hexadecanoic Acid	373-49-9	16:1	$C_{16}H_{30}O_2$	254.42	
Stearic Acid	Octadecanoic Acid	57-11-4	18:0	$C_{18}H_{36}O_2$	284.48	
Oleic Acid	cis-9-Octadecenoic Acid	112-80-1	18:1	$C_{18}H_{34}O_2$	282.47	
Linoleic Acid	cis-9,12-Octadecadienoic Acid	60-33-3	18:2	$C_{18}H_{32}O_2$	280.46	
Linolenic Acid	cis-9,12,15-Octadecatrienoic Acid	463-40-1	18:3	$C_{18}H_{30}O_2$	278.44	
Arachidic Acid	Eicosanoic Acid	506-30-9	20:0	$C_{20}H_{40}O_2$	312.54	
Gondoic Acid	cis-11-Eicosenoic Acid	5561-99-9	20:1	$C_{20}H_{38}O_2$	310.53	
Behenic Acid	Docosanoic Acid	112-85-6	22:0	$C_{22}H_{44}O_2$	340.60	
Erucic Acid	cis-13-Docosenoic Acid	112-86-7	22:1	$C_{22}H_{42}O_2$	338.58	

Even with the above-mentioned caveats, a few important compositional features are apparent, particularly with respect to carbon chain length and degree of unsaturation. One obvious feature is that all common triglycerides are dominated by even-numbered carbon chains, with C_{16} and C_{18} being the largest components. (Renewable diesel, produced by hydroprocessing of triglycerides, is therefore dominated by C_{15} and C_{17} molecules, since the carboxyl carbon within each fatty acid is removed during this processing.) Another important feature is that some oils are dominated by saturated carbon chains, while others are dominated by unsaturated chains.

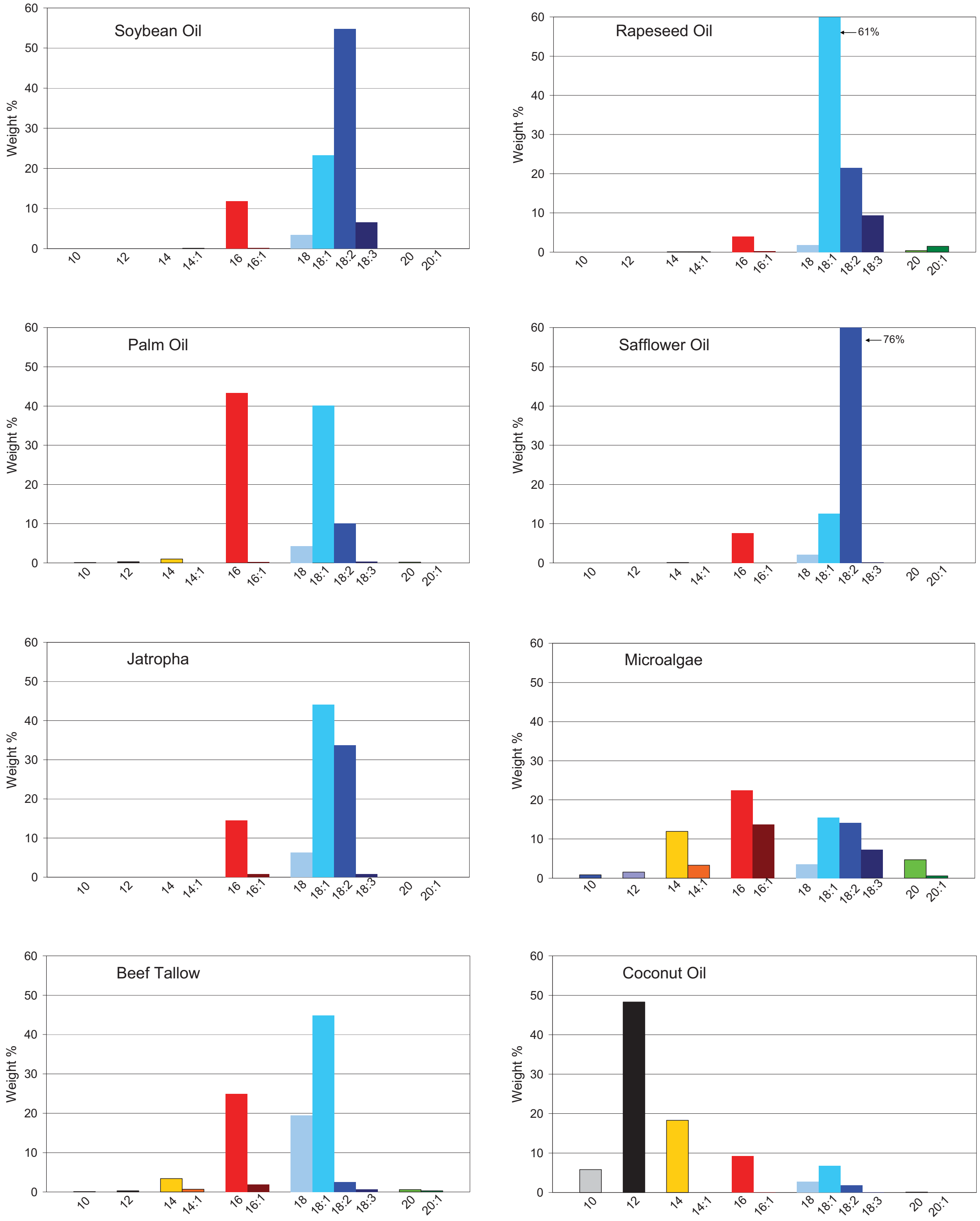


Figure 22. Compositional Profiles of Common Triglycerides

Examples of this extreme diversity are provided by coconut oil (which is about 90% saturated) and safflower seed oil (which is about 90% unsaturated).

A further illustration of this compositional variability is presented in Fig. 22 above, which graphically depicts the composition of 8 biodiesel precursors. This shows that the two most commonly used biodiesel feedstocks (soybean oil in the U.S.; rapeseed oil in Europe) differ significantly in the relative composition of C_{18} fatty acids, with soybean being dominated by linoleic acid (18:2) and rapeseed being dominated by oleic acid (18:1). This compositional difference leads to differences in fuel properties (especially oxidative stability) as will be discussed later. [Although not shown in Fig. 22, it should be mentioned that there are other species of rapeseed that contain substantial levels of erucic acid (22:1), which can contribute to poor low temperature handling.]

5.2. Physical Properties of Biodistillates and their Precursors

As already mentioned, hundreds of vegetable oils and animal fats have been investigated as feedstocks for production of biodiesel. Important physical properties of many of these feedstocks are given in Appendix IV-3; properties of biodistillates (FAME and renewable diesel) are given in Appendix IV-4.

One of the most critical properties of the triglyceride feedstocks is viscosity at 40°C, which typically ranges from 20 to 50 mm^2/sec, or about an order of magnitude higher than biodiesel FAME or petroleum diesel. The mass energy content (also called lower heating value) of most triglyceride feedstocks are similar to FAME, but are 5-10% below the energy content of No. 2 petroleum diesel or renewable diesel.

Due to their considerably higher molecular weight (MW), the flash point of triglyceride feedstocks are higher than for FAME or petroleum diesel. At the same time, this higher MW leads to poorer low temperature operability for triglycerides (as measured by higher cloud point and pour point) compared to FAME, petroleum diesel, and renewable diesel.

5.3 Biodistillate Fuel Standards

Several standard-setting organizations have developed sets of standards to define acceptable quality of biodistillate fuels. The two most widely accepted organizations are ASTM (in the U.S.) and the European Commission (in Europe). ASTM has established standard specifications for biodiesel fuel blendstocks (B100) for middle distillate fuels, called ASTM D 6751-08,(194) as well as for biodiesel blends of B6 to B20 in petroleum diesel, called ASTM D 7467.(195) The European Commission has only established standard specifications for B100, called EN 14214.(196) In addition, a consortium of international automobile and engine manufacturers has issued a set of guidelines for biodiesel quality, known as the Worldwide Fuel Charter.(195)

Important aspects of the biodiesel (B100) specifications are shown in Table IX. Table X shows the same biodiesel specifications, along with B100 specifications from other countries, ASTM specifications for biodiesel blends (B6-B20) and standard specifications for petroleum diesel in the U.S. and Europe. At the present time, only the U.S. has established a separate standard for biodiesel blends. In all other locations, low level biodiesel blends (B5-B20) are acceptable if both the biodiesel component and petroleum diesel component meet their respective standards. No special standards have been established for renewable diesel, but diesel fuel containing renewable diesel must comply with the appropriate standards for No. 2 diesel fuel (ASTM D 975 in the U.S.; EN 590 in Europe).

A major reason for many of the specifications in the B100 standards is to ensure high purity FAME, free of contaminants and unreacted starting materials that could lead to poor performance with respect to storage stability, injection quality, corrosion, deposit formation, emissions, or other aspects. Further explanation of the ASTM B100 specifications – including rationale for their establishment – is provide below, as well as some comparisons with European and other fuel specifications. This information was obtained from several literature sources, (102,192,195,193)as well as from the fuel standard documents themselves.

5.3.1 Water and Sediment

B100 should be clear in appearance and free of water and sediment. A centrifuge-based test method, D 2709, is used to determine the cleanliness of the fuel. The same test is used for both B100 and petroleum diesel (as defined in D 975). In both cases, the acceptable maximum limit of water and sediment is 0.05 vol.%.

For several reasons, this is a very important test for B100. For example, available water can react with FAME to produce fatty acids, can support microbial growth in storage tanks, and can lead to excessive corrosion. As described earlier (Section 4) water is formed by certain side reactions (saponification and esterification of free fatty acids) that occur during the production of FAME. Also, water is deliberately added during the washing process to purify the produced biodiesel.

Sediments are of concern because of the potential to plug fuel filters and adversely affect the performance of fuel injectors. Modern fuel injectors operate under extremely high pressures, up to 200 MPa, (193)which requires very small orifice sizes and component clearances. Proper functioning of these fuel injectors is jeopardized by excessive sediment levels, potentially leading to engine damage.

In addition to the D 2709 water and sediment specification, the European Biodiesel Standard (EN 14214) includes a specification for “Total Contamination.” This is a mass-based determination of non-water solid contaminants in the fuel. The maximum allowable level of such contaminants is 24 mg/kg. The U.S. standards do not include a comparable specification for total contamination.

Table IX. U.S. and European Biodiesel Standards (B100)

Property	ASTM D 6751-08		EN 14214		Worldwide Fuel Charter	
	Limits	Method	Limits	Method	Limits	Method
Water and Sediment (% vol., max)	0.05	D 2709	0.05	EN 12937	0.05	D 2709
Total Contamination (mg/kg, max.)			24	EN 12662	24	EN 12662, D 2276, D 5452, D 6217
Kinematic Viscosity @ 40° C (mm^2/s)	1.9-6.0	D 445	3.5-5.0	EN 3104/3105	2.0 - 5.0	EN 3104, D 445,
Flash Point, Closed Cup (°C, min.)	93	D 93	120	EN 3679	100	ISO 2719, D 93
Methanol (wt.%, max.)	0.20[a]	EN 14110	0.20	EN 14110	0.20	EN 14110,
Cetane No. (min.)	47	D 613	51	EN 5165	51	ISO 5165, D 613,
Cloud Point (°C)	Report[d]	D 2500	Country Specific			
Sulfated Ash (wt.%, max.)	0.020	D 874	0.020	EN 3987	0.005	EN 6245, D 482,
Total Ash (wt.%, max.)					0.001	EN 6245, D 482,
Gp I metals Na + K (mg/kg, max.)	5	EN 14538	5	EN 14108/14109	5	EN 14108/14109, EN 14538
Gp II Metals Ca + Mg (mg/kg, max.)	5	EN 14538	5	prEN 14538	5	EN 14538
Total Sulfur (ppm, max.)	15[b]	D 5453	10	EN 20846	10	EN 20846/20884, D 5453, D 2622
Phosphorous (ppm, max.)	10	D 4951	10	EN 14107	4	EN 14107, D 4951, D 3231
Acid No. (mg KOH/g, max.)	0.50	D 664	0.50	EN 14104	0.50	EN 6618, EN 14104, D 664, D 974,
Carbon Residue (wt. %, max)	0.05	D 4530	0.30[e]	EN 10370	0.05	D 4530
Free Glycerin (wt.%, max.)	0.02	D 6584	0.02	EN 14105/14106	0.02	EN 14105/14106, D 6584
Total Glycerin (wt.%, max.)	0.24	D 6584		EN 14105	0.24	EN 14105, D 6584
Mono Glyceride (wt.%, max)			0.80	EN 14105	0.80	EN 14105
Di glyceride (wt.%, max)			0.20	EN 14105	0.20	EN 14105
Triglyceride (wt.%, max)			0.20	EN 14105	0.20	EN 14105
Distillation (T-90 °C, max.)	360[c]	D 1160				
Copper strip corrosion (3-hr. at 50° C, max.)	No. 3	D 130	No. 1	EN 2160	Light Rusting	D 665-Procedure A
Oxidation Stability (hrs @ 110°C, min)	3	EN 14112	6	EN 14112	10	EN 14112, prEN 15751
Linolenic acid methyl ester (wt.%, max)			12	EN 14103	12	EN 14103 mod
Polyunsaturated acid methyl esters (wt.%,max)			1	prEN 15799	1	prEN 15799
Ester Content (wt.%, min)			96.5	EN 14103	96.5	EN 14103 mod, EN 14078
Iodine Number (gl/100g, max.)			120	EN 14111	130	EN 14111, prEN 15751
Density (kg/m^3)			860-900	EN 3675	860-900	EN 3675, D 4052, EN 12185

Footnotes:

a Alternatively, flash point must be > 130 °C

b For blending with ULSD. For other fuels, higher sulfur levels are allowed

c Atmospheric equivalent T-90 point

d Low temperature properties are not strictly specified, but should be agreed upon by the fuel supplier or purchaser

e This limit is based on the bottom 10% fraction of the fuel, not the entire fuel

Table X. Selected Biodiesel and Diesel Standards

Property	Biodiesel Fuels (B100)						Biodiesel Blends	No. 2 Diesel Fuels		
	U.S. (ASTM D6751-08)	Europe (EN 14214)	Worldwide Fuel Charter	South Africa	Brazil	Japan (JIS K2390)	U.S. (ASTM D7467-08[d])	Europe (EN 590)	U.S. (ASTM D975)	Worldwide Fuel Charter (Category 4)
Water and Sediment (% Vol., max)	0.05	.05 w/w	0.05 w/w	0.02	0.02	0.05	0.05	0.02 w/w	0.05	.02 w/w
Total Contamination (ppm, max)		24	24	24		24		24		10
Kinematic Viscosity @ 40° C (mm^2/s)	1.9-6.0	3.5-5.0	2.0 - 5.0	3.5 - 5.0		3.5-5.0	1.9-4.1	2.0-4.5	1.9-4.1	2.0 - 4.0
Flash Point, Closed Cup (°C, min.)	93	120	100	100	100	120	52	55	52	55
Methanol (wt.%, max.)	0.20[a]	0.2	0.2	0.2		0.2				
Cetane No. (min.)	47	51	51	45	45	51	40	46	40	55
Cetane Index, (min.)						51	40[b]		40[b]	55
Cloud Point (°C)	Report[e]	Country Specific			Report	Report	Report[e]		Report[e]	
Sulfated Ash (wt.%, max.)	0.02	0.02	0.005	0.02	0.02	0.02	0.01	0.01		
Total Ash (wt.%, max.)			0.001					0.01	0.01	0.001
Gp I metals Na + K (mg/kg, max.)	5	5	5	10	10	5				
Gp II Metals Ca + Mg (mg/kg, max.)	5	5	5	5		5				
Total Sulfur (ppm, max.)	15	10	10	10	10	10	15	50	15	10
Phosphorous (ppm, max.)	10	10	4	10	10	10				
Acid No. (mg KOH/g, max.)	0.5	0.5	0.5	0.8	0.8	0.5	0.3			0.08
Carbon Residue (wt.%, max)	0.05	0.3	0.05	0.05	0.05	0.3	0.35	0.3	0.35	0.2
Free Glycerin (wt.%, max.)	0.02	0.02	0.02	0.02	0.02	0.02				
Total Glycerin (wt.%, max.)	0.24	0.25	0.24	0.38	0.38	0.25				
Mono Glyceride (wt.%, max)		0.8	0.8	1.00	1.00	0.8				
Diglyceride (wt.%, max)		0.2	0.2	0.25	0.25	0.2				
Triglyceride (wt.%, max)		0.2	0.2	0.2	0.25	0.2				
Distillation (T-90 °C, max.)	360[c]			360 @ T95	360 @T95	360	343	360	282-338	320
Copper strip corrosion (3-hr.@ 50° C, max.)	No. 3	No. 1	Light Rusting	No. 1	No. 1	No. 1	No. 3	No. 1	No. 3	No. 1
Oxidation Stability (hrs @ 110°C, min)	3	6	10	6	6	2	6			
Linolenic acid methyl ester (wt.%, max)		12	12	12		12				
Polyunsaturated methyl esters (wt.%, max)		1	1	1		1				
Ester Content (wt.%, min)		96.5 min.	96.5 min	96.5 min		96.5 min	6-20 vol.%	0 - 5		
Iodine Number (g I_2/100g, max.)		120	130	140		120				
Density (kg/m^3)		860-900	860-900	860		860 - 900		820-845		820 - 840
Aromatics (% vol., max)							35[b]		35[b]	15 % m/m
Lubricity @ 60 °C, WSD, microns (max)							520	460	520	400
Polycyclic Aromatic Hydrocarbons (wt.%, max)								11		
Cold Soak Filterability, °C, max				-4 - 3						

Footnotes

[a] Alternatively, flash point must be > 130 °C

[b] Either aromatics spec or Cetane Index spec (40, min) must be met

[c] Atmospheric equivalent T-90 point

[d] Biodiesel component of the blend must conform to requirements of ASTM D6751

[e] Low temperature properties are not strictly specified, but should be agreed upon by the fuel supplier or purchaser

5.3.2 Kinematic Viscosity

According to ASTM D 6751, test method ASTM D 445 is required to determine the viscosity of B100. This is done by measuring the time required for a specific volume of the sample to flow through a prescribed capillary tube under gravity. As viscosity is highly dependent upon temperature (see Fig. 14), the temperature of this test is carefully controlled at 40°C.

Viscosity affects the behavior of fuel injection, with high viscosity leading to larger drops, poorer atomization, and greater in-cylinder penetration of the fuel spray. These conditions can also lead to engine deposit formation, poor combustion, higher emissions, and increased engine oil dilution.

As previously mentioned, triglyceride oils and fats have unacceptably high viscosity levels, which prevent them from being used as neat fuels. Biodiesel fuels produced from these triglycerides have considerably reduced viscosity levels, but they still typically exceed the levels of No. 2 diesel fuel. Because of this, the allowable viscosity limits for B100 are slightly higher than for petroleum diesel. The ASTM standards specify a viscosity range of 1.9 – 4.1 mm^2/sec for petroleum diesel, but a larger range of 1.9 – 6.0 mm^2/sec for B100. [Note: the units used to express viscosity, mm^2/sec, are sometimes referred to as centistokes (cSt).] The European B100 standards are somewhat more restrictive, having a narrower acceptable viscosity range of 3.5 – 5.0 mm^2/sec.

5.3.3 Flash Point

Flash point is determined by ASTM D 93, which involves slowly heating a sample of fuel in a closed, stirred cup. The cup is opened at various time intervals, and an ignition source is moved over the top of the cup. The flash point is defined as the minimum temperature at which the fuel will ignite upon application of this ignition source.

Flash point varies inversely with volatility. The presence of even small amounts of volatile substances can lower the flash point of a fuel substantially. Thus, the flash point specification is used to protect against excessive contamination by methanol, which may be left over from the production of FAME. Besides the safety hazard resulting from a low flash point, excessive methanol can affect fuel pumps, seals, and elastomers, and contribute to decreased lubricity.

The minimum flash point limit in ASTM D 6751 is 93°C. The European biodiesel standard defines a somewhat higher flash point limit of 120°C. These are both substantially higher than the ASTM D 975 limit of 52°C for conventional No. 2 diesel fuel. Consequently, the flash point test for biodiesel is not an effective means of detecting methanol in biodiesel blends.

5.3.4 Methanol Content

As described above, methanol contamination in B100 can contribute to a number of safety and performance problems. Despite this, ASTM D 6751 does not require explicit measurement of methanol. However, if methanol is not measured, the B100 sample must meet a more stringent flash point specification of 130°C. If methanol is measured directly, it is done using a gas chromatographic-based method, EN 14110, which is also required by the European B100 standard. The maximum allowable amount of methanol is 0.02 wt.%, according to both the U.S. and European standards.

5.3.5 Cetane Number

Cetane number is a measure of a fuel's ignition and combustion characteristics. It is determined experimentally in a standardized laboratory engine, by comparing the ignition performance of a test fuel with the performance of other fuel blends having known cetane numbers. A minimum cetane number of 47 is required for B100. This is considerably higher than the cetane number limit of 40 required by ASTM D 975 for conventional No. 2 diesel fuel. The European limit for B100 is higher yet, at 51. However, FAME materials have naturally high cetane numbers, so meeting either the U.S. or European standard is generally not a problem.

For petroleum diesel, a calculated cetane index is sometimes used to define the fuel's combustion characteristics, rather than a measured cetane number. The cetane index calculation is based upon the fuel's specific gravity and distillation curve, both of which are quite different for B100 compared to petroleum diesel. Consequently, the established cetane index calculations are not accurate predictors of cetane number for biodiesel.

5.3.6 Cloud Point

Cloud point is the temperature at which a visible haze of wax crystals first appears in a fuel as it is cooled down under conditions prescribed in ASTM test method D 2500. Cloud point is an important feature in cold weather performance for all distillate fuels. Typically, B100 has higher cloud points than conventional diesel fuel, largely due to the presence of saturated FAME species such as methyl palmitate (16:0) and methyl stearate (18:0). As discussed in later sections, the cloud point of B100 can be modified by use of additives and by blending with other feedstocks.

Despite the importance of cloud point, no numeric standards have been established by either U.S. or European organizations. However, fuel producers are required to measure the fuels' cloud point, and report this to the customer.

5.3.7 Sulfated Ash

ASTM D 874 is used to determine the sulfated ash content of biodiesel. In this test, the sample is ignited and burned until only ash and carbon remain. The residue is then treated with sulfuric acid and heated to completely oxidize and remove all carbon. The remaining sulfated ash is then weighed. According to ASTM D 6751, the maximum allowable amount of sulfated ash in B100 is 0.020 wt.%.

The primary purpose of this sulfated ash procedure is to ensure minimal contamination by the alkaline catalysts used in the esterification method of producing biodiesel; namely sodium (Na) and potassium (K). Excessive levels of Na and K can lead to engine deposits and other harmful consequences. Of particular concern is the susceptibility of modern diesel particulate filters (DPF) to impairment from excessive ash levels.

Conventional diesel fuel does not have a specification for sulfated ash, but does have a total ash spec. Total ash is determined by a different method, D 482, and has a maximum allowable level of 0.01 wt.%. This total ash spec also applies to B6-B20 blends, as defined in ASTM D 7467, but does not apply to B100.

5.3.8 Group I and II Metals

As described above, a sulfated ash method (ASTM D 874) is required primarily to determine contamination of biodiesel by Na and K. Another method, EN 14538, is also required to determine the same Group I metals (Na and K) as well as the Group II metals, calcium (Ca) and magnesium (Mg). Method EN 14538 involves optical emission spectral analyses with inductively coupled plasma (ICP-OES). In this method, Na and K are measured together. The maximum allowable sum of Na and K is 5 ppm. Similarly, Ca and Mg are measured together, and also have a total allowable sum of 5 ppm.

5.3.9 Sulfur Content

The total sulfur content of biodiesel is determined by ASTM Method D 5453. In this method, a small volume of fuel is injected into a high temperature combustion tube, where all the sulfur is converted to SO_2. The combustion gases are then exposed to UV irradiation that converts SO_2 to a high energy excited form. As this high energy species reverts to its stable state, it emits light which is detected by a photomultiplier tube. The intensity of this fluorescence is proportional to the amount of sulfur in the sample.

Biodiesel meant for blending with ULSD must meet the ASTM sulfur specification established for ULSD; namely, 15 ppm maximum. The European standard for biodiesel requires a slightly lower maximum of 10 ppm. The major concern about sulfur contamination is its adverse effects on the performance of exhaust emissions control systems. Fortunately, most biodiesel fuel feedstocks are naturally low in sulfur. However, it is possible for sulfur contamination to arise from neutralization agents used in the FAME production process. In addition, some low grade feedstocks such as fats, greases, and used vegetable oils can contain appreciable levels of sulfur.

5.3.10 Phosphorus

The U.S. standard for B100 requires ASTM Method D 4951 to be used in determining total phosphorus (P) concentrations. A maximum limit of 10 ppm P is allowed, which is the same limit specified in the European standard for B100. (The Worldwide Fuel Charter recommends a lower limit of 4 ppm.) Method D 4951 involves inductively coupled plasma with atomic emission spectrometry (ICP-AES). The ASTM standard for conventional diesel (D 975) and for B6-B20 blends (D 7467) do not include a specification for phosphorus content.

As with sulfur, the concerns about phosphorus contamination are related to emissions control system degradation. Biodiesel naturally contains very little phosphorus, but some contamination is possible if triglyceride feedstocks are not adequately refined prior to being used in the transesterification process. In particular, some phospholipids can remain in vegetable oils, and proteins can remain in animal fats.

5.3.11 Acid Number

The most common method for determining acid content in biodiesel is ASTM D 664, which involves titration of free fatty acids with a solution of KOH. The maximum allowable limit for acid number is 0.50 mg KOH/g fuel, according to both the U.S. and European standards. ASTM standards for conventional diesel and B6-B20 blends of biodiesel do not contain specifications for acid number.

The presence of free fatty acids can promote corrosion in fuel injection systems and other metallic components. Generally, freshly prepared biodiesel will have a very low acid number, since the base catalyst used in the transesterification process will remove all available fatty acids. However, upon degradation of the fuel by exposure to water and air free fatty acids may be produced. The Worldwide Fuel Charter suggests that a change in total acid number (ΔTAN) following an accelerated fuel aging test be used as an indication of fuel stability. So far, no standards-setting organization has adopted a ΔTAN specification.

5.3.12 Carbon Residue

Carbon residue is a measure of how much residual material remains after combustion. This test involves vaporization of the fuel at high temperature (550°C) in the absence of oxygen. For conventional diesel fuel, ASTM D 975 requires use of Method D 524, which first involves removal of 90% of the fuel by distillation. Carbon residue is then determined on the remaining 10% fraction. For No. 2 diesel, the specification limit from this test (often called the Ramsbottom carbon residue) is 0.35 wt% of the 10% bottoms.

When dealing with biodiesel, it is difficult to obtain a 10% bottoms fraction by distillation, so the carbon residue determination is conducted on the neat, undistilled fuel, according to Method D 4530. The maximum carbon residue limit for B100 is 0.05 wt.% of the entire fuel. The same test method and carbon residue limit apply to B6-B20 blends under ASTM Standard D 7467. However, the European B100 standard is based upon a 10% bottoms fraction, and therefore has a higher limit of 0.30 wt%.

While not directly correlating with injector and engine deposits, carbon residue is thought to give a reasonable estimate of the depositing tendencies of a fuel. In biodiesel samples, high levels of carbon residue can be caused by contamination with unreacted glycerides. As discussed below, B100 standards include other specifications to directly address this issue.

5.3.13 Free and Total Glycerin

Free and total glycerin are measured by the same gas chromatographic method, ASTM D 6584, which involves derivatization of the materials to facilitate chromatographic separation and detection. Free glycerin (also called glycerol) results from incomplete separation of the FAME product after transesterification. High levels of free glycerin may cause problems during fuel storage by settling to the bottom of tanks, or in the fuel system by clogging filters and injectors. “Bonded glycerin” refers to monoglycerides, diglycerides, and triglycerides that remain in the fuel due to incomplete transesterification. High levels of these glycerides can lead to injector fouling and can contribute to engine deposits.

The glycerin limits established in ASTM D 6751 for B100 are 0.02 wt.% for free glycerin and 0.24 wt.% for total glycerin. The European Standards are similar, but also have individual limits for monoglycerides, diglycerides, and triglycerides. Neither conventional diesel fuel nor B6-B20 blends of biodiesel have any specifications for glycerin (either free or total).

5.3.14 Distillation Temperature (T_{90})

For conventional No. 2 diesel fuel, ASTM D 975 establishes both a minimum (282°C) and a maximum (338°C) limit on the 90th percentile distillation point (T_{90}). These limits are not appropriate for B100, which consists of a narrow range of chemical species, and hence exhibits a much narrower distillation range compared to conventional diesel.

Typically, B100 has a slightly higher boiling point than the T_{90} level of conventional diesel. ASTM D 6751 has defined a maximum T_{90} limit of 360°C for biodiesel as a precaution to ensure that the fuel is not contaminated with high boiling material, such as used motor oil. The required test method, D 1160, involves distillation under reduced pressure, but the limit of 360°C is expressed as an atmospheric equivalent boiling point.

The European B100 Standard (EN 14214) does not contain a specification for distillation temperature. B6-B20 blends defined by ASTM D 7467 have a T_{90} maximum limit of 343°C (slightly higher than conventional diesel at 338°C), but do not have a T_{90} minimum.

5.3.15 Copper Strip Corrosion

The copper strip corrosion test, ASTM D 130, is used to determine the corrosiveness of fuels towards copper surfaces. In this test, a polished copper strip is immersed in a fuel sample for 3 hours at 50°C. After removal and washing, the copper strip is qualitatively rated by comparing its appearance with known standards. The limit for B100 specified in ASTM D 6751 is a maximum rating of No. 3. (Higher numbers indicate a greater degree of corrosiveness.) The same test method and limit apply to conventional diesel fuel (ASTM D 975) and B6-B20 blends (ASTM D 7476). The European standards for both conventional diesel and B100 are more stringent, with a maximum allowable rating of No. 1.

The presence of free fatty acids in B100 can contribute to excessive corrosiveness of the fuel. However, as discussed above, B100 standards (both U.S. and European) have other specifications for total acid number, which are generally regarded as being more protective against excessive free fatty acids.

5.3.16 Oxidative Stability

An accelerated oxidation test, EN 14112 (also called the Rancimat Test), is used to determine the oxidative stability of biodiesel. In this test, a stream of heated air (110°C) is bubbled through a sample of fuel. Volatile oxidation products (such as light organic acids) are carried by the air stream into a vessel containing distilled water. The electrical conductivity of this water is continuously measured until it rises rapidly. The time between the start of test and the point where the conductivity sharply rises is called the induction period. The induction period limit in ASTM D 6751 for B100 is 3 hours. The limit for European B100 (and for B6-B20 blends in the U.S.) is 6 hours. Conventional diesel fuel does not require a specific test for oxidative stability.

Due to their relatively high concentrations of unsaturated compounds, biodiesel fuels can more readily oxidize, forming peroxides and acids. These oxidation species can damage plastics and elastomers, and can contribute to formation of sludges and deposits. Oxidative stability is regarded as one of the most critical fuel quality issues for biodiesel. Due to this concern, the European Biodiesel Standard (EN 14214) also includes a separate specification for linolenic acid methyl esters (which contains 3 double bonds) and for polyunsaturated acid methyl esters (which contain 4 or more double bonds).

5.3.17 Ester Content

ASTM D 6751 includes no specification for ester content of B100. However, a specification is included in ASTM D 7467 for B6-B20 blends. With these blends, an infrared spectrometric method, ASTM D 7371, is required to ensure that the FAME concentrations are in the range of 6 to 20 vol.%. In contrast, the European biodiesel standard does include a specification for minimum FAME content. A gas chromatographic method, EN 14103, is used to ensure a minimum FAME concentration of 96.5 wt.%.

5.3.18 Iodine Number

Iodine number provides a measure of the number of double bonds (or degree of unsaturation) in the FAME molecules. There is a general correlation between unsaturation and oxidative stability. ASTM standards do not include a specification for iodine number, believing that the Rancimat oxidative stability test, EN 14112, provides an adequate measure of biodiesel's stability. The European biodiesel standard does contain a specification for iodine number, determined by Method EN 14111. The specification limit is a maximum of 120 mg I_2/100g of fuel.

This iodine number specification has been the source of some controversy. The European maximum limit of 120 is quite restrictive, so that some common FAME feedstocks, such as soybean oil, have difficulty meeting it. Even more highly unsaturated feedstocks, such as sunflower and safflower, are precluded from use, unless blended with other low-unsaturation FAME materials.

5.3.19 Density

ASTM standards do not include a specification for B100 density, though the European standards do. Neat biodiesel is significantly more dense than conventional diesel. Dilution of biodiesel, either deliberately or inadvertently, is likely to reduce its density. As a precautionary measure, a density range of 860 to 900 kg/m^3 is specified in EN 14214.

5.4 Quality Control/Quality Assurance Measures

To ensure satisfactory product quality, biodiesel producers and marketers must have an established quality control/quality assurance (QC/QA) program. In Germany, the Association for Quality Management of Biodiesel (abbreviated AGQM in German) was established in 1999 to deal with in-use fuel quality.(197) More recently, the National Biodiesel Board has addressed this concern in the U.S. by establishment of the National Biodiesel Accreditation Commission that oversees and directs the BQ-9000 Quality Management System.(23) This Commission has recently issued two sets of requirements: one for B100 producers;(198) the other for B100 marketers.(199)

The BQ-9000 Producers Requirements define acceptable documentation practices, management responsibilities, laboratory operations, sampling and testing methods, fuel blending and loading requirements, and other aspects of a Quality Management System. The BQ-9000 Marketers Requirements include many of the same elements with respect to documentation, management responsibilities, and laboratory procedures, but also address issues of fuel storage, blending, and distribution.

A critical aspect of fuel quality is establishment and operation of a competent fuel testing laboratory. A minimal level of quality control testing should be conducted at the fuel production site, for every batch of fuel that is produced. This is routinely done for conventional diesel fuel produced at a petroleum refinery, but for biodiesel, this is not always the case.

Small “Mom and Pop” producers of biodiesel will generally not have the necessary equipment or expertise to conduct the full range of tests specified in ASTM D 6751 for B100. Even in such cases, however, a subset of the most critical QC tests should be conducted on-site for every batch, with other tests being conducted periodically, using outside laboratories. This distinction between critical and less critical QC laboratory testing has been discussed in some detail by Van Gerpen et al., who recommended a set of 8 tests be performed on each biodiesel batch.(102) They also determined that the total capital cost of equipment necessary to conduct these 8 tests was about $80K (in 2004).

In Table XI below, we provide our recommendations for laboratory QC tests that should be conducted to ensure high quality biodiesel. The tests recommended for every batch of B100 are the same ones recommended by Van Gerpen et al., with the addition of the Rancimat oxidative stability test.

Table XI. QC Laboratory Testing Recommendations for B100

QC Tests Conducted on Every Batch		QC Tests Conducted Periodically	
Property	Test Method	Property	Test Method
Water and Sediment	D 2709	Cetane Number	D 613
Viscosity	D 445	Methanol	EN 14110
Flash Point	D 93	Metals (Na, K, Ca, Mg)	EN 14538
Cloud Point	D 2500	Total Sulfur	D 5453
Sulfated Ash	D 874	Phosphorous	D 4951
Acid Number	D 664	Carbon Residue	D 4530
Free and Total Glycerin	D 6584	T_{90}	D 1160
Copper Strip Corrosion	D 130	Ester Content*	EN 14103
Oxidative Stability	EN 14112	Iodine Number*	EN 14111

* Only required for European biodiesel

6. In-Use Handling and Performance of Biodiesel Fuels

As described in the above section, some properties of biodiesel differ from those of conventional diesel fuel. Consequently, precautions must be taken to ensure that proper handling practices are followed, so that products having acceptable quality are being delivered to the end customer. Because renewable diesel fuel is virtually identical to petroleum-derived mid-distillate blendstocks, and it is generally blended into a final fuel at the refinery, the issues and practices described in this section pertain only to biodiesel, not to renewable diesel.

Under special circumstances, B100 may be utilized. However, for use as a transportation fuel, only blends of biodiesel with conventional diesel are recommended. (An exception exists in Germany, where B100 is commonly used as a transportation fuel.) The literature is replete with studies where various blend ratios of biodiesel have been used. For research and development purposes, investigations of wide blending ranges are valuable, since this provides a better understanding of fuel effects on injection behavior, engine performance, emissions, materials compatibility, and other factors. For commercial use, however, a much narrower range of biodiesel blend ratios is desirable.

In the U.S. today, two biodiesel blend levels are most common; B2 and B20. B2 is frequently used to provide sufficient lubricity for ULSD to meet ASTM D 975 requirements. In these cases, if biodiesel were not included, some other lubricity additive would be used. B20 is the highest blend level specified by ASTM and permitted by many engine and vehicle manufacturers.

As early as 1996, the National Biodiesel Board began to focus on B20 as the preferred blend of biodiesel.(200) Many other groups, including DOE, consider B20 to represent a good balance of cost, emissions, cold weather performance, materials compatibility, and solvency.(192,89) Furthermore, B20 (which imparts approximately 2.2% oxygen content to the fuel blend) is the minimum accepted level for vehicle fleets to satisfy the alternative fuel vehicle requirements of the Energy Policy Act (EPAct). Due to its now common usage, B20 is frequently referred to simply as “biodiesel,” and B100 is referred to as “biodiesel blendstock.”

B20 blends (and lower concentration blends) are commonly prepared by mixing B100 with conventional diesel fuel at one of three different steps in the distribution chain: (1) blending by the end user, (2) blending by a jobber or distributor who then provides the finished fuel, or (3) blending at a petroleum terminal or rack by the facility operator. Additionally, three different methods of blending are used:

1. Splash blending. B100 and diesel fuel are added separately into a fuel delivery truck or individual vehicle fuel tank. Mixing occurs by means of agitation while the vehicle is in motion.
2. In-tank blending. B100 and diesel fuel are added separately or at the same time into a mixing tank. Agitation provided by a rapid filling rate may be sufficient to cause adequate mixing, though additional stirring or recirculation may be necessary in some cases.
3. In-line blending. B100 is added in pulses or continuously into a flowing stream of diesel fuel as it travels through a pipe or hose to a larger holding tank.

In-line blending is preferred because it provides the greatest accuracy and control over the blending operation. However, it is also the most expensive method, as it requires use of metered pumps and injector systems. Other precautionary measures to ensure successful blending include use of multiple B100 tanks (with quality testing being performed on the contents of each tank before blending), and maintenance of a constant temperature (70°F) in all biodiesel tanks and blending equipment.(201) Additional guidelines regarding blending and handling of biodiesel are provided in a recent DOE document.(192) A recent study sponsored by the Canadian Trucking Association also highlights challenges and precautions when integrating biodiesel into the infrastructure already used for conventional diesel fuel.(202)

6.1 Fuel Quality Surveys

One of the biggest concerns of the biodiesel industry is the quality of finished fuels being used in the marketplace. The use of poor quality fuels can lead (and has led) to field problems and customer complaints, which reduce public confidence and jeopardize the future of the industry. Steps to address these concerns have been taken in recent years by adoption (or modification) of ASTM Standards D 6751 (for B100) and D 7467 (for B6-B20), and by development of the BQ-9000 Quality Management System.

Another aspect of ensuring overall product quality is application of in-use surveys. The first systematic field survey in the U.S. was conducted by NREL in 2004, and reported in 2005.(203) In this study, 27 samples of B100 and 50 samples of B20 were obtained from blenders and distributors around the country. Based upon questionnaires, it was determined that most blenders and distributors did not conduct product testing of their own, but relied upon the biodiesel manufacturers to ensure fuel quality. Laboratory tests conducted as part of this study showed that 85% of the B100 samples met all ASTM D 6751-03 standard specifications. However, it was noted that only 4 of the 27 samples would meet a minimum inhibition period of 3 hours as measured by the Rancimat oxidation test. (The Rancimat test was not included in ASTM D 6751 at the time of this study, but was added in 2007.) Similar problems with oxidative stability of the B20 samples were noted. This survey also highlighted blending problems in producing B20, as 18 of the 50 samples tested had biodiesel concentrations outside the accepted range of B18-B22 – 7 were considerably higher (maximum of B98) and 11 were considerably lower (minimum of B7).

In 2006, NREL conducted another nationwide fuel quality survey of B100 intended for use as a blendstock.(204) Specification testing of 37 B100 samples showed that 59% failed to meet the ASTM D6751 requirements applicable at this time. The main reasons for failures were excessive levels of total glycerine and low flash point. Such problems suggest insufficient quality control in the production and clean-up of FAME. These results were quite disturbing because they indicate a worsening of B100 quality between the 2004 and 2006 survey periods. Oxidative stability was again pointed out as an area of concern. Although still not a standard specification at the time of this survey, the Rancimat test was conducted on 10 of the 37 B100 samples. Only 3 of these 10 had an induction period in excess of 3 hours.

The most recent nationwide B100 quality survey was conducted by NREL in 2007.(205) In this case, all known biodiesel producers in the U.S. were approached, with 56 of the 107 producers supplying samples for testing and evaluation. These 56 samples were binned according to producer size, with 25 samples coming from small producers (<0.1 mg/y), 16 samples from medium-sized producers (0.1 – 1.0 mg/y) and 15 samples from large producers (>1.0 mg/y). Results from laboratory specification testing showed that the large producers nearly always met ASTM D 6751 specifications. However, fuels from small and medium-sized producers still had significant failures, with oxidative stability having the highest failure rate at 30%. (The Rancimat oxidative stability test was included in ASTM D 6751 by this time.) It was also noted that B100 produced from used vegetable oils failed the specifications more often than B100 produced from other feedstocks. Based upon certain assumptions regarding production volumes, it was concluded that 90% of B100 produced in the U.S. met all specifications; a significant improvement over previous survey results. However, a point not discussed by the authors is that all B100 samples in the 2007 survey were voluntarily provided by willing producers. In the earlier surveys, samples were obtained from blenders and distributors, not from producers. This change in procedure could raise questions about sampling bias.

The 2004 biodiesel quality survey conducted by NREL included B20 samples, while the 2006 and 2007 surveys did not. Results from the 2004 survey raised questions about quality control in blending operations, as 36% of the samples had biodiesel contents outside the acceptable range of B18-B22. More recent work by other organizations has also highlighted concerns about blending problems. One study involving analysis of B20 obtained from retail fueling stations in 2007 showed that of the 19 samples tested, 8 were actually <B17, with 4 being <B5.(206) This study also reinforced concerns about oxidative stability, as 45% of the samples failed to meet the Rancimat test specification.

In another recent report, a ^{14}C radiocarbon analysis method was developed and applied to U.S. biodiesel samples acquired in 2006.(207) This method does not measure FAME content directly, but determines the amount of modern carbon (from recently living biological materials) as opposed to fossil carbon. Of the 10 retail B20 samples tested, 6 were actually B10-B17 and 1 was B74.

Measurement of biodiesel blend concentrations has been an area of investigation for many years. Excellent reviews of analytical methods have been published recently.(208) Commonly used methods include chromatographic, spectroscopic, and wet chemical methods. However, many of these methods are expensive and time consuming. The new U.S. standard for B6-B20 blends (ASTM D 7467-08) specifies use of method D 7371, which utilizes mid-infrared spectroscopy.(195) Although not widely practiced, it appears possible to include an on-board fuel sensor for real-time determination of biodiesel content. It has been demonstrated that the same type of dielectric-based sensor used for gasoline/ethanol blends provides reasonably accurate measurements of biodiesel/diesel blends.(209)

6.2 Biodiesel Stability

Ensuring satisfactory stability of biodiesel in the market place is an important, but complex problem. No single test method is able to accurately assess the stability with respect to different degradation pathways. In broad terms, chemical reactivity of biodiesel can be described as involving oxidative and thermal processes. Both sets of processes are influenced by the degree of unsaturation, and the configuration of the double bonds, in the fatty acid chain component of FAME. In the field, unstable fuel can lead to increased viscosity, as well as formation of gums, sediment, and other deposits. Further insights into these degradation processes are provided in recent literature reviews on the topic.(210,211) (Having no unsaturated fatty acid chains, renewable diesel is not highly susceptible to these types of degradation.)

Oxidative instability is initiated by extraction of a hydrogen atom from a carbon adjacent to a double bond – the so-called allylic position.(212) Following removal of this hydrogen, rapid reaction with molecular oxygen leads to formation of allylic hydroperoxides. Subsequent reactions involving isomerization and radical chain propagation reactions produce numerous secondary oxidation products such as aldehydes, alcohols, and carboxylic acids. FAME molecules containing a carbon that is adjacent to two double bonds (a bis-allylic group) are particularly susceptible to this type of oxidative instability. It is for this reason that the European biodiesel standard (EN 14214) includes a separate specification for linolenic acid methyl ester.

The Rancimat oxidative stability test (EN 14112) is based upon detection of these volatile, secondary oxidation products that result from reaction of biodiesel with oxygen at elevated temperature. This test is considered a good indicator of a fuel’s oxidative stability, but is not necessarily a good indicator of long-term storage stability or thermal stability.(213) Thermal polymerization of biodiesel occurs through Diels-Alder reactions, which require the presence of two double bonds in a conjugated configuration. Isomerization of FAME to produce these conjugated structures occurs at much higher temperatures (250-300°C) than encountered in the Rancimat test procedure. Therefore, thermal polymerization is not generally regarded as a serious problem for biodiesel, except in cases where the fuel is repeatedly heated by the engine and recycled to the fuel tank.(211)

Several groups have investigated other laboratory oxidative tests to predict stability of biodiesel under different conditions. A European study utilized the Rancimat test apparatus, but applied numerous conditions of time, temperature, and oxygen levels to better estimate storage and thermal stability.(213) Somewhat mixed results were obtained, with no single set of test conditions being ideal. A similar approach using variations of Rancimat tests conditions was recently reported, and mathematical models were developed to predict oxidation stability as a function of temperature.(214) These oxidative tests provide a measure called “Oxidative Stability Index” (OSI; sometimes also called “Oil Stability Index”). The Rancimat test specified in the U.S. and European biodiesel standards (EN 14112) provides a particular measure of OSI.

A group at Southwest Research Institute (SwRI) explored numerous test methods for assessing biodiesel stability, and concluded that two were most useful: (1) Rancimat test method (EN 14112) and a modification of ASTM D 2274.(215) D 2274 is an accelerated storage stability test that is often used with conventional diesel, although it is not a requirement under the standard specifications for diesel fuel, D 975. This test involves heating the fuel at 95°C for 16 hours, while oxygen is bubbled through the sample. After this time, the fuel is cooled and filtered to determine the mass of insoluble oxidation products that have been produced. However, FAME is better able to solubilize these oxidation products, which in petroleum diesel would normally be insoluble. This behavior can lead to situations where a seemingly stable B100, when mixed with ULSD, can produce B20 having unacceptable levels of insolubles.(210,211)

More recently, a group from NREL and SwRI conducted a detailed experimental study on the stability of biodiesel and biodiesel blends.(216,217) Several samples of B5, B20, and B100 were studied under conditions meant to represent three real-world aging situations: (1) storage and handling, (2) fuel in a vehicle's tank, and (3) high temperature engine fuel systems. In part, this work was conducted to establish a technical foundation upon which to base specification requirements for biodiesel stability. Results showed that the best predictor of B5 and B20 stability is the inherent stability of the B100 used in making these blends. Using B100 that met the Rancimat test requirement (induction period of longer than 3-hours) was concluded to be an effective way of ensuring satisfactory storage stability of B5 and B20 for up to 1 year.

An extreme illustration of B100 instability was recently published by a group of Japanese researchers, who showed that the oxidative degradation reactions of FAME are highly exothermic.(218) They cautioned that under certain conditions, this could lead to a potential fire risk due to spontaneous ignition of unstable biodiesel.

6.2.1 Anti-Oxidants

Raw vegetable oils are known to contain varying levels of natural anti-oxidants such as tocopherols and carotenoids. These are high-boiling materials that remain unreacted during the transesterification process of producing FAME, but are removed upon distillation of the FAME. Many literature reports indicate that raw FAME has greater oxidative stability than refined (distilled) FAME. However, synthetic anti-oxidants have been found to be much more effective than these natural anti-oxidants.(211,213,219,220,221)

Effectiveness of anti-oxidants is generally determined using the Rancimat test. Identifying the optimum anti-oxidant formulation and dosage often requires extensive testing, as the results are quite variable from one fuel to another. It has also been noted that FAME produced from old or recycled vegetable oils is less stable than FAME produced from fresh oils.(220,222) It generally appears that the most effective anti-oxidants for biodiesel include t-butyl hydroquinone (TBHQ) and pyrogallol (1,2,3 tri-hydroxy benzene). Butylated hydroxy toluene (BHT) materials are also somewhat effective, but may not be the preferred additive for biodiesel as they often are for petroleum diesel fuels. Typical dosages of anti-oxidants used in biodiesel range from 200 to 1000 ppm, with little or no enhanced performance observed at higher concentrations.(211,223,221)

6.2.2 Other Approaches to Enhance Stability

Fundamentally, biodiesel instability is a consequence of its high degree of unsaturation, particularly poly-unsaturation. Attempts have been made to address this by chemical processes that reduce the degree of unsaturation. For example, deliberate oxidative treatments of biodiesel with hydrogen peroxide(224) and ozone(225) have been conducted with claims of improved stability and other properties. However, much more testing and evaluation is required before such practices could be accepted.

A different approach involves selective hydrogenation of poly-unsaturated FAME to produce mono-unsaturated FAME.(226) This partial hydrogenation is different from the processes used to produce renewable diesel, where total saturation of the double bonds generally occurs. While an attractive concept, partial hydrogenation is far from commercialization, as it has been applied only in the laboratory using very expensive catalysts.

Another means of reducing the unsaturation of FAME involves nitration by use of nitric acid.(227) In this case, the main goal is not to improve the oxidative stability of the FAME, but to produce nitrated materials that can be used as cetane improvers.

The goal of reducing the poly-unsaturated content of biodiesel is also driving biotechnology efforts to develop modified soybean plants which produce higher concentrations of oleic acid chains (18:1) at the expense of reduced linoleic acid (18:2) and linolenic acid (18:3) chains.(33,32)

6.3 Low Temperature Operability

For many users, low temperature operability is the greatest biodiesel concern, particularly during cold seasons of the year. Just as with conventional diesel fuel, precautions must be taken to ensure satisfactory low temperature operability of biodiesel and its blends.(228) Poor low temperature operability may be exhibited in several ways, but principally by filter plugging due to wax formation, and engine starving due to reduced fuel flow.

As with fuel stability, there is no single best test to assess low temperature operability. U.S. fuel standards do not include explicit specifications for low temperature operability – either for conventional diesel or biodiesel (or blends of the two). However, the fuel seller is generally required to give an indication of low temperature operability by reporting the cloud point (CP) of the fuel. A number of other laboratory tests are commonly used to define low temperature operability of biodiesel (and conventional diesel). These are listed below in Table XII.

Table XII. Commonly Used Low Temperature Operability Tests for Biodiesel

Test Name	Abbreviation	Test Method(s)
Cloud Point	CP	EN 23015, ASTM D 2500, ASTM D 5773
Pour Point	PP	ASTM D 97, ASTM D 5949
Cold Filter Plugging Point	CFPP	EN 116, IP 309, ASTM D 6371
Low Temp Filterability Test	LTFT	ASTM D 4539
Wax Appearance Point	WAP	ASTM D 3117

6.3.1 Factors Influencing Low Temperature Operability

An excellent review of cold weather properties and performance of biodiesel is available in the literature.(229) Poor operability results from the presence of long-chain paraffinic hydrocarbon groups, as are present in biodiesel. In general, the longer the carbon chain, the higher the melting point, and poorer the low temperature operability. The presence of carbon–carbon double bonds lowers the melting point of a molecule (hydrocarbon or fatty acid alkyl ester) significantly. Therefore, to a certain degree, there is a trade-off between fuel stability and low temperature operability. With increasing extent of unsaturation, stability decreases but low temperature operability improves.(230,231)

In large part, the fatty acid composition of the fats and oil precursors to biodiesel dictate the low temperature operability of the final fuels. Feedstocks with highly saturated fatty acid structures (such as palm oil and tallow) produce biodiesels with poor operability; whereas feedstocks with highly unsaturated fatty acid structures (such as rapeseed and safflower oil) have better operability.

The presence of a methyl ester head group lowers the melting point of its parent fatty acid by about 40°C. Thus, FAME has considerably better low temperature operability than do free fatty acids. Replacing methanol with ethanol to produce FAEE results in slightly improved operability, as the ethyl esters typically have melting points 5-10°C lower than the comparable methyl esters.(232,112,233,99,234)

Blending of B100 with conventional diesel often results in non-linear effects with respect to low temperature operability parameters.(235) Cloud Point (CP) is determined primarily by the presence of saturated fatty acid esters, which crystallize as the temperature is lowered. Unsaturated fatty acid esters serve to solubilize these waxy saturated materials, but when blended with conventional diesel, the solvency effectiveness may be reduced.

Of all the low temperature properties listed above in Table XII, only CP can be defined thermodynamically, as it is governed by solid-liquid equilibrium as a function of temperature. CP is the temperature at which the least soluble biodiesel component crystallizes from solution. Thus, CP is determined by the type and amount of saturated fatty acid esters, with other components of biodiesel having no effect. Several researchers have developed predictive models for CP, based upon these thermodynamic relationships.(236,237,232) In general, these models show good agreement with laboratory measurements. Also, because of the thermodynamically driven mechanism for crystallization, small amounts of impurities in biodiesel can significantly affect CP. In particular, it has been noted that low concentrations of unreacted monoglycerides and diglycerides increase CP, although PP is not affected.(229)

6.3.2 Approaches for Improving Low Temperature Operability

In his literature review, Dunn described 5 general approaches to improving the cold flow properties of biodiesel.(229) Each of these approaches (as well as others) is described below:

6.3.2.1 Blending with Petroleum Diesel

Diluting biodiesel with petroleum diesel is on effective means of improving low temperature operability. As B20 is the most commonly used form of biodiesel in the U.S., this type of addition is routinely conducted. However, during particularly cold seasons, further dilution may be desirable, thus producing a blend of <B20. Alternatively, blending with No. 1 diesel may be used rather than No. 2 diesel. While dilution with petroleum diesel improves all measures of cold flow, the effect is not linear with all properties. For example, it has been reported that CP and PP decrease nearly linearly with dilution, while CFPP and LTFT are only slightly affected.(229,238)

6.3.2.2 Use of Commercial Petroleum Diesel Additives

Cold flow improver (CFI) additives have been developed and applied to conventional diesel fuel for many years. These additives are synthetic polymers of various compositions. CFI additives interact with the wax crystals as they form in the fuel, and modify their size, shape, and degree of agglomeration. CFI additives are commonly referred to as pour point depressants, flow improvers, wax modifiers, and paraffin inhibitors. Determining the optimum CFI additive type and dosage for a particular fuel is something of an art, and requires extensive testing. Studies have shown that some CFI additives are very effective in reducing PP of biodiesel blends, but have little or no benefit with respect to CP or LTFT.(229,239,240,241)

6.3.2.3 Use of New CFI Additives for Biodiesel

Little information is available in the open literature about new CFI additives designed for use in biodiesel. There are reports of using glycerol in the synthesis of highly hindered glycerol ether derivatives, which improve cold flow properties, although only at high concentrations (>1%).(169)

Also reported in the literature is use of ozonized vegetable oil to improve low temperature operability of biodiesel.(242) Ozone reacts with the carbon-carbon double bonds in the oils to produce undefined products which, when added to biodiesel at about 1%, significantly reduced PP, although CP was not affected.

Another recent report describes the use of nickel and manganese based additives produced from resinic acids that are by-products in pulp manufacturing.(243) While somewhat effective in reducing PP, there are clear disadvantages to using metallic additives.

6.3.2.4 Use of Higher Alcohols for Transesterification

As already mentioned, using ethanol in place of methanol reduces CP of the fatty acid alkyl esters by 5-10°C, and improves overall low temperature operability. Even greater improvement results from use of isopropyl- or butyl-alcohol.(229,244) Apparently, these bulky head groups disrupt the molecular spacing, increasing disorder and weakening crystal structures. Although this approach is effective, it is usually not economically viable, as methanol is much cheaper to use than the higher alcohols.

6.3.2.5 Crystallization Fractionation

Crystallization fractionation is the separation of fatty acid derived materials on the basis of differences in crystallizing (or melting) temperature. Commercial processes for this have been developed in the animal fats and vegetable oils industries, where this practice is sometimes called “winterization.” Applying these processes to biodiesel on a large scale introduces significant engineering and economic challenges. Other adverse fuel quality impacts can result, as removal of the highest melting point components leaves a biodiesel that is enriched in unsaturated components, thereby decreasing cetane number and oxidative stability. In addition, a commercial outlet for the removed waxy fraction must be found. Nevertheless, crystallization fractionation remains an active area of research. A recent article reported improved efficiency in the process by using micro heat exchangers having very small chamber diameters of 0.2 mm.(245)

6.3.2.6 Other Methods

As previously mentioned, genetic engineering approaches are being pursued to develop seed oil compositions that are more favorable for both oxidative stability and for low temperature operability.(246,230,234) A different approach, still in the research stage, involves structural isomerization of FAME by reaction with solid acid catalysts.(247) While effective in reducing CP, this approach is unlikely to become economically viable in the near term.

6.4 Viscosity of Biodiesel

Viscosity is defined as a measure of resistance to flow of a liquid due to internal friction of one part of a fluid moving over another.(248) Dynamic viscosity (η) is the ratio of shear stress existing between layers of moving fluid and the rate of shear between the layers.(229) Kinematic viscosity (υ) is the resistance to flow of a liquid under gravity. Kinematic viscosity equals the dynamic viscosity of a fluid divided by its density (ρ); that is $\upsilon = \eta/\rho$.

The viscosity of biodiesel is typically higher than that of petroleum diesel – often by a factor of two. The viscosity of straight vegetable oil is much higher yet, and is the main reason why such oils are unacceptable as diesel blendstocks. Viscosity has significant effects on the injection quality of diesel fuels and fuel blends. In general, the higher the viscosity, the poorer the fuel atomization.(249) Higher viscosity has been shown to result in narrower injection spray angle, longer penetration length, and lower fuel vaporization in the combustion chamber.(250) Several investigators have shown that with its higher viscosity, biodiesel also produces larger mean droplet sizes upon injection.(251,252,253) In addition, due to higher viscosity, the delivered fuel volume (or rate of fuel injection) of biodiesel can be lower than with petroleum diesel.(254) Alternatively, a higher pressure is required with biodiesel to deliver the same volume of fuel as with petroleum diesel.(252)

Viscosity can vary among different biodiesel fuels by as much as 100%.(251) This may be one reason for the relatively large performance and emissions differences reported in the literature for biodiesel fuels. Also, viscosity is extremely sensitive to temperature, increasing nearly exponentially as temperature is reduced.(234) Thus, concerns about poor atomization with biodiesel are exacerbated at low temperature. One recent study has shown that as temperature is reduced, the distribution of B100 fuel among individual injectors within an injector assembly becomes very unequal.(255) This, in turn, could lead to engine performance and emissions problems.

Viscosity of biodiesel is affected by the compositional make-up of the fuel. In general, viscosity increases with carbon chain length and degree of saturation.(248,256) Carbon-carbon double bond conjugation also influences viscosity, with *cis* configuration giving a lower viscosity than *trans*. Position of the double bonds within the carbon chain, and chain branching, have little effect on viscosity. The alcohol used in transesterification to produce biodiesel also has an influence, as

FAEE has slightly higher viscosity than FAME. Empirical models have been developed to predict the viscosity of biodiesel fuels with reasonable success.(257,258)

Biodiesel users have very few options to improve the viscosity of the fuel. The only practical approach is to dilute with petroleum diesel (or renewable diesel). Low concentration blends of biodiesel (B20 and below) generally have acceptable viscosity, and do not cause significant field problems. The viscosity range specified for B6-B20 blends in ASTM D 7467 is identical to that of ULSD, at 1.9 - 4.1 mm^2/s. Adherence to this specification should ensure satisfactory biodiesel quality with respect to viscosity. Exceedance of this viscosity limit is an indication of fuel contamination with unreacted (or partially reacted) vegetable oils,(259) or a blending problem causing higher biodiesel contents than B20.

6.5 Lubricity

Lubricity can be defined as the ability to reduce friction between solid surfaces in relative motion.(193) In most applications, two mechanisms contribute to the overall lubricity: (1) hydrodynamic lubrication and (2) boundary lubrication. In hydrodynamic lubrication, a liquid layer (such as diesel fuel within a fuel injector) prevents contact between opposing surfaces. Boundary lubricants are compounds that adhere to the metallic surfaces, forming a thin, protective anti-wear layer. Boundary lubrication becomes important when the hydrodynamic lubricant has been squeezed out or otherwise removed from between the opposing surfaces.

Good lubricity in diesel fuel is critical to protect fuel injection systems. To provide better engine performance and lower emissions, modern injection systems have become more sophisticated than older systems. For example, not only do today's systems control injection timing, they also have capabilities for injection rate shaping, multiple injections per cycle, pilot injections, and other features. Today's common rail injection systems also operate at much higher pressure than in the past, reaching pressures as high as 200 MPa.(193)

In many cases, the fuel itself is the only lubricant within a fuel injector. With the increasing operational demands described above, maintaining adequate lubricity is more critical than ever to ensure satisfactory performance of fuel injection systems. However, as the need for improved lubricity has increased, the natural lubricity of diesel fuels has decreased. This was first noticed in the U.S. following introduction of low sulfur diesel fuel standards in 1993, which established a maximum sulfur limit of 500 ppm for on-road No. 2 diesel fuel.(260) (The previous maximum sulfur limit was 5000 ppm.) The refinery hydrotreating processes used to reduce sulfur levels were found to also reduce the fuel's lubricity.(261,262)

It was discovered that this reduction in lubricity was not due to sulfur removal itself, but to simultaneous removal of trace level lubricity-imparting materials during the hydrotreating processes.(263,264) Studies have shown that molecules containing hetero-atoms (O, N, and S) generally have improved lubricity compared to hydrocarbons, with oxygen-containing materials being especially effective.(265) Lubricity effectiveness decreases in the order of O>N>S>C. Within the class of oxygen-containing materials, carboxylic acids are more effective than alcohols, esters, and ethers.(118) In fact, low concentrations (10-50 ppm) of carboxylic acids are frequently added to petroleum diesel as lubricity improvers.(193)

With introduction of ULSD in 2006, having a maximum sulfur limit of 15 ppm, fuel lubricity has become a more critical issue. The extreme degree of hydrotreatment necessary to achieve these low sulfur concentrations effectively removes all other hetero-atom containing molecules, thereby producing a hydrocarbon fuel having very high purity, but low lubricity. Because of this, U.S. standards for No. 2 diesel fuel (ASTM D 975) were recently modified to include a lubricity specification for the first time. This specification is based upon ASTM Method D 6079, which determines lubricity using a High Frequency Reciprocating Rig (HFRR) test apparatus that involves moving a steel ball across a hardened plate immersed in the test fuel. To pass this specification test, the wear scar that appears on the steel ball must be no larger than 520 µm in diameter. An alternative lubricity test is ASTM D 6078, which uses a Scuffing Load Ball on Cylinder Lubricity Evaluator (SL-BOCLE, or simply BOCLE). In some instances, the BOCLE test may provide a better indication of in-use wear than the HFRR test.(263)

In the U.S., lubricity specifications apply to both conventional diesel and B6-B20 blends of biodiesel. B100 does not have a lubricity specification. In fact, the natural lubricity of neat B100 is so high that a 1-2% blend of it with ULSD is generally sufficient to meet the lubricity specification of D 975.(265) In part, biodiesel's good lubricity can be attributed to the ester group within the FAME molecules, but a higher degree of lubricity is due to trace impurities in the biodiesel. In particular, free fatty acids and monoglycerides are highly effective lubricants.(265,266) It has been noted that purification of biodiesel by means of distillation reduces its lubricity because these high-lubricity impurities are removed. The effect of unsaturation upon lubricity is unclear, with some researchers reporting positive effects of carbon-carbon double bonds(265) while others report no effect.(267)

6.6 Materials Compatibility and Wear

Due to its different physical and chemical properties, introducing biodiesel into systems designed for petroleum diesel raises questions about materials compatibility and other potentially adverse impacts on fuel or engine systems. Some of these issues are discussed below.

6.6.1 Materials Compatibility

The issue of materials compatibility pertains to the impacts of biodiesel upon seals, gaskets, hoses, metal surfaces, and other materials that the fuels contact. It is well known from laboratory studies and in-use experience that changes in fuel composition can affect the integrity of elastomeric materials. In particular, changes in swelling, shrinkage, embrittlement, and tensile strength are of concern, as extreme changes in these properties can lead to seal failures, leaks, and subsequent problems.

Materials compatibility issues are of greatest concern with use of B100, and are another reason why use of B100 is generally discouraged. With B20, these concerns are greatly reduced, but not eliminated. In 2005, the Coordinating Research Council (CRC) sponsored a thorough assessment of materials compatibility using low level blends of biodiesel (B5 and B20) produced from rapeseed methyl ester (RME) and soy methyl ester (SME).(268,269) To further stress these fuels, some of the SME blends were prepared using B100 that had been deliberately oxidized, using conditions more extreme than are likely to be encountered in the field. Several common fluorocarbon elastomeric materials were immersed in the fuel blends under prescribed conditions and then tested for changes in appearance and physical properties. Two of the five elastomers were reported as being most compatible with the test fuels, though the others may also be acceptable in most applications.

In a similar study,(270) researchers from NREL and SwRI investigated the compatibility of five elastomeric materials (in the form of o-rings) with three fuels: (1) baseline certification diesel fuel (having 346 ppm sulfur), (2) baseline fuel blended with 15% ethanol, and (3) baseline fuel blended with 20% soy-based biodiesel. No significant impacts of B20 upon elastomer deterioration were observed, and the authors concluded that all five elastomers appeared to be fully compatible with this fuel. However, the E15 blend did show noticeable deterioration, and may be expected to cause operational problems in certain field applications.

More recently, researchers from DuPont conducted an elastomeric compatibility study with various biodiesel fuels and blends.(271) While all the elastomers performed well with fresh, pure biodiesel, severe swelling occurred when the elastomers were exposed to fuels that were contaminated with water and/or free fatty acids. In field use applications, such conditions could be encountered, possibly leading to seal leakage or other operational problems. Both contaminated B20 and B100 fuels were found to be aggressive towards several conventionally-formulated elastomers. This work illustrates the need to formulate elastomeric materials that will be sufficiently durable even under worst case field conditions.

6.6.2 Wear Impacts

With its superior lubricity, it might be expected that use of biodiesel would result in lower wear of metal surfaces. The literature contains some information to support this expectation. In a 2003 paper, an Indian research group conducted long-term engine endurance testing (up to 512 hours) using engines fueled with conventional diesel and biodiesel blends, with rice bran methyl ester being used as biodiesel.(272) Periodic sampling and analysis of the lube oil revealed 30% lower concentrations of wear metals from the biodiesel blends. In the same study, a bench rig was used to investigate wear between two rubbing metal surfaces; e.g. a section of piston ring and a section of cylinder lining. Scanning electron microscopy (SEM) showed less surface damage when using B20 compared to conventional diesel fuel.

In a follow-up to this Indian study, more extensive tribological examinations were performed on the used lube oils drawn from engines running on conventional diesel and B20.(273) Overall, the condition of the lube oil from the B20 fueled engine was considered superior to that from conventional diesel, containing lower amounts of wear debris, soot, resinous compounds, and oxidative products. Due to fuel dilution, the viscosity of the lube oil decreased over time, though the extent of dilution was lower from the B20 case. However, there is evidence that while the extent of dilution is reduced with B20, the fuel that does enter the oil is more oxidatively unstable.(89) Others have suggested that dilution of lube oil with biodiesel can become a problem in some cases, and attribute this to the higher boiling range of biodiesel as compared to conventional diesel.(208)

More recently, this Indian research group investigated in-cylinder wear of medium-duty diesel engines fueled with conventional diesel and B20.(274) After 100 hours of operation, the engines were disassembled and inspected. Use of B20 resulted in less deposits on cylinder parts, and lower overall wear. Wear metals were again analyzed in the used oil, and were found to be reduced in the B20 case. However, Pb and Al contents were slightly higher in lube oils from B20, possibly due to attack by FAME on paints and bearings.

In the U.S., an extensive field test was conducted using U.S. Postal Service vehicles.(275) After four years of operation, engines and fuel systems were removed from eight vehicles: four 1993 Ford cargo vans and four 1996 Mack tractors. For each set of four, two had been running on B20 and two on conventional diesel. All eight systems were disassembled and carefully inspected for wear and other performance attributes. With the Ford cargo vans, no significant differences were observed between the diesel and B20 cases. However, noticeable differences were observed with the Mack tractors. In particular, cylinder heads from the B20 engines contained more sludge. Additionally, over their use, the B20 engines required injector nozzle replacement, whereas the conventional engines did not. The authors commented that both of these problems could have been due to use of B20 fuel that was out of spec.

In the previously mentioned CRC study, extensive bench testing and analysis was conducted to investigate the effects of B5 and B20 on the wear and performance of fuel injection systems.(268,269) A 500-hour injector wear test showed satisfactory performance of all fuels, except the highly oxidized B20 fuel that caused fuel filter plugging and terminated the test. Pump lubricity tests also indicated satisfactory performance with all fuels except the highly oxidized B20. Finally, a common rail test rig was built and used in a 500-hour test procedure to assess fuel performance under realistic conditions. No unusual wear was found on any of the common rail test pumps used in this study with any fuel. Overall, it a appears that except for the highly-oxidized B20 fuel, the biodiesel blends exhibited satisfactory lubricity performance in all tests.

A more recent report indicates that use of B100 in light-duty indirect injection engines can lead to injector fouling, resulting in flow reductions and power loss.(276) The extent of this problem with more advanced LD injection systems is not known, but this may be yet another reason to discourage use of biodiesel blends above B20.

6.7 Other In-Use Issues

A variety of other fuel issues are occasionally of interest with respect to in-use handling and performance of biodistillates. One example is surface tension, which can affect spray atomization, droplet size, and other functions of fuel injection.(277,250) Although the surface tension of biodiesel is somewhat higher than that of typical No. 2 diesel fuel, this does not seem to be an important determinant in causing noticeable performance effects. Much more important is fuel viscosity, which generally correlates with surface tension, and is responsible for numerous effects as described above.

Water solubility and water contamination are other issues of some concern. At room temperature, water is very slightly soluble in conventional diesel fuel (<100 ppm), but has significant solubility in B100 (up to 1200 ppm).(271) Water solubility in B20 is intermediate between these two extremes. The generally higher water levels in biodiesel can exacerbate problems with corrosion, wear, suspension of solids, and microbial growth. Due to these problems, U.S, Navy researchers have recommended that biodiesel not be used in water-compensating fuel tanks on-board marine vessels.(278)

When dealing with biodiesel, extra "housekeeping" precautions may be necessary to remove excess water and sediment. In particular, this is required when first introducing biodiesel into tanks previously used for conventional diesel, as accumulated water and sediment may become dispersed and plug filters under these conditions.(228)

Fuel economy of biodiesel is another in-use operational issue. As already mentioned, biodiesel typically has 10% lower mass energy content than No. 2 diesel fuel (expressed as BTU/lb, or kJ/kg). However, due to its somewhat higher fuel density, the fuel economy of biodiesel expressed on a volumetric basis (i.e., miles/gallon) is only lower than that of conventional diesel by a few percent. In actual use, B20 is unlikely to result in any noticeable decrease of volumetric fuel efficiency.

Another measure of fuel efficiency is brake specific fuel consumption, meaning the amount of fuel required for the engine to perform a given amount of work. This can be expressed as either mass or volume of fuel used per bhp-hr work performed. However, due to the above-mentioned differences in energy content between biodiesel and conventional diesel, these brake-specific fuel consumption metrics can also be confusing. Perhaps the best metric for comparison is energy-specific fuel consumption, meaning the energy of fuel required to perform a given amount of work (i.e., BTU of fuel/bhp-hr). On this basis, there is no difference between biodiesel and conventional diesel.(277,279,250)

A final in-use operational issue with biodiesel is its effect on injection timing. Fuel is injected into a diesel engine as a consequence of a pressure wave that propagates from the fuel pump (or common rail reservoir) to the injector nozzle. The speed of this propagation is influenced by a fuel property called the bulk modulus of elasticity, which is determined by the fuel density and the speed of sound through the fuel. (Bulk modulus is the product of fuel density and the square of the sound velocity.) Compared to conventional diesel, biodiesel has slightly higher density and sound velocity. Consequently, the pressure wave propagation is slightly faster in B100, resulting in injection timing that is advanced by 1-2°.(250) The consequences of this slight timing change on engine performance and emissions are unclear, with conflicting reports appearing in the literature. However, it is likely that with low concentration blends (B20 and below), any injection timing effects would be too small to be noticeable.

7. Exhaust Emissions Impacts

7.1 Background

Diesel vehicles are a significant source of both NO_x and PM emissions and, to a lesser extent, CO, HC, and other toxic species (e.g., carbonyls). Since NO_x is a precursor to ozone (O_3) formation, it is also a key variable in the development of control strategies to reduce this secondary pollutant; any increase in NO_x emissions could negatively impact ambient O_3 levels. Further, California regulations state that no fuel modification can result in an increase in regulated emissions. A potential increase in emissions could prohibit the introduction of biodistillate blends in that state. Hence, one of the key issues related to the use of biodistillates is their influence on exhaust emissions.

An earlier review of the impact of B20 on dynamometer-based emissions conducted by EPA(280) reported substantial decreases in HC, CO, and PM emissions, and a slight increase in NO_x emissions (see Table XIII and Fig. 23). These findings raised serious questions as to the potential impact on NO_x emissions following the introduction of biodistillate fuels. More recently, McCormick et al.(281) performed an analysis using updated data and concluded that, on average, there was no net increase in NO_x emissions using B20; although the results varied greatly depending upon individual engines (Table XIII). Both studies reported significant reductions in CO, HC, and PM emissions. The discrepancy in NO_x emissions results between these studies is a critical issue that needs to be resolved. Using the extensive literature review compiled as part of this study, we address here the range of reported biodistillate emissions results to develop a better understanding of the true impacts of these fuels.

Table XIII. Average Percent Change in Emissions from use of B20 in Dynamometer Tests

Pollutant	EPA (2002)	McCormick et al. (2006)
NO_x	+2.0	+0.6*
CO	-11.0	-17.1
HC	-21.1	-11.6
PM	-10.1	-16.4**

*Reported as statistically insignificant.
**Excludes engines equipped with DPF.

7.2 Methodology

All references compiled as part of this study were reviewed for emissions data, and the results of this task are contained in Appendix V. We identified ninety four references reporting a total of 346 distinct emissions test results for all engines [heavy-duty (HD), light-duty (LD), and single-cylinder test engines (TE)], blends (B20, B50, B100, etc.), biodistillate source, test cycles, control technology, operating conditions, and model year. With respect to the latter parameter, it should be noted that the year when the engine was manufactured was generally not reported. For this parameter, we chose to use the date of publication as a surrogate for the model year.

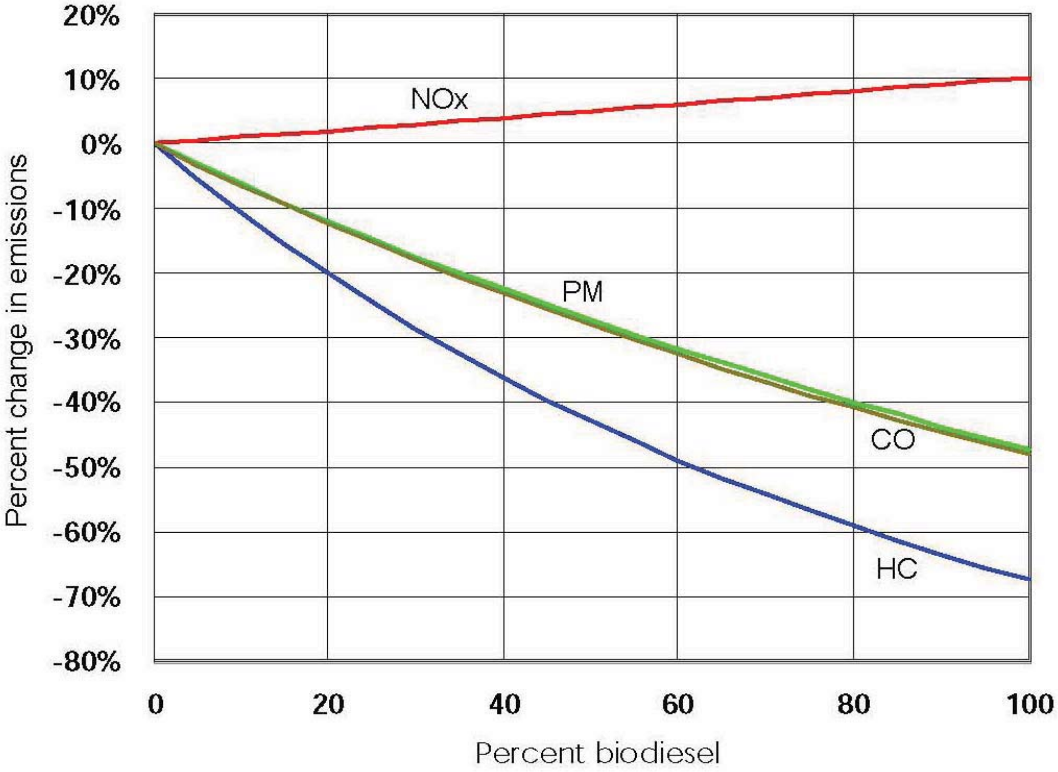


Figure 23. Average Emission Impacts of Biodiesel for HD Highway Engines (EPA, 2002)

In performing the analysis described in this section we chose to report the change in emissions using biodistillate vs. a reference diesel fuel (non-biodistillate fuel) rather than evaluating absolute emission rates. By taking this approach, we were able to clearly identify the impact of specific biodistillate blends on emissions. If a publication did not list a reference diesel fuel for comparison, the results were not used to evaluate a percent change in emissions; however, all emissions data, with corresponding units are shown in Appendix V. Outliers were also omitted from the analysis based on a simple two tier selection:

- In studies reporting a single biodistillate and reference fuel result, did the emissions difference between the two vary by more than 250%?
- In studies reporting several biodistillate and reference fuel results, did the average emissions difference vary by more than 150%?

If either of these criteria were met, the results were considered to be an outlier, and were not included in further analysis.

To assess the change in emissions with respect to the blend fraction of biodistillate, the data were segregated based on engine type (HD, LD, and TE) and the percent change in emissions for NO_x, HC, CO, and PM from the referenced diesel fuel with respect to the biodistillate blend. Due to the large variability in emissions, a series of graphs was developed as follows:

1. A data point is shown for the average of each reported test in an individual study at a given biodistillate level. This assessment is designed to show the variability in the reported emissions tests.

2. A data point is shown for the average of all tests from all studies at a given biodistillate level, with error bars representing the minimum and maximum percent change. This simplifies the previous representation by collapsing the test results to a single point for each blend level.
3. Using the average dataset, a third graph was developed showing only a logarithmic trend line based on the average emissions result at each biodistillate level. This representation is similar to what was used in the 2002 EPA document, and is a simple way of showing the trend in each emission species as the biodistillate percentage increases.

Given that the most commonly tested blends were B20 and B100, we focused our evaluation of the change in emissions by model year (year of publication) on these two blends. As before, a graphical analysis was employed. We plotted the percent change in emissions from the reference diesel fuel based on the reference publication year. Each data point represented an average reported emission level. Included in the analysis are the results for all engines, operating conditions, and biodistillate types. The data were sorted by engine size, emission control, and test procedure. It should be noted that there was no differentiation between biodistillate type (i.e. soybean, rapeseed, algae, etc.) and operating conditions.

7.3 Impact of Blend Level on Criteria Emissions

To evaluate the impact of biodistillate blend level on criteria emissions, a total of nine graphical analyses were generated as follows:

- Three engine classes: HD, LD, TE, with each chart containing data for NO_x, CO, HC, and PM.
- Three representations of the emissions data:
  - Individual test results vs. blend level.
  - Average of all test results at a given blend level vs. blend level.
  - A logarithmic fit of the average of all test results at a given blend level vs. blend level.

This approach was designed to clearly show the wide range of results, while providing an increasing level of clarity by which the observations could be interpreted. While the results have been segregated by engine class, within each engine class the reported observations are for all biodistillate sources, test cycles, control technologies, operating conditions, and model years.

The three representations for HD, LD, and TE are presented in Figures 24, 25, and 26, respectively. Each graph displays the percent change from a referenced diesel fuel with respect to biodistillate percentage. The top panel in each figure contains a data point for the average of each individual test result (i.e., studies generally reported a range of emission rates for a given engine and fuel) at a given biodistillate level and is color coded by pollutant (NO_x, CO, PM and HC). To display the full range of observations, the y-axis spans a percent change of +/- 100%. A linear trend line for each of the species is included, which provides an assessment of the overall change in emissions with increasing levels of biodistillate. The middle panel collapses the data from the top panel by displaying the average of all test results at a given blend level vs.

blend level. Error bars represent the minimum and maximum percent change from a reference diesel fuel for all test results within at a specific biodistillate blend level. Again, they are color coded based on the four pollutants and a linear trendline is displayed for each of the species. The bottom panel in each figure uses the same dataset as the middle panel, but displays a logarithmic trend line based on the average of all emissions for a given biodistillate level. This is the simplest way of showing the trend in emissions for each pollutant as a function of biodistillate level. Note that for this case, the range in the y-axis is from +20% to -40%.

For all three approaches, trendlines were not fit through zero (i.e., 0 % change for 0 % biodistillate) so the magnitude of the trendline at the lowest biodistillate levels should be treated with caution. This is especially true for the logarithmic result, where both the magnitude and direction of the trendline is primarily determined by the lowest % biodistillate data point.

Using the information presented in Figures 24-26, we can draw a number of conclusions regarding the potential impact of biodistillate blend levels on emissions, with the caveat that the approach does not allow for the assessment of the impact of specific biodistillate sources, test cycles, control technologies, operating conditions, and model years. A further limitation of this approach is that by not evaluating specific biodistillate sources, a linkage between biodistillate fuel properties and emissions could not be determined. Given these limitations, we can draw the following conclusions:

- Heavy-duty engines:
  - NO_x emissions are elevated for all B levels and increase slightly with increasing % B.
  - CO, HC, and PM are decreased for all B levels and decrease further with increasing % B.
  - There is a greater impact of % B on HC and PM than on NO_x and CO.
- Light-duty engines:
  - NO_x emissions are elevated for all B levels and increases slightly with increasing % B.
  - The magnitude of the NO_x increase is greater than for the HD case.
  - CO, HC, and PM are decreased for all B levels and there is less of an impact of % B on emissions than for the HD engines.
  - There is a greater impact on HC and PM than on NO_x and CO.
  - The downward trend in the logarithmic PM curve for the lowest biodistillate levels is an artifact and is driven by the lowest reported data values.
- Test engines:
  - The emissions from all species are decreased for all biodistillate blend levels.
  - NO_x emissions increase slightly with increasing % B.
  - CO and HC emissions are relatively flat and do not appear to be influenced by % B.
  - PM emissions decrease with increasing % B.

Overall, the HD and LD results are fairly similar in that they both exhibit elevated NO_x emissions and reduced CO, HC, and PM emissions, with the magnitude of the effect on CO emissions being less than that on HC and PM emissions. For the TE case, the tighter range in the change in emissions and decrease in NO_x emissions for all B levels could be a function of fewer data points (HD had the greatest number of tests), greater control over engine operating parameters, and greater reliance on steady-state emissions tests (i.e., fewer transients).

To compare the results of this analysis with the findings of other studies, we can use the regression equations derived from the logarithmic trendlines to predict the % change in emissions of a given pollutant for a specified % B. The regression equations determined from the logarithmic fits in Figures 24-26 are presented in Table XIV.

Table XIV. Regression Equations Derived from the Logarithmic Fits Presented in Figs. 24-26 where x is the % biodistillate and y is the predicted change in emissions

Pollutant	**HD**	**LD**	**TE**
NO_x	y=0.9632*LN(x)+0.0216	y=2.8031*LN(x)+2.4126	y=3.9711*LN(x)-20.017
CO	y=-2.8267*LN(x)-7.7784	y=-1.3709*LN(x)-5.9866	y=-1.768*LN(x)-8.0626
HC	y=-11.953*LN(x)+17.775	y=-3.9273*LN(x)-4.8293	y=-0.552*LN(x)-13.722
PM	y=-13.069*LN(x)+23.367	y=1.8053*LN(x)-41.424	y=-8.6181*LN(x)+12.93

Since the greatest number of test results were obtained using B20 and B100, one outcome of this analysis would be an estimate of the impact of these blend levels on emissions. Using the equations provided in Table XIV, we can predict a change in emissions for a given blend level. The results for both B20 and B100 are presented below in Tables XV.

Table XV. Predicted Changes in Emissions using B20 and B100 based on the regression equations listed in Table XIV

	Pollutant	**HD**	**LD**	**TE**
B20	NO_x	+2.9	+10.8	-8.1
	CO	-15.7	-10.1	-13.4
	HC	-18.0	-16.6	-15.4
	PM	-15.8	-36.0	-12.9
B100	NO_x	+4.5	+15.3	-1.7
	CO	-20.8	-12.3	-16.2
	HC	-37.3	-22.9	-16.3
	PM	-36.8	-33.1	-26.8

For the HD and LD cases, going from B20 to B100 increases the change in emissions for all pollutants except LD PM, with major decreases in CO, HC, and PM emissions for both blends. Slight increases in NO_x emissions are predicted for B20 and B100. For the TE case, emissions of all species are reduced when using B20 and B100 relative to a reference diesel fuel.

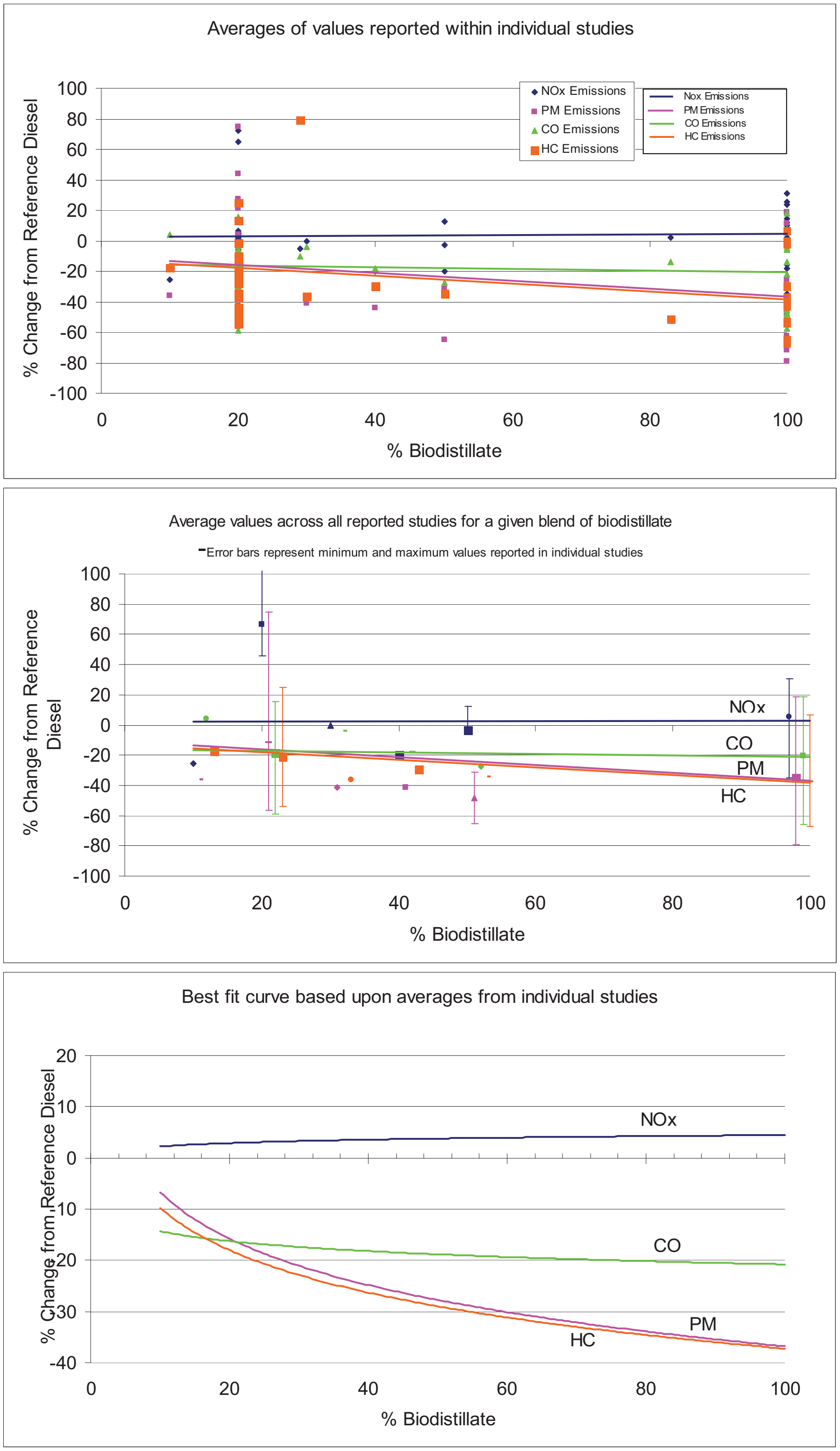


Figure 24. Effects of Biodistillate Blends on Exhaust Emissions from HD Engines

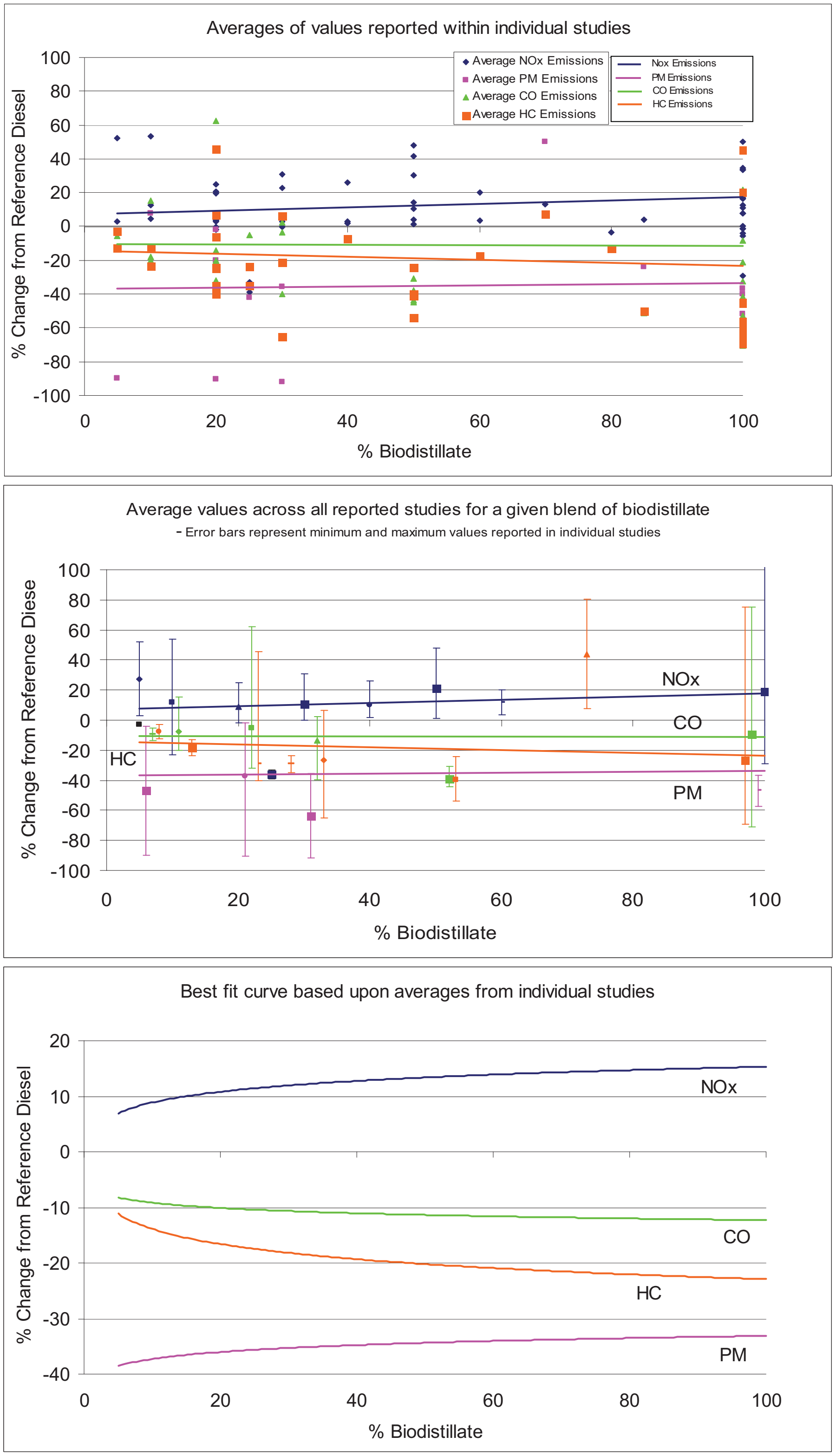


Figure 25. Effects of Biodistillate Blends on Exhaust Emissions from LD Engines

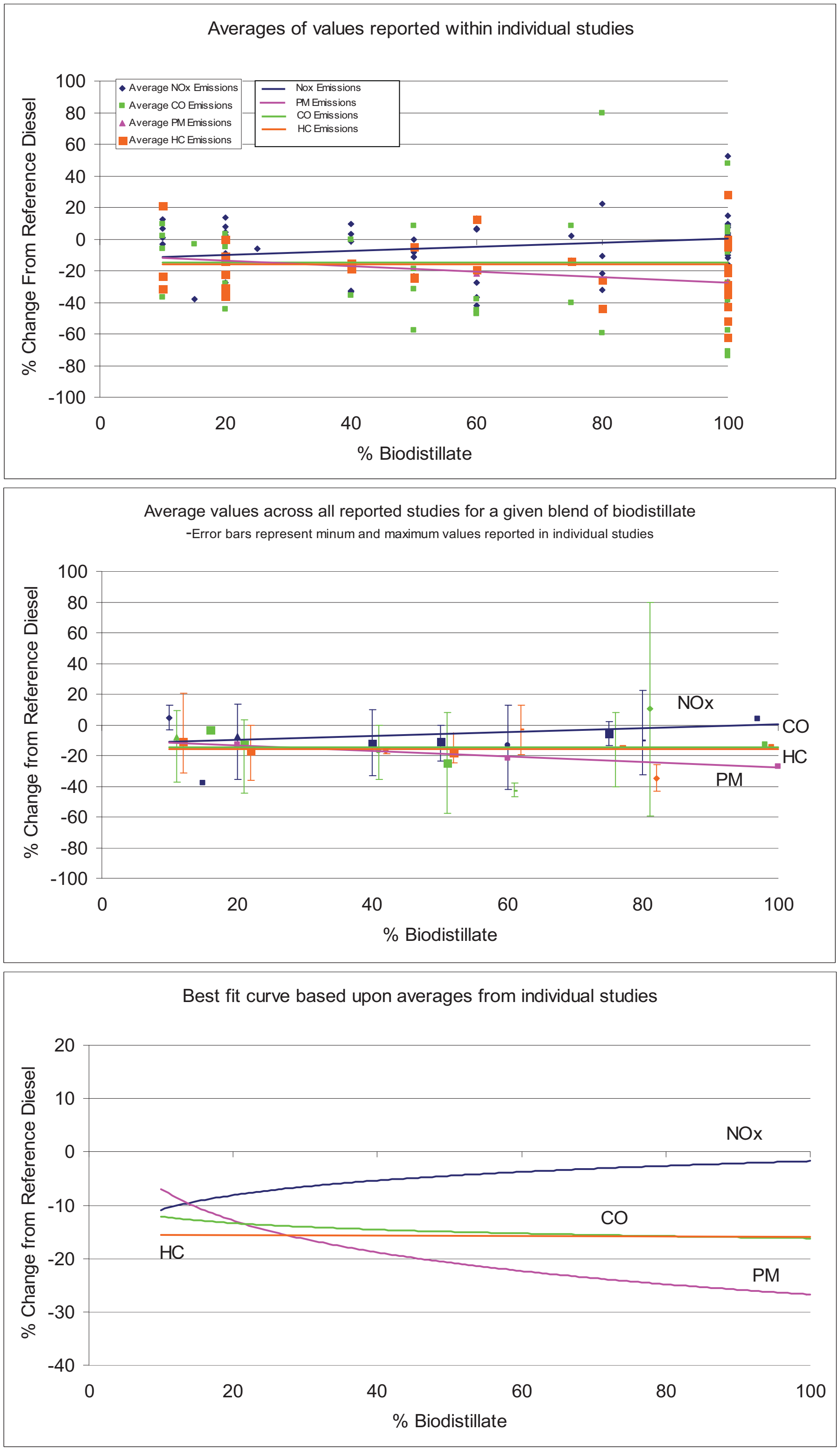


Figure 26. Effects of Biodistillate Blends on Exhaust Emissions from TE

As a check on the analyses reported in this section, we can compare our results against those of EPA (2000) and McCormick et al. (2006) listed in Table XIII. The B20 emissions findings from those studies and this study are summarized in Table XVI. The predictions for all species are comparable, with the primary difference being an increase in NO_x emissions predicted in this and the EPA (280) studies, and no change predicted by McCormick et al. (281) Based on these findings, we can conclude that the use of biodistillate blends could have a positive impact on diesel CO, HC, and PM emissions, while slightly increasing NO_x emissions.

Table XVI. Comparison of Average Change in Emissions from HD Dyamometer Tests using B20

Pollutant	EPA, 2002	McCormick et al., 2006	This Study
NO_x	+2.0	+0.6*	+2.9
CO	-11.0	-17.1	-15.7
HC	-21.1	-11.6	-18.0
PM	-10.1	-16.4**	-15.8

*Reported as statistically insignificant.
**Excludes engines equipped with DPF.

We can also compare the HD results for all blend levels reported in this study with the EPA (2002) findings shown in Fig. 23. Overlaying the data from Fig. 24 (bottom panel) with those of Fig. 23 yields the chart shown in Fig. 27. The solid lines represent the findings from this work, while the dashed lines present the EPA (2002) findings. It is important to remember these data represent a compendium of engines and control technologies, model years, biodistillate sources, and test cycles, with the EPA (2002) observations reflecting an older set of experiments and engines. Given this caveat, the findings are similar, with NO_x emissions increasing and CO, HC, and PM emissions decreasing for all blend levels. Although, the percent change in emissions for all pollutants relative to a base diesel fuel is lower for this study than in the previous report. One possible explanation for this discrepancy is emissions from the newer engines (and more advanced control technologies) compiled as part of this study are lower overall, leading to a reduced impact from the introduction of biodistillate blends.

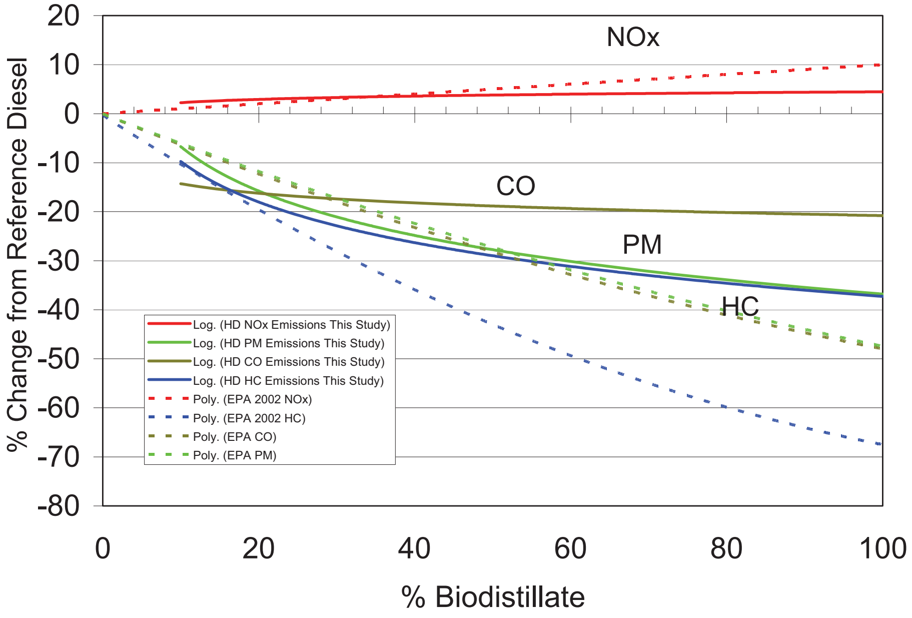


Figure 27. Comparison of the HD Engine Results from this Study with EPA (2002)(280)

7.4 Influence of Model Year on Emissions

One possible influence on emissions and the change in emissions following the introduction of biodistillate fuels is the model year of the test engine, and as a consequence, the engine technology. Newer engines, with improved emissions control systems and lower overall exhaust emissions could affect the observed impacts of biodistillates. Using the emissions data contained in Appendix V and the year of publication as a surrogate for model year (and as a consequence technology), we used a similar graphical analysis technique as previously described to evaluate potential emissions trends with model year.

Two graphs for each pollutant were created; one was for B20, while the second was for B100. Each emissions test was represented by a data point for the average change in emissions presented in the reference. Error bars represent the minimum and maximum reported values in the reference. The data were further sorted by engine size (HD, LD or TE), emission control (yes/no = dotted/solid error bars), and testing procedure (engine or chassis dynamometer test). This approach allows for observing the variability in the reported data with the caveat that there is no differentiation between biodistillate type (i.e. soybean, rapeseed, algae, etc.), test cycle, and operating conditions.

The graphs of % change in emissions at fixed biodistillate levels (B20 and B100) for a given year of publication (surrogate for model year/technology) are shown in Figs. 28-31. Given the limited results for each year, coupled with large error bars associated with most data points, it is difficult to draw quantitative conclusions. However, qualitatively it appears that the % change in all emissions (for both B20 and B100) is largely unchanged with model year/technology. The only case where there may be a discernable trend is a decrease in PM when using B100 in newer vehicles.

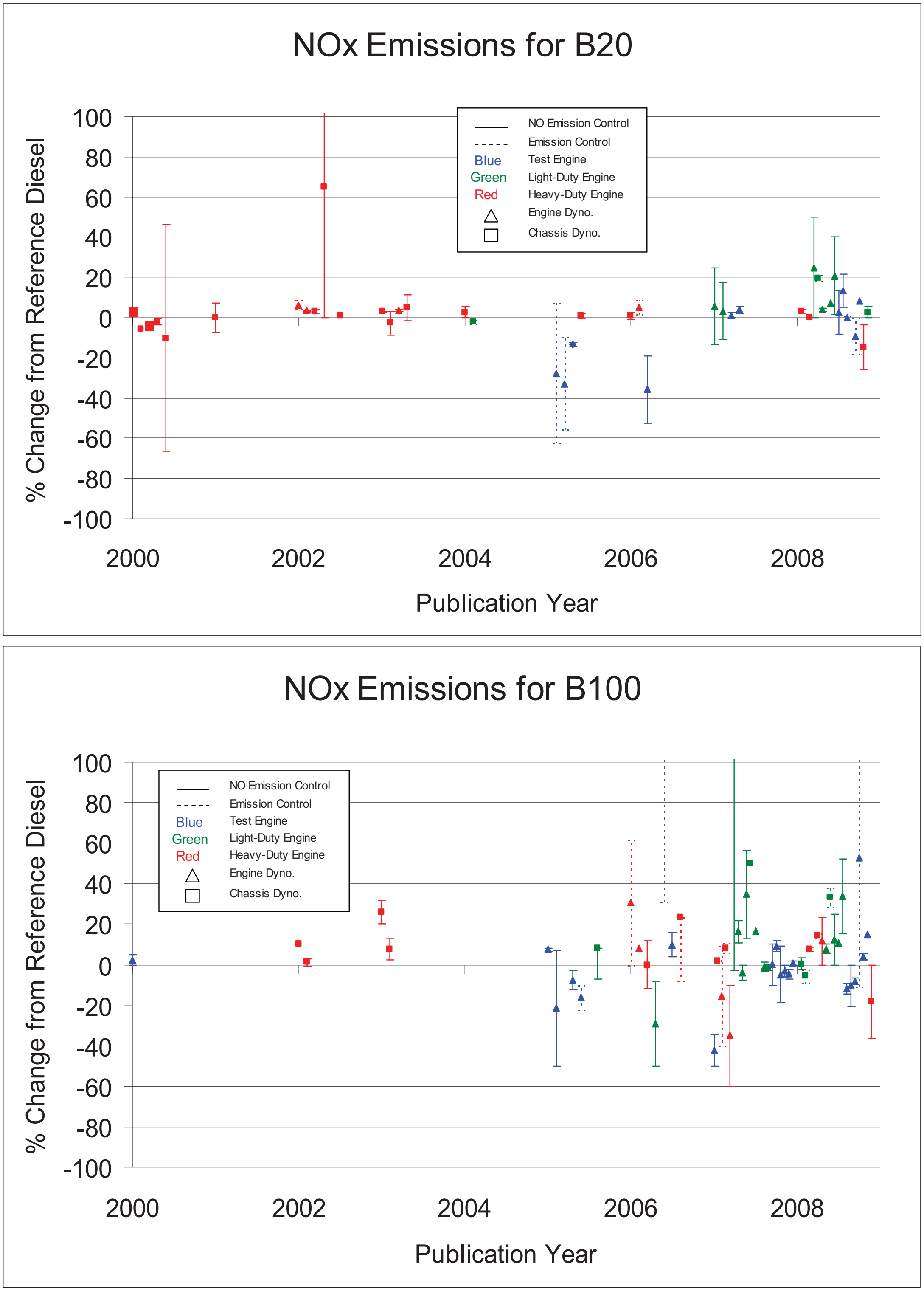
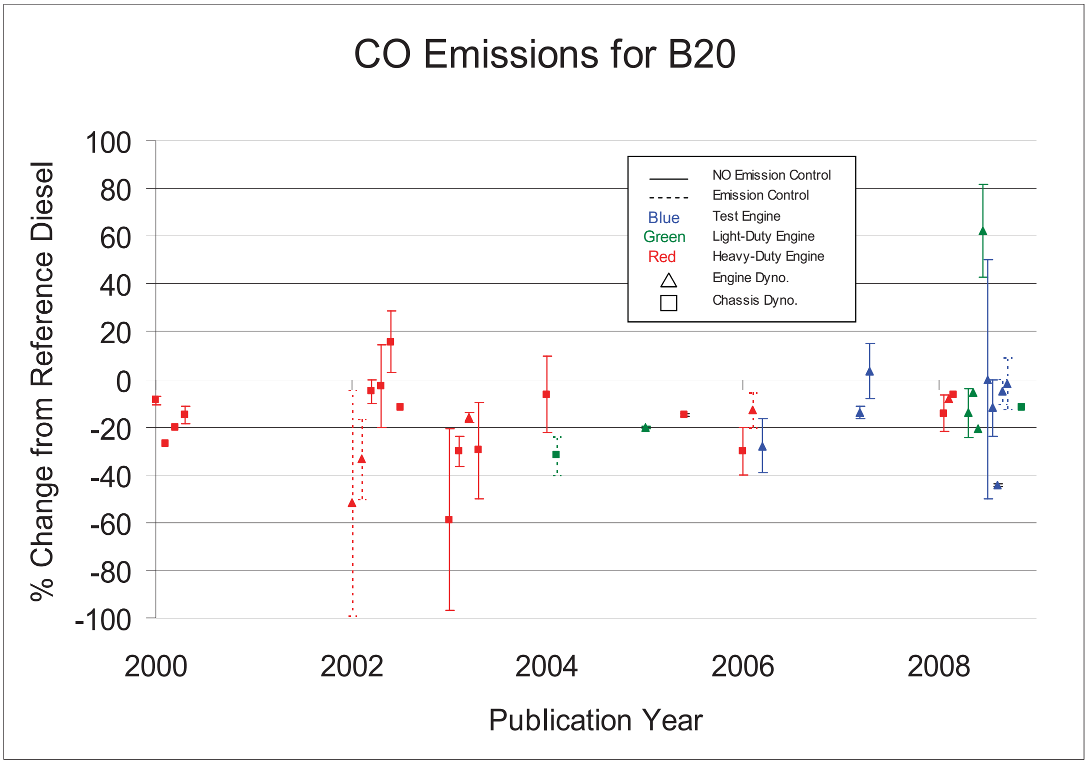


Figure 28. NO_x Emssions for Biodistillate Fuels Compared to Reference Diesel Fuel



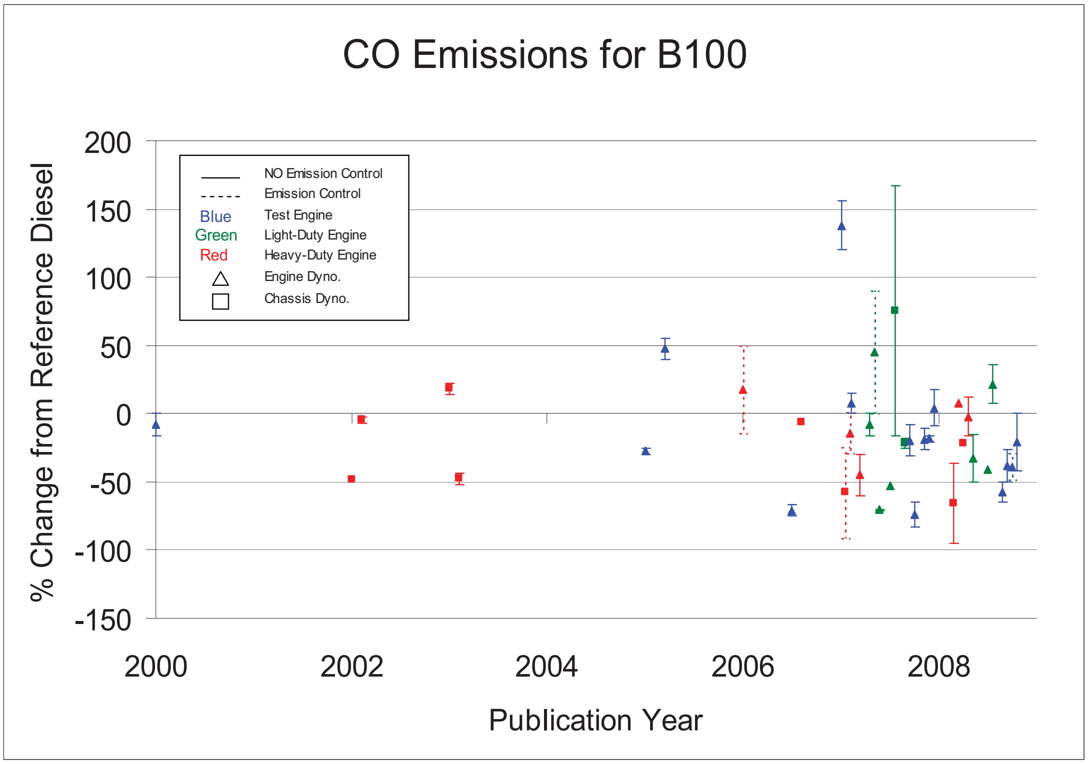


Figure 29. CO Emissions for Biodistillate Fuels Compared to Reference Diesel Fuel

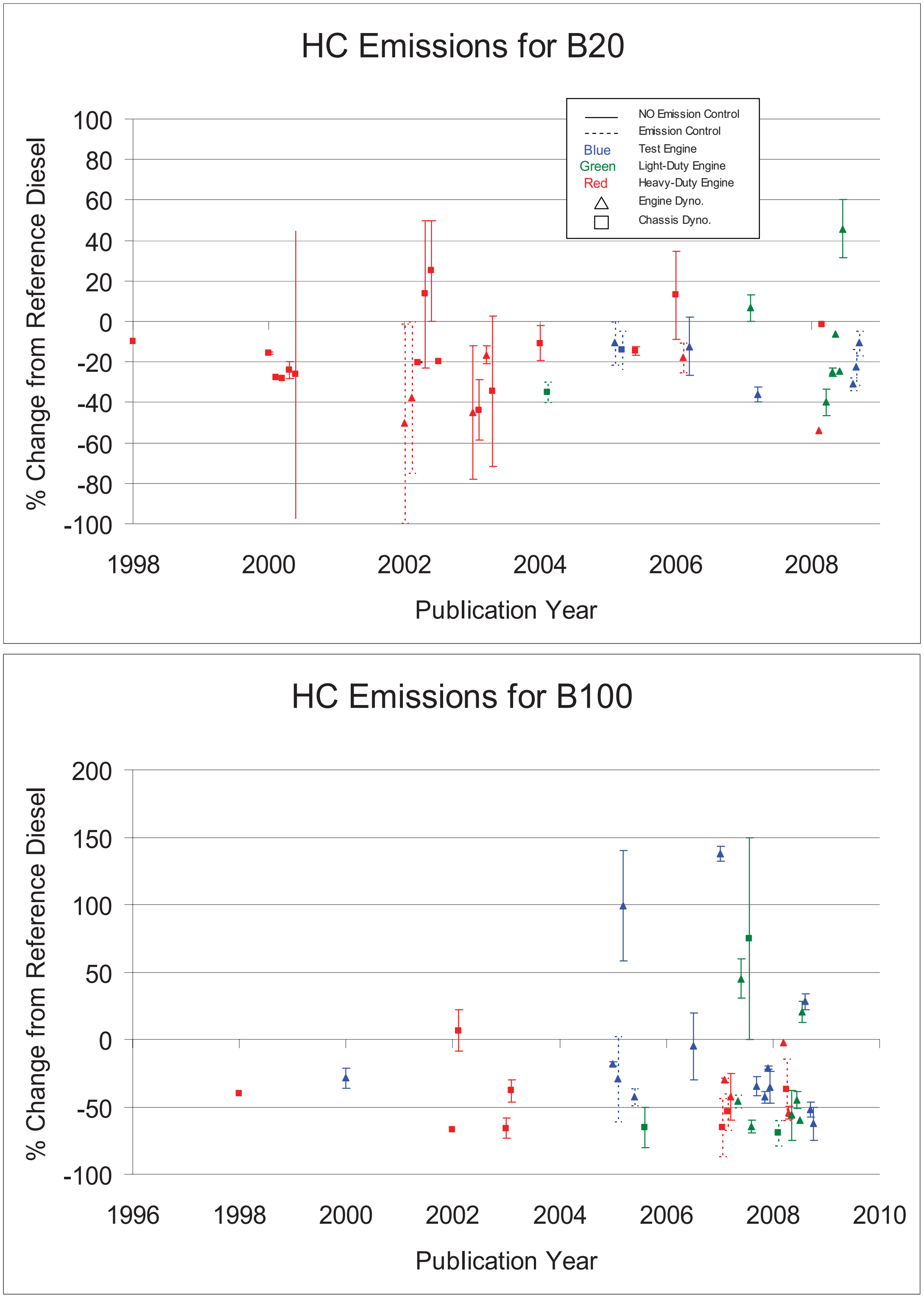
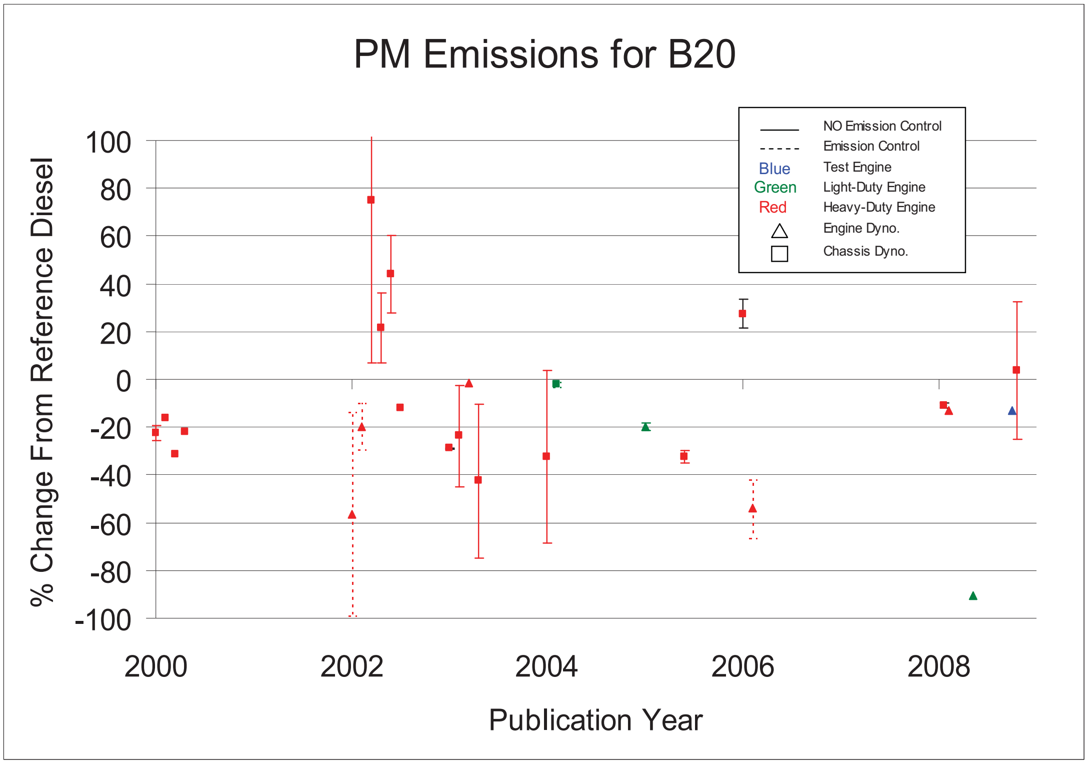


Figure 30. HC Emissions for Biodistillate Fuels Compared to Reference Diesel Fuel



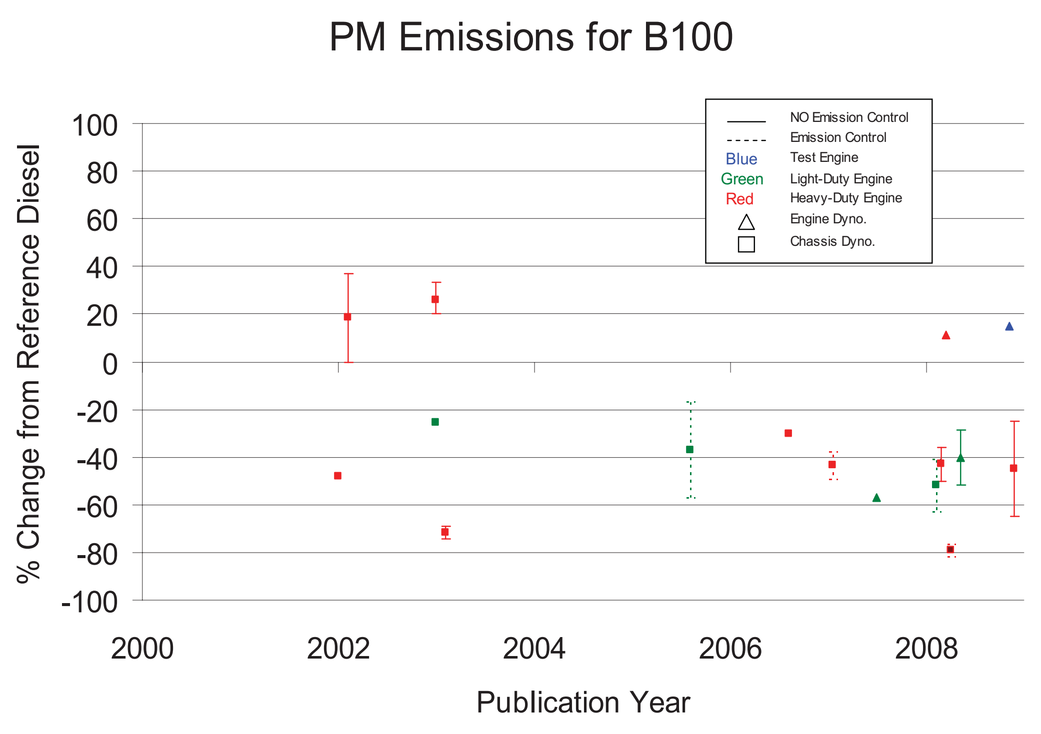


Figure 31. PM Emissions for Biodistillate Fuels Compared to Reference Diesel Fuel

7.5 Impact of Blend Level on Carbonyl Emissions

One of the other questions associated with the use of biodistillate blends is the potential impact on emissions of toxic species. To address this issue, we reviewed the database for emissions data beyond the criteria species of NO_x, CO, HC, and PM. The findings were limited, with most of the observations being for carbonyls. A total of seven papers contained information on the change in emissions compared against a reference diesel fuel. While some of the papers contained results for speciated carbonyls, a number only reported total carbonyl emissions. These results for the major species (formaldehyde and acetaldehyde) and total carbonyls are contained in Appendix V-2 and presented graphically in Figure 32. The previously described methodology to evaluate emissions was applied in this case. Due to the limited number of data points, Figure 32 contains the results for both HD and LD engines, along with a logarithmic fit to the complete data set. Overall, the results imply there is a decrease in emissions with increasing blend level; although a number of studies reported increasing emissions for B20. This conclusion runs is somewhat surprising since biodiesel, which consists of oxygenated species (FAME), might be expected to increase aldehyde emissions.

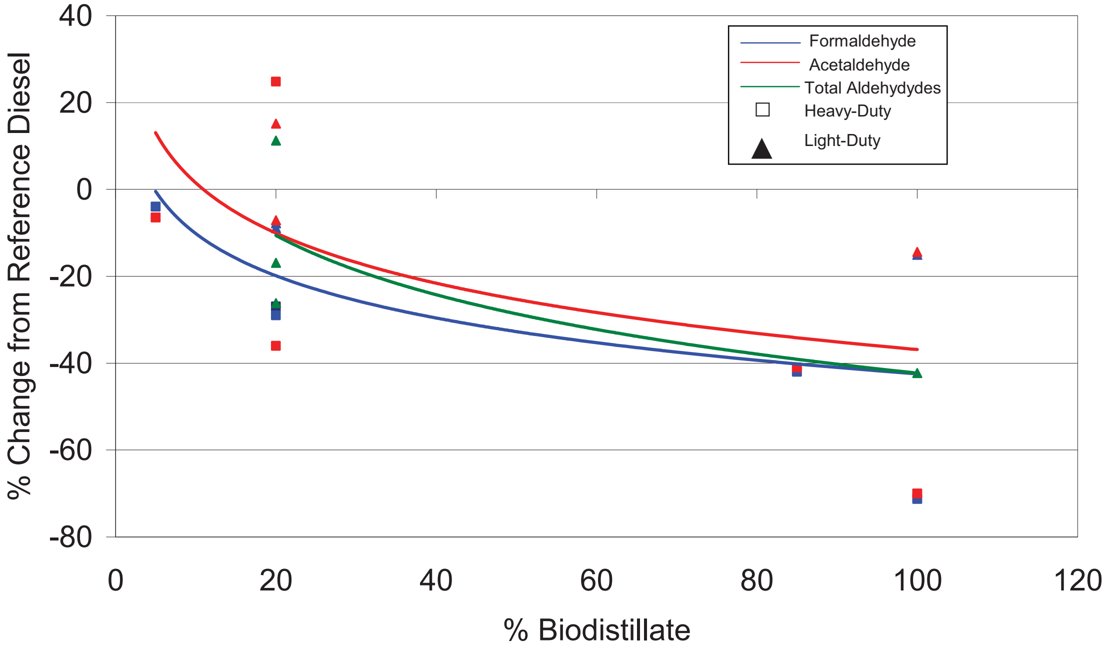


Figure 32. Effects of Biodistillate Blends on Carbonyl Exhaust Emissions
(Both HD and LD engines)

7.6 Emissions Reduction via Oxygenate Blending

To address potential NOx emissions problems resulting from use of biodiesel, many researchers and organizations have investigated approaches involving the blending of additional oxygenated components. Use of fuel/water emulsions is one such approach. In one of the earliest reports, straight vegetable oils were emulsified with 5-10% water and the combustion performance was examined in the laboratory.(282) Evidence of "explosive combustion" of the oil-water emulsion droplets was obtained, and simultaneous reduction of NOx and PM emissions was demonstrated.

More recently, academic researchers from Taiwan reported on emulsification of soy-derived biodiesel with water.(283,284) Various emulsion formulations were investigated, including 2-phase water/oil (W/O) and 3-phase oil/water/oil (O/W/O) blends, having total water concentrations of about 10%. It is noteworthy that the viscosity of these emulsions was considerably higher than that of neat biodiesel – by almost a factor of two. Emissions results using an engine dynamometer test stand showed small, but significant reductions in NOx with all the emulsion blends. The greatest NOx reduction was obtained using an emulsion that included aqueous ammonia.

In another recent study, researchers from Oak Ridge National Laboratory tested a soy-derived biodiesel and a 10% water emulsion in a 4-cylinder light-duty diesel engine.(285) This work showed that the NOx increase in using B100 compared to ULSD could be completely offset by use of the biodiesel/water emulsion. The emulsion fuel also reduced PM emissions significantly when EGR was used, but not without use of EGR.

Fuel blends of ethanol with biodiesel have also been explored. This could be especially relevant to biodiesel composed of FAEE, where excess ethanol remains in the product mixture.(286) However, addition of ethanol has a critical effect upon the fuel's vapor pressure, with very low ethanol concentrations resulting in dramatic increases in vapor pressure, along with a significant increase in flash point. Thus, ethanol blends (with both conventional diesel and biodiesel) introduce safety concerns regarding handling of the blends.

Blends of conventional diesel fuel with ethanol are sometimes referred to as "diesohol." Besides the problems of vapor pressure and flash point mentioned above, diesohol blends are often unstable with respect to phase separation, particularly when contaminated with low concentrations of water.(287) It has been reported that including biodiesel as an additional blending component improves the stability of diesohol. In one case, a blend of 80% diesel, 15% biodiesel, and 5% water was reported to give optimum performance, though no NOx emissions reductions were observed with this blend.(288)

This same approach of using biodiesel to stabilize diesohol may be employed with the commercial product called O_2Diesel™. This material is reported to consist mainly of conventional diesel fuel, with 7.7% ethanol and a small amount of proprietary "fatty acid-based stabilizer additive."(289) O_2Diesel™ has been shown to reduce NOx slightly (about 2%) and PM more substantially (about 20%) compared to conventional diesel fuel. However, due to the flammability concerns resulting from its high vapor pressure and flash point, special precautions are required for storing and using O_2Diesel™. In particular, its use is limited to centrally-fueled fleets, where both the vehicles' fuel tanks and the refueling storage tanks are equipped with flame arrestors.

Various other oxygenates have been blended with biodiesel in an effort to improve emissions. For example, Japanese researchers have investigated blends of dimethyl ether (DME) in biodiesel produced from palm oil and used cooking oil.(290) Benefits reported include reduced viscosity and pour point of the fuels, slight NOx reductions, and substantial reductions in smoke levels. Nothing was stated about the flash point of DME/biodiesel blends, but this surely would be a matter of concern if used commercially. Similar benefits have been reported for blends of diethyl ether (DEE) with biodiesel.(291)

In a very recent report, blends of conventional diesel and biodiesel were emulsified with a "biosolution" consisting of 96.5% organic enzyme and 3.5% water.(292) Emissions of PM and PAH were reduced when using these emulsion fuels, but NOx emissions were not measured.

8. Life-Cycle Analysis and Land Use Impacts

In comparing energy and environmental impacts of different fuels, it is increasingly recognized that the entire life-cycle of the fuel must be considered. In fact, life-cycle models have become a common aid for policy regarding the use of alternative fuels. (4,13,18,293,294) Life-cycle assessments (LCA) provide a tool to evaluate the "cradle-to-grave" energy and environmental impacts that result from all stages of a product's life, from manufacturing through disposal. These environmental impacts can include energy use, emissions produced, water consumption, eutrophication and acidification potential, and other factors. According to an EPA report,(295) there are three steps involved in conducting an LCA to assess these energy and environmental impacts:

1. Compiling an inventory of relevant inputs and outputs of a process stream
2. Evaluating the potential impacts associated with the inputs and outputs
3. Interpreting the results to make informed decisions

A full-fuel LCA starts with raw material extraction and ends with fuel consumption.(296) For a biofuel, this includes all inputs and requirements for feedstock growth, harvesting, fuel production, distribution and combustion as well as intermediate transportation steps. Fig. 33 shows a typical pathway for biodiesel production from soybeans.

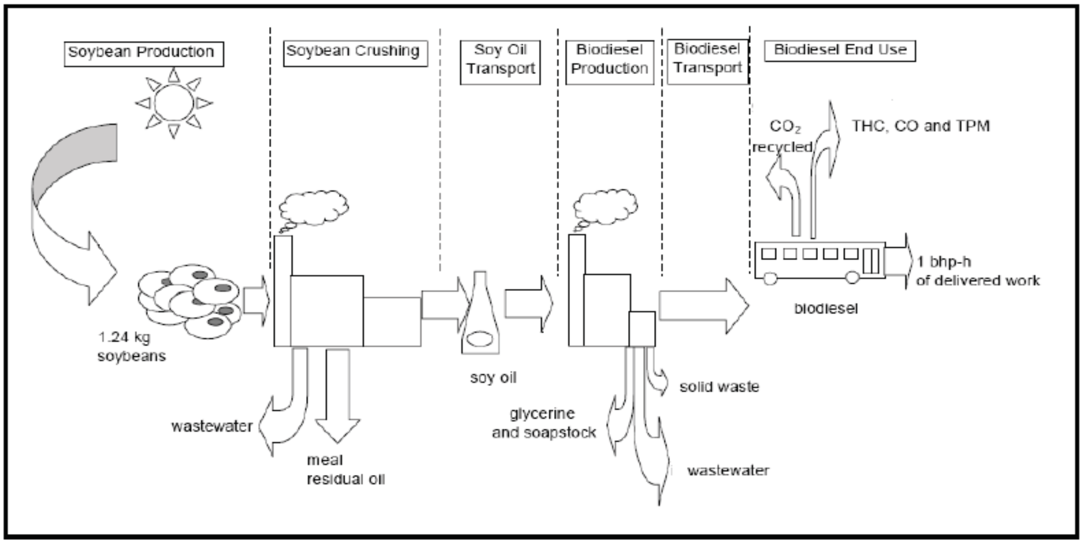


Figure 33. Biodiesel from Soybean Pathway.
Taken from Reference(297)

The pathway of a bio-fuel is data-intensive, requiring specific inputs for fertilizer use, harvest yields, electricity mixes, processing efficiencies, and many other factors. Due to these intensive data requirements, clearly defined boundaries are crucial for calculating robust results. Data used is often specific for a particular feedstock or process and may be regionally specific, although some databases use averages for a larger region.(297,298,299,300,301) Because of variations in pathway boundaries and assumptions among studies, LCA results are best used for comparison of energy use and emissions relative to conventional petroleum fuels and other products within the study itself, and not for direct comparisons among different studies.(297)

LCA are frequently used to assess the relative attractiveness of various transportation fuels, and are becoming a common aid in determining the most desirable options for sustainable fuel and energy processes. Numerous LCAs have been conducted for ethanol fuels; by comparison, the LCA literature on biodiesels is scant. A literature review we undertook for biodiesel-specific LCA studies considered approximately publications. These studies are discussed below in further detail, with emphasis given to results for energy and GHG emissions.

8.1 Fuel LCA Overview

Full-fuel LCAs in general take into account all energy flows and emissions associated with production of the final energy source in its consumable form. These steps can be broken into two parts: well-to-tank (WTT) and tank-to-wheels (TTW). The combination of the two parts represents the complete well-to wheels (WTW), or cradle-to-grave, life-cycle for a transportation fuel.

The WTT pathway for a biodistillate fuel commonly includes growth of the crop which may involve land-use change (LUC) and farming inputs like fertilizers, harvesting of the crop, processing or crushing to extract the oil, production (via transesterification or some other method), and distribution to the fuel-pump. This also includes any intermediate transportation steps. The TTW analysis includes combustion of the fuel in a vehicle, and depends on the type of vehicle, its efficiencies and type of driving. However, common practice for biofuels is to assume a carbon-neutral principle in which the amount of CO_2 emitted by a bio-fuel during combustion is the same as that absorbed by the plant during its growth through photosynthesis.(30) In this case, the WTT results for GHG emissions are similar to the complete WTW results.

8.1.1 LCA Modeling Tools

The complete WTW pathway of a biofuel is extremely data-intensive. However, there are numerous existing LCA modeling tools and other databases that can be used, many of which are available in the public domain. Existing models usually include a specific pathway with a given set of default assumptions that may or may not be changed by the user. Several private companies have also developed their own LCA models to aid in their decision making. ST&T2 Consultants recently performed a review of existing LCA tools, and found approximately 37 models.(297) Of those 37, the ten listed in Table XVII are applicable for biofuels. However, pathways for biodiesel are quite limited in these models, as described below.

The GREET model is one of the most comprehensive LCA tools available in the public domain, and includes over 100 fuel production pathways and more than 70 vehicle/fuel systems. The GREET model is used as an aid for policy decisions in the US. Similarly, GHGenius is used for Canadian policy. Many of these publicly available models include default assumptions for energy mixes and transportation distances that minimize differences between models. However, the default assumptions can be adjusted with more site-specific details for individual analysis.

Table XVII. LCA Tools for Transportation Fuels
Taken from References(297,302)

Model	Biodiesel Pathways	Region	Publicly Available	Notes
BEES	None	US and EU data	Yes	Adapted for bio-based products
BESS	None	US	Yes	Specific for corn-to-ethanol
EBAMM	None	US data	Yes	Excel model uses data from 9 difference studies and outcomes from each dataset
EIO-LCA	None	US and EU data	Yes	
GaBi	None	EU (Germany)	Yes - $$	Can model ethanol
GEMIS	From forest residue	EU data	Yes	Limited pathways.
GHGenius	From soybeans, canola, palm, tallow, yellow grease and marine oils.	US and Canadian Data	Yes	200 pathways. Used in Canadian policy decision making.
GREET	Soybeans	US Data	Yes	100 pathways, used in US policy.
LEM	Soybeans	US data	No	Basis of GHGenius.
SimaPro	None	EU and US data.	Yes - $$	Has biodiesel processes, but no pathways.

This list of models is not exhaustive; it does not include many LCA models that do not have biodiesel pathways. Additionally, many companies conduct LCA independently of these modeling tools. Several databases also exist in the public domain to support fuel LCAs. Some agencies, including NREL and EcoInvent, have made their databases publicly available.(298,299)

8.1.2 Variations in Modeling

Although established databases and modeling tools exist, differences in LCA modeling approaches are still common. Two models can be run with the same types of assumptions and produce different results.(303) However, standards have been implemented to maintain consistency in data. ISO 14044:2006 provides requirements and guidelines, and ISO 14048:2002 outlines standards for data documentation and format within the model.(304,305) However, the standards do not specify methodologies that should be used, so results of different assessments can be highly varied. Therefore, fuel LCA models are typically used to determine the relative benefits of different scenarios in which conventional petroleum fuels are displaced with alternative fuels.

Differences in methodologies arise from variations in defining fuel pathways, scenario boundaries, input assumptions, and dealing with co-products. Most LCA data inputs are specific to the process, fuel type, or region that is being evaluated. For example, crop yields can vary dramatically based upon type of crop or growing location; also, energy use for a 2nd Generation production process may not be well established and must be estimated from scant data. Generally, LCA inputs and assumptions represent reported industry-wide averages.(306,301,307)

However, some data may come from literature rather than process technology, especially in cases of new technology.

The quality of input data clearly affects LCA results for biofuels. As defined by Wang,(308) some of the key issues (several of which are discussed below) include the following:

- land use changes
- nitrogen fertilizer for plant growth
- conversion factor of nitrogen fertilizer to N_2O
- crop yields
- other farming energy or chemical requirements
- energy use in biofuel processing plants -- including the type and amount of process fuel
- credits given to co-products
- scale of production

8.1.2.1 Land-Use Change

The growth of crops to support a bio-fuel industry would require some existing crop lands to be converted to bio-fuel crops, as well as conversion of other arable lands to crop-land. This topic of land use change (LUC) and the way that it is considered (or not considered) in LCA modeling has drawn considerable attention, partly due to recent publications by Searchinger et al. (309) Fargione et al.(310) and Crutzen et al.(311) Both direct and indirect LUC may have significant impacts on the overall life-cycle of a fuel. Direct impacts are those that are associated directly with the cultivation of feedstocks used to produce a biofuel in the region where it is used. Indirect effects are those that could potentially arise when a crop is produced in one region of the world in response to fuel demand in another region.

Most LCA models include some type of direct LUC assessment to address changes in GHG emissions resulting from modifications to soil carbon, or variations in above ground biomass from preparation of existing crop-lands or conversion to new crop-land.(297) Methods of including direct LUC are somewhat controversial, specifically with respect to biologically-produced N_2O emissions.(311) The IPCC consensus is that N_2O has a global warming potential (GWP) 296 times that of CO_2, so small changes in N_2O can result in significant differences in GWP.(312) Therefore, it is crucial to account for all N inputs and outputs from cultivation of land to grow biomass -- including crop residues, fertilizer, N fixation, manure, deposition, gaseous losses, crop output, runoff, N transfer between co-rotated crops, and others. It is also important to know how these factors change over time.(313)

The IPCC recommends use of an N_2O conversion factor for LCA modeling to estimate the amount of N_2O emitted per gram of Nitrogen fertilizer input. This factor has a significant impact on the overall GHG emissions during the agricultural stage of biodiesel's life-cycle, but its value is very controversial. Many models use the IPCC-recommended factor of 1.325% or something similar. The GREET model uses the IPCC value(308) and the GHGenius model uses a factor of 1.125%.(297) Using these relatively low conversion factors generally results in favorable life-cycle GHG emissions for biodiesel relative to conventional diesel. However, Crutzen et al.(311) concluded that the IPCC emissions factor for N_2O was seriously underestimated, and recommended a conversion value equivalent to an IPCC factor of 2.24-3.74.(308) This change results in biodiesel having increased life-cycle GHG emissions relative to conventional diesel. Delucchi's LEM model, which includes a more complete Nitrogen balance than other models, shows a 50% increase in life-cycle GHG emissions for biodiesel relative to petroleum diesel, largely because of N_2O impacts.(314,313,315)

Indirect LUC has been a topic of recent publicity and concern as having potentially serious adverse GHG impacts. Searchinger's paper discusses the principal that as crops are diverted to fuels in one geographic location, increased crop production will be required elsewhere to compensate. This increased production could occur through displacement of existing crops, expansion of croplands, or intensification of existing production -- though economic equilibrium only occurs for expansion or intensification.(303) Expansion of croplands may require reducing forest lands or other fallow lands elsewhere, which could result in an extremely large release of CO_2 previously sequestered by roots and soil. Intensification of production may require more fertilizer usage. Both could have a net-negative GHG effect on the biofuel.

Many LCA models do not include the effects of indirect LUC because they are much more difficult to analyze and require subjective assumptions that contain substantial uncertainty. However, policy is trending toward including indirect LUC into already required LCA models.(316) To do this, some type of economic model is required to estimate the economic supply and demand of developing new crop lands. Possible models to accomplish this include GTAP (Global Trade Analysis Project from Purdue University), FASOM (Forest and Agricultural Sector Optimization Model from Texas A&M University), and FAPRI (Food and Agricultural Policy Research Institute at Iowa State University).(316)

8.1.2.2 Method of Dealing with Co-products

Several by-products are also produced during the manufacturing of biodiesel; for example, animal feed meal is produced during the oil extraction process, and glycerin is produced during transesterification. Other co-products such as naphtha or propane may be produced in 2nd Generation biodiesel manufacturing involving hydroprocessing. (174) Common practice in LCA modeling is to allocate some of the energy and emissions produced during the fuel life-cycle to these co-products since they can replace other similar products in the market. Several different methods of allocation are commonly used. (317,318,319) These are described below in more detail.

- ***Physical Allocation***—Environmental impacts are allocated to each by-product and the biofuel based upon a common physical parameter such as mass (kg) or energy (MJ). A drawback of this method is that it does not consider the environmental impacts that have been offset by replacing other products.

- ***Economic Allocation***—Calculations are performed on the basis of the economic value of the biofuel and other valuable by-products. The economic allocation method has similar drawbacks to the physical allocation method in that it does not consider changes to environmental impacts from replacement of other materials.

- ***Expanded Allocation*—**By-products are assumed to replace existing products. The environmental impacts from the replaced product are subtracted from the emissions and energy needed to produce the biodiesel. Changes in assumptions, however, can have significant effects on the results. Additionally, the expanded allocation method does not make corrections for changes in scale. This could be a problem for large-scale production, for example, once the glycerin market becomes saturated.

- ***No Co-Product Allocation*—**All energy and emissions incurred in the lifecycle are attributed to the final biofuel product. While perhaps the easiest approach to use, failing to allocate any energy or environmental impacts to co-products is clearly an over-simplification of reality.

The choice of allocation method may significantly affect the final results of the LCA. Several studies included in the literature review examined the effects that different allocation methods have on the results. Bernesson, et al. studied the effects of all four allocation methods listed above, as well as a range of production plant sizes. (317) They found that differences in plant size were almost negligible in some cases, but the allocation method had significant impacts, reducing GWP by a factor of 2 to 3 compared to no allocation, and possibly resulting in the process becoming a net-supplier of energy for the expanded allocation method. A quick scan of LCA methodology by Guinee and Heijungs found that different allocation methods could result in up to a 250-fold difference in extreme cases. (319) Numerous other studies included cases for one allocation method compared to no allocation, which generally produced large differences in LCA results.

The allocation of by-products is also controversial; the choice of methods is not clearly defined, but has a large effect on the LCA results. For example, many studies give glycerin a by-product credit; however, in some regions, the glycerin market is already saturated from the soap making industry, which is not expected to change as biofuel production is increased. In the EU, a 5% replacement of diesel fuel with biodiesel would result in 1.5 MMT of additional glycerin. (301) Since the market is already saturated, it would not be able to accommodate this extra product. To legitimately allocate energy or emissions to the by-product, another market must be identified. Definition and boundaries of allocation methods need to be more clearly defined to make meaningful comparisons between different LCA studies.

8.2 Biodiesel LCA Literature Review and Results

A literature review of LCA studies of biodiesel pathways was conducted. The review considered 39 published papers and reports covering a broad range of feedstocks and methods of production. Some studies compared biodiesel to conventional diesel while others looked at only a single fuel, but investigated differences in assumptions, processes, or life-cycle scenarios. The most common feedstocks were rapeseed (in many EU studies) and soybeans (in many U.S. studies). Most studies considered biodiesel production via transesterification with methanol, though a few also investigated renewable biodiesel produced via hydroprocessing. Each paper is identified and briefly summarized in Appendix VI-1 and VI-2.

To compare the differences in the results among these 39 studies, the environmental impacts are shown both on an absolute basis and relative to the reference fuel used. Both the energy and CO_2 equivalent emissions are discussed further.

8.2.1 Energy

The life-cycle energy use required to produce and/or use a unit of fuel is one of the impacts most frequently assessed in an LCA. The overall energy benefit or energy return (ER) of the entire process is determined by dividing the energy out of the process (the heating value of the fuel) by the total life-cycle energy inputs. A net energy benefit results when the ER is greater than one; an ER less than one indicates more energy is required to produce the fuel than is contained in the final product. [This value of ER is sometimes called Energy Return on Investment (EROI).] Common practice in biofuel LCA is to report only the required fossil energy inputs in the EROI, but not any renewable energy inputs, such as the energy content of the plant itself. This typically results in an ER greater than one for biodistillates. In contrast, the energy requirements to make conventional diesel are almost entirely fossil energy, (including the energy content of petroleum itself) which typically results in a life-cycle ER of less than one.

Of the 38 studies included in the literature review, 18 reported an ER value -- or something equivalent that could easily be converted to ER. Fig. 34 shows the ranges of ER results from each. A single point in the figure depicts a study in which a single result was reported; vertical bars represent the minimum and maximum of a range of values reported. In some cases, the range represents the high and low values for a single scenario; in other cases, the range encompasses values for numerous scenarios in a particular study. The numbering refers to the study numbers provided in Appendix VI-1 for each reference, which provides a more detailed summary of results for each paper.

Note that the x-axis in Fig. 34 (and subsequent figures) is a time line, representing the year in which the study was published. Additional spacing along the x-axis was used to avoid overlapping of data points – see for example the three results shown for Study No. 5 in the year 2003. Also note that different symbol shapes and colors are used to distinguish biodiesel life-cycle cases from renewable diesel cases and different colors represent different feedstocks.

Several studies compared the biodiesel ER to a reference fuel (typically conventional diesel), which is shown in Fig. 34 as solid black circles. (In a few cases, the reference fuel was some other alternative fuel such as ethanol, which is not shown here). The shaded horizontal band in Fig. 34 represents a selected range of ER for petroleum diesel. Some results were excluded from the designated range because of reporting differences or unrealistic values(320). For most cases, the life-cycle ER for petroleum diesel was below one, indicating an additional benefit for any fuel that resulted in an energy return greater than one.

Figure 34 clearly illustrates the variability in results among different studies, whether for traditional methods of production (biodiesel via transesterification) or 2nd Generation methods (renewable diesel via hydroprocessing or gasification). Although the results are quite diverse, generally a net energy benefit (ER>1) for biodiesel is shown. The mean value reported is 3.1, and all but five cases fall below an ER value of 4. Of the four studies reporting larger values, one of them is for a 2nd Generation fuel type: Study No. 22 is for hydroprocessing soybean oil using the UOP Ecofining process.(174) Study No. 39 (321) is also for the UOP Ecofining process, but only when tallow is used as a feedstock is the ER greater than 4. The differences between these two studies will be discussed in more detail in the next section on critical references. Study No. 26 is the only LCA reported for Jatropha.(322) The range is extremely large due to a wide range of sensitivity analyses for both best case and worst cases. Study No. 20 reports a high and low value for transesterification of rapeseed based on allocation of co-products or no allocation for specific use on an organic farm.(323) The assumptions used in this paper are specific to the farm and its proximity to a production plant, which results in the higher estimates. Study No. 9 has been identified as a critical study and will be discussed in more detail in the next section.(296)

Many of the studies were completed within the EU, and make comparisons between rapeseed and sunflower oil as a feedstock. However, even these results are not consistent. Studies numbered 5, 14, 16, and 36 (Venturi,(324) Cocco,(325) Edwards,(301) and Prieur,(326) respectively) all compared rapeseed and sunflower within specific regions in the EU. Study Nos. 5 and 14 were both within Italy, No. 36 was for French conditions, and No. 16 was a broad study for average EU 25 conditions. Although the three studies for specific countries showed rapeseed to have a slight advantage over sunflower, the average EU conditions showed the opposite. Similar inconsistencies are reported throughout the literature. The following critical studies will be discussed in more detail to help identify the origin of the differences.

8.2.1.1 Critical LCA Studies for Energy

Some of the 38 studies we evaluated were identified as critical based on the frequency of citation in other studies, the quality of the assumptions, the number of scenarios studied, and the robustness of the results. A brief description of the energy results of each of these critical studies is given below.

Study No. 1 was reported by NREL in 1998.(307) This is a frequently cited study, and is considered one of the most authoritative references for biodiesel LCAs in the U.S. It compares the environmental impacts of biodiesel with those of petroleum diesel, and includes a comprehensive assessment of each, as well as a detailed sensitivity analysis of the inputs. The ER range shown in Fig. 34 represents a single high and single low value, where the high value (3.2) includes only the fossil energy inputs to produce biodiesel, and the low value includes all energy inputs. A net energy benefit results when considering only the fossil energy inputs. (ER for biodiesel is most frequently reported for fossil energy inputs only.) The fossil ER of 3.2 is frequently cited and is used as a reference value for comparison in numerous studies. The ER calculated for petroleum production was less than 1, resulting in nearly a four-fold energy benefit for biodiesel compared to petroleum diesel. This study also included a detailed emissions analysis (for CO_2) and comparison between petroleum and biodiesel use in an urban bus. (The LCA results for CO_2 emissions will be discussed in the next section.)

Study No. 5 (Venturi(324)) compared biodiesel production from rapeseed, soybeans and sunflower seeds in Italy, with a range of crop yields, based on differing regional productivity and compares co-product allocation by energy versus none. The ER falls below one for each feedstock when no co-product allocation method is used. However, even when co-product allocation is used, sunflower and soybean both result in an energy dis-benefit for low crop yields. Rapeseed is the only favorable energy return for all crop yield ranges when some of the energy use is allocated to the co-products, due to higher yields in the growing climate in the study. The results of the study are compared to ethanol produced from both lignocellulosic and traditional feedstocks, and no reference value for petroleum diesel is reported.

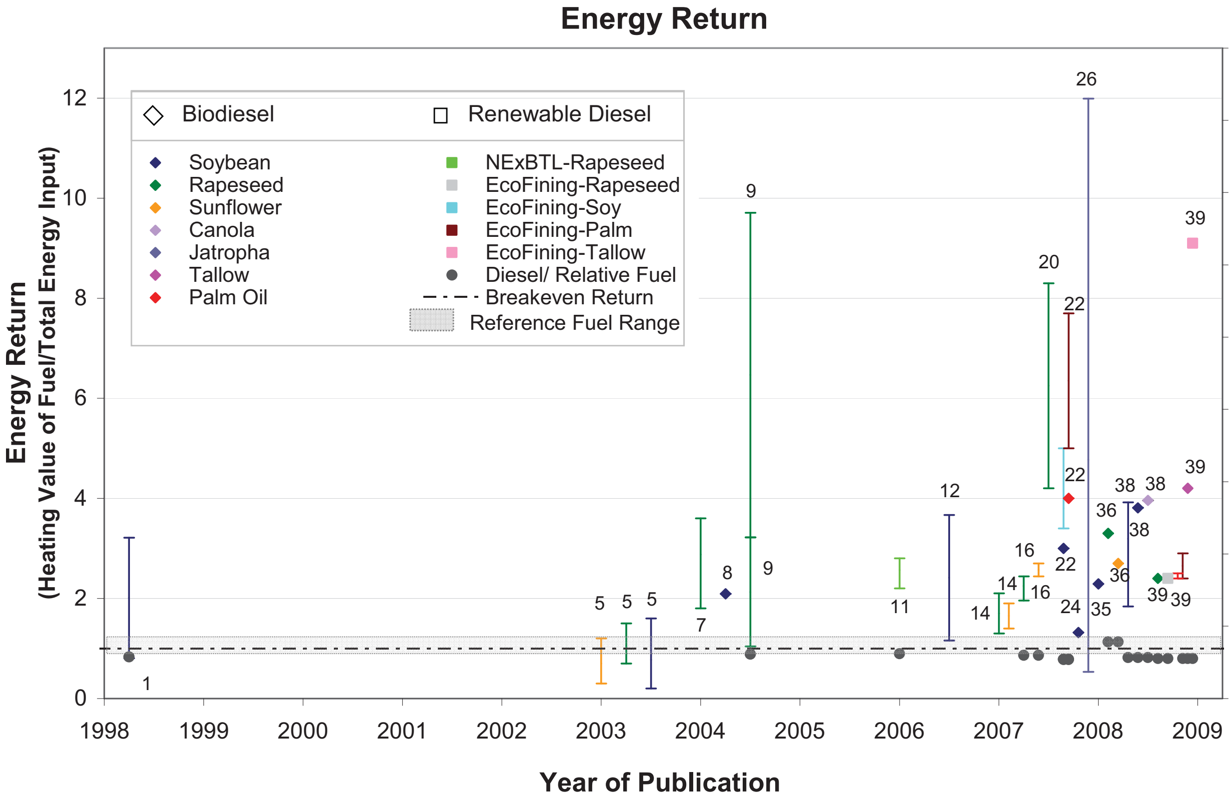


Figure 34.Energy Return for 17 LCA Models
Study No. provided in Appendix VI-1 and VI -B

Study No. 7 (Bernesson$^{(317)}$) investigated how changing the allocation of co-products affects both energy and global warming impacts of biodiesel. (This study was conducted by a group at the Swedish University of Agricultural Sciences, who also published Study No's. 20 and 28, which were not identified as critical studies due to the narrower scope of each.) This study clearly demonstrates how different allocation methods for co-products dramatically affect the final LCA results. All four allocation methods discussed in Section 8.1.2.2 were applied to small, medium and large-scale production facilities. Results showed that the size of the plant had little impact on the final energy balance of the fuel, but the allocation method had significant effects. No allocation to by-products resulted in the lower range of the energy return. Any of the allocation methods increase the ER. Not shown in the Fig. 34 is the ER for the expanded allocation method, which allows compensation for the energy requirements for the displaced product. When using the expanded allocation method, biodiesel production for all three sizes of plants resulted in a negative energy balance (-2.74, -2.92 and -6.91 for small, medium and large facilities, respectively), indicating that the process is a net supplier of energy. A reference value for energy return of diesel is not given in the paper.

Study No. 9 (Janulis[296]) investigated transesterification of rapeseed oil in Lithuania. Although the scope is very specific, it is identified as a critical study due to the broad range of impacts quantified and the frequent citation of this paper throughout the LCA literature. In total, over 20 scenarios were investigated and three different methods of calculating an energy ratio were used. The scenarios included different harvesting yields, use of classic agro-technologies compared to new seed preservation and bio-fertilizer technology, use of methanol compared to ethanol for transesterification, and cold pressing oil extraction versus higher productivity hot pressing technology. The results in Fig. 34 represent all three ER methods that were calculated: the bar at 3.2 is the upper value for ER using the traditional calculation (LHV of fuel/ life-cycle energy inputs). The other two ER calculation methods include different approaches of assessing co-product energy: the second method compares the energy accumulated in all products with total energy consumed; the third method (called the ecobalance) compares the energy in the fuel with the energy related solely to the biofuel production (subtracting energy for co-product production). The second method, which includes all energy contained in co-products, results in high energy ratios, which is why the ER range is well above the average in Fig. 34. This study is a comprehensive assessment of how changes in technology can help improve the overall energy balance of biodiesel. The results show that REE has slightly higher energy efficiency than RME, and that advancement in technology can help to further improve the energy efficiency compared to biodiesel. By adjusting the allocation of co-products, the energy return may increase by a factor of three.

Study No. 11 (Gartner et al. [327]) investigated 2nd generation biodiesel production via the NExBTL ™ process. The evaluation is based on a facility located in Poorvoo, Finland, and utilizes production data collected at the plant, but also includes analysis for average EU conditions. The main difference between locations is the energy mix and use of natural gas. The study investigates both energy and GHG benefits of production from rapeseed oil or palm oil with a variety of origins (grown in Europe or Malaysia). The ER values were reported per ton of NExBTL produced, where the energy content of NExBTL is 44GJ t. An ER of 2.2 to 2.8 for rapeseed results. The main differences depend on where the rapeseed was grown: a higher ER results when rapeseed is grown locally (in the EU) either on land that was set aside, or for natural land that was converted. The lower ER occurs when the rapeseed has to be transported from overseas. The energy savings for producing NExBTL was found to be over 60% relative to conventional diesel.

Study No. 16 (Edwards et al.[301]) is a complete WTW investigation conducted by the Institute for the Environment and Sustainability in the EU, along with EUCAR and CONCAWE, to aid EU policy decisions regarding alternative fuels. This study includes detailed descriptions of a large array of alternative fuel pathways, with comprehensive appendices for both WTT, TTW and WTW results for each fuel type. The results for biodiesel and the petroleum diesel reference fuel are included in Fig. 34, but the analysis also included synthetic diesel and DME from biomass sources like waste wood and farmed wood. The focus of the study is on policy in the EU, so EU feedstocks of rapeseed and sunflower were investigated. The expanded allocation method was applied in all cases, with glycerin use as both an animal feed and a chemical feedstock being investigated. Additionally, both methanol (to produce RME) and ethanol (to produce REE) were considered as a process fuel, which broadens the range of results for rapeseed compared to sunflower seed.

Study No. 38 was also identified as a critical study due to its level of detail.(297) Two separate analyses were performed in the study: one to compare the results of the GHGenius model to the GREET model, depicted by the first range of values in the figure, and one to compare the GHG and ER results for biodiesel production from different feedstocks using the GHGenius model, which is depicted by the two different points for canola and soybean. The model provided detailed assumptions as well as a sensitivity analysis for the results. The sensitivity analysis is not depicted in the figure for ER, but is included in the GHG results discussed in the following section.

Kalnes et.al. published two studies for UOP's Ecofining Process: Study No. 22 (174) and Study No. 39 (321). Study No. 39 investigated three different feedstocks for the Ecofining process (rapeseed, palm oil, and tallow). It also investigated how using biogas will affect the energy and GHG emissions. Study No. 22 investigated both soy and palm oil. Both compared the Green Diesel results to biodiesel from transesterification of each feedstock, and to low-sulfur petroleum diesel. In each case, the Green Diesel range for each feedstock is reported in Fig. 34 as well as the biodiesel and petroleum diesel reference. The differences in the results from the two studies are quite significant: Study No. 22 reports nearly double the ER for Green Diesel from palm oil than Study No. 39. The most notable difference in the studies is that N_2O emissions were neglected in Study No. 22, but included in Study No. 39. However, this should be more noticeable in GWP than in ER (GWP will be discussed in more detail in the following section). Not enough detail is given in either publication to discern if this is the only difference between the studies. In both studies, Green Diesel results in a favorable energy benefit relative to both its biodiesel counterpart and to conventional diesel. In Study No. 39, using biogas (a co-product) to produce power that could be used at the processing facility was also investigated, which provides the range of results for palm oil: the lower result does not include the use of biogas, the upper result does. Tallow as a feedstock for the green diesel process provides an ER of 9.1. The energy benefit is substantial due to the fact that tallow is considered a waste product from a meat rendering plant, and its only energy inputs come from transportation to the processing facility and from the production of the Green Diesel itself. Studies No. 22, 39 and 11 for second generation methods of biodiesel production do not show a substantial increase in energy return relative to biodiesel production from transesterification, except when using tallow as a feedstock.

More detail on the remaining studies included in Fig. 34 can be found in Appendix VI-1 and VI-2.

8.2.2 Green House Gas Emissions

Frequently in LCA of transportation fuels, GHG emissions results are aggregated and reported on the basis of total global warming potential (GWP). GHGs are converted to a CO_2 equivalent basis using factors recommended by IPCC (312) (shown in Table VIII) or by similar factors. Of the 38 studies included in our literature review, 16 reported GHG impacts or GWP potential. Results from these 16 are shown in Fig. 25 – 13 of them also have corresponding ER data shown in Fig. 34. The studies that reported a range of results for a particular feedstock are designated by vertical bars; studies reporting a single result are designated by a point.

Table XVIII. IPCC GHG Equivalency Factors

Greenhouse Gas	tCO_2 eq/ t
CO_2	1
Methane (CH_4)	23
Nitrous Oxide (N_2O)	296
CFC-12	10,600
HFC-134a	1,300
O_3	6

The 16 LCA studies for GWP shown in Fig. 35 reported GWP as g CO_2 equivalent per MJ of fuel, or other similar value that could be easily converted to this unit. However, some studies investigated the complete WTW lifecycle, while others only completed the WTT portion. A frequent assumption, however, is that the carbon emitted during combustion of biofuels is offset by the carbon uptake during the plant's growth, resulting in minimal overall contribution from combustion (there is some minor contribution to GWP due to other pollutants like NO_x). This is a significant difference when comparing to GWP of conventional diesel fuel, since a large portion of total life-cycle GHG emissions from diesel fuel occurs during combustion.

Although direct comparison among studies is not straight forward, since each study varies significantly in its assumptions and pathways, Fig. 35 still shows a relatively tight range of GWP results, with most of the results falling between 10-60 grams of CO_2 equivalent per MJ of fuel produced. The range of conventional diesel GWP values reported in these studies is from 22 to 240 grams of CO_2 equivalent per MJ of fuel.

The relative GWP difference between the biofuel and conventional fuel reported in each study is illustrated in Fig. 36. (Figs. 35 and 36 consist of slightly different sets of studies due to differences in reporting: many studies only reported a percent increase or decrease, while some reported GWP for biodiesel but not for petroleum diesel). When possible, the complete WTW GHG emissions of biodiesel are compared to the complete life-cycle of the reference diesel fuel. However, the relative impact is widely varied among different studies: several showed a 90% or greater decrease in GHG emissions, while several others showed less than 10% benefit. With the exception of Delucchi's Study No. 32 however, biodiesel LCA results in a significant improvement in GWP relative to fossil diesel.(315) The results of Delucchi's model demonstrate the potentially severe impacts of N_2O emissions due to land use change. His model does not include indirect effects, but illustrates the general issues with LUC impacts, which in this case results in a 50% increase in GWP relative to fossil diesel. Indirect impacts have the potential to be even more severe.

Figures 35 and 36 illustrate the extreme variability in LCA results, even when looking at similar feedstocks in similar locations. For example, soybean oil was the feedstock examined in six of the studies shown in Fig. 35. Three of them reported a single value, which correspond quite well with each other, although they are in different locations: No. 1 (Sheehan(307)) and No. 12 (Hill(328)) are for production in the U.S.;, and No. 35 (Panichelli(329)) is for production in Argentina. However, the three remaining studies (No. 8 is for Italian conditions; (330) No's. 24 and 38 are for U.S. and Canadian conditions (320,297) report a range of values that are much lower. When comparing these values to the reported GWP for petroleum diesel, the variability is even more pronounced. Although the GWP for biodiesel in the NREL study (Study No. 1) was quite high relative to the other soybean LCA models, it also showed the largest benefit relative to petroleum diesel in Fig. 36 at about an 80% decrease in GWP. Study No. 12 (Hill(328)) determined a GWP value was comparable to that in the NREL Study, but it resulted in a benefit of only about 43% compared to the reference diesel fuel. Both Study No. 8 (Carraretto(330)) and Study No. 24 (Kreider(320)) had lower GWP values, and lower benefits relative to conventional diesel fuel.

Three studies reported on the absolute GWP for renewable diesel life-cycles: Kalnes et al.(174,321) on Ecofining (Studies No. 22 and 39) and Gartner et al,(331) on NExBTL hydrotreating (Study No. 11). Gartner actually reports higher than average GWP for NExBTL compared to other studies, while the EcoFining process results in low-range GWP. Kalnes also reports corresponding GWP for biodiesel, which shows that the EcoFining process results in a reduction in GWP emissions relative to production of biodiesel from the same feedstocks. Additionally, when compared to a reference diesel fuel, all 2nd Generation biodiesel LCA studies report significant GWP benefits (usually 50% or greater). This is seen in Fig. 36 for Studies Nos. 11, 22, 23,25, and 39. Reports that include gasification to DME or FTD are also shown in Fig. 36. This technology shows the most consistent results and significant potential for reducing GHGs with respect to conventional diesel (Studies No's. 6, 16 and 28).

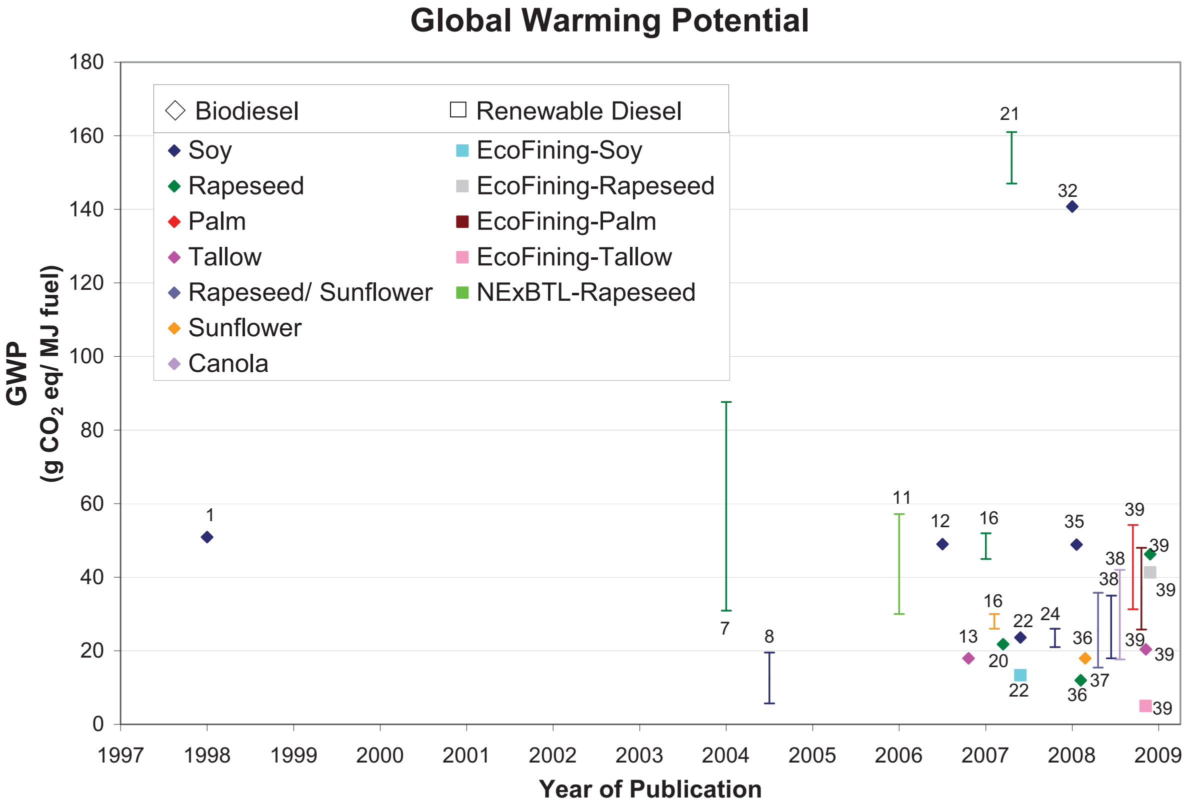


Figure 35. Absolute GWP from Sixteen Biodiesel LCA Studies

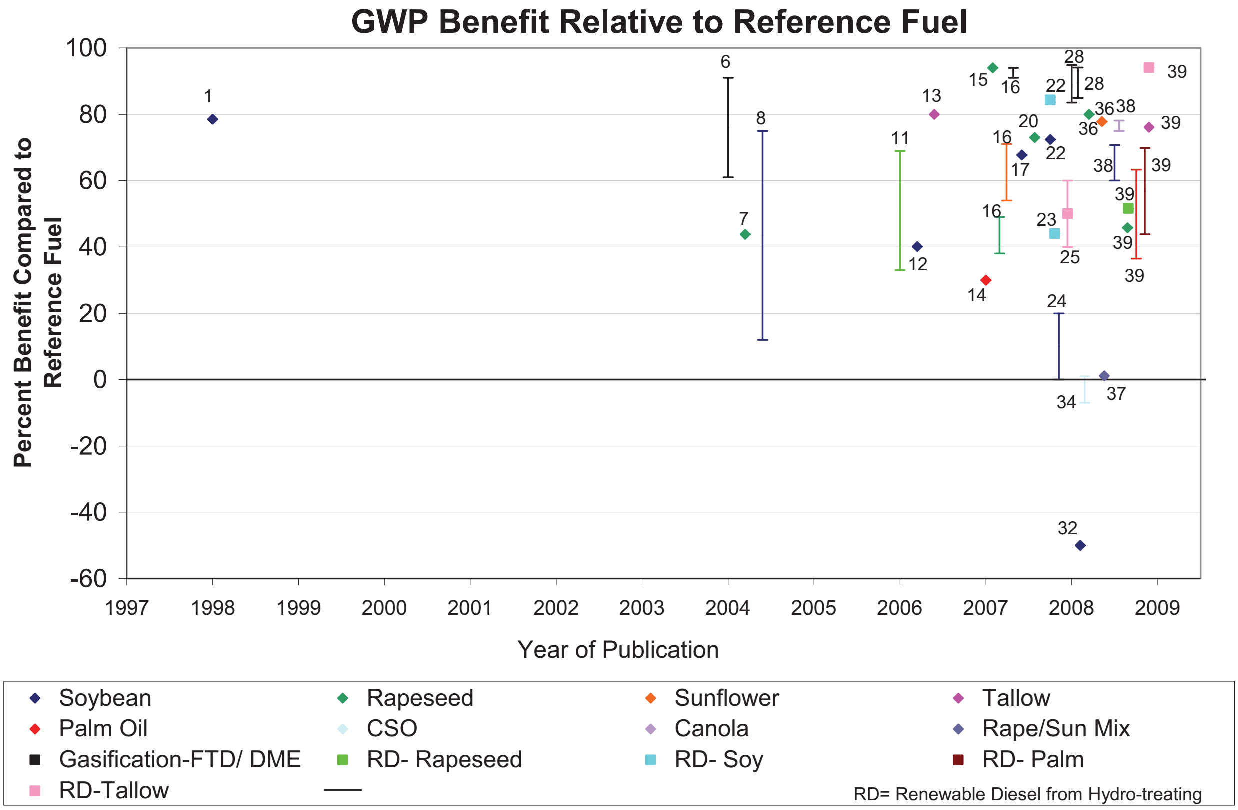


Figure 36. Relative GWP from 20 Biodiesel LCA Studies

8.2.2.1 Critical Studies for GWP

In addition to the critical studies previously discussed for energy return that include GWP, additional studies were identified as critical for GWP results based upon similar criteria. The level of detail in the critical studies was enough to provide a breakdown of GWP contributions from each stage of production for comparison. Fig. 37 shows the breakdown by contribution to GWP from agriculture, oil extraction, conversion, transportation and combustion as well as any carbon offsets (due to the carbon neutral principle or co-product allocation) arranged by feedstock and technology type (transesterification or hydro-processing). The reference diesel fuel value is also shown in Fig. 37 for comparison.

Contributions from each category, as well as total GWP values and amount of reduction relative to fossil diesel vary. Of the three studies included for soybean methyl ester (SME) in Fig. 37, two showed comparable reduction in GWP relative to the fossil reference fuels used, although the total GWP levels varied significantly. Similar reductions relative to reference fuels were demonstrated for the three critical studies for rapeseed methyl ester (RME). Fig. 37 demonstrates how variations in assumptions during each lifecycle stage contribute to the differences in the final GWP results for these biofuels. Contributions from the agricultural stage vary most significantly. Delucchi's high N_2O emission rates attribute significant GWP to the agricultural phase, causing a detriment for biodiesel relative to fossil diesel (Study No. 32).(315)

Although the NREL study (Study No. 1) included an inventory analysis of GHG emissions, the total inventory was not converted to equivalent CO_2 emissions, so the reported GWP depicted in the figures is the straight CO_2 emissions determined, and does not included contributions for N_2O or CH_4. However, the total inventory for these gases is quite small, and would contribute less to total GWP than would the comparable inventory for petroleum diesel. The contributions from the agricultural phase are also quite low (Fig. 37), but most of the N_2O and CH_4 emissions of the life-cycle come from this phase, which would bump up its contribution slightly, if included. Most of the GWP comes from fuel production and final use. The offsets in the Fig. 37 are from CO_2 uptake from plant growth, which nearly counteracts all combustion emissions. Thus, the total life-cycle CO_2 emissions in this study are reduced by nearly 80% relative to conventional diesel (Fig. 36).

The Delucchi report[315] (Study No. 32) was considered a critical study because of its attention to soil nitrogen emissions. In Delucchi's estimation, the contribution of nitrogen emissions during the agricultural phase is large enough to result in a net-negative GWP effect relative to conventional diesel. Besides the major GHG gases (CH_4, N_2O and CO_2), Delucchi's calculation of total GWP includes other trace gases (CFC-12, HFC-134a, and O_3), which further increase the total GWP dis-benefit of biodiesel compared to conventional diesel. The displaced emissions in Fig. 37 are from both credits to co-products and CO_2 uptake in plant growth.

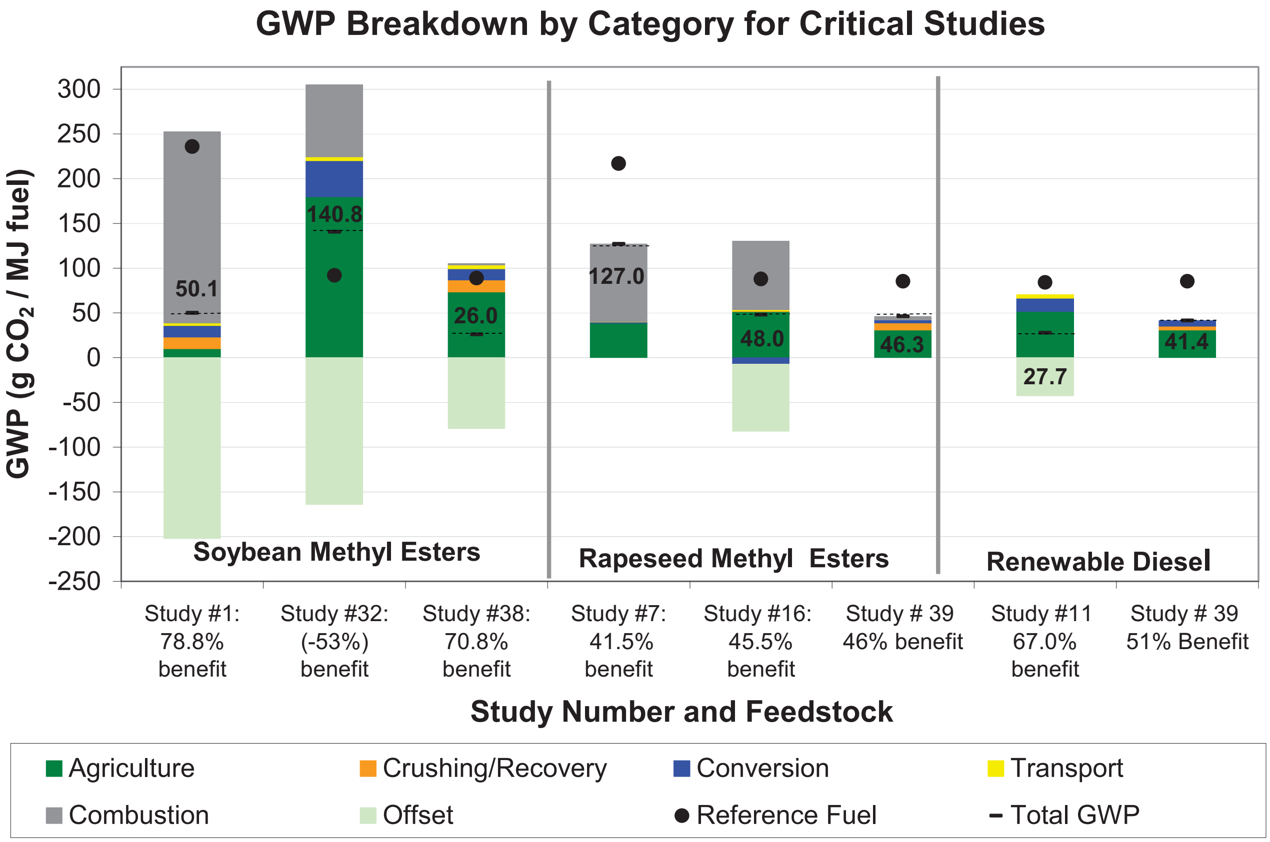


Figure 37. Contribution of Individual Life-Cycle Stages to Overall GWP

Study No. 38 (S&T2(297)) includes multiple scenarios for canola oil and soy oil. The baseline scenario for both feedstocks showed that biodiesel from canola results in a lower GWP due to its lower nitrogen requirements, leading to lower LUC contributions compared to soy oil. The ranges of GWP in Fig. 35, however, show that canola could have a potentially higher GWP than soy oil. This is due only to higher level of detail in the sensitivity analysis for canola. Therefore, the benefit relative to conventional diesel is higher for canola than for soy oil because the comparison is made from base case value ranges and not the ranges included in the sensitivity analysis. Only the base-case for soy oil is pictured in Fig. 37 to show the breakdown for contributions from each life-cycle stage. The contribution from combustion is minimal due to carbon offsets already calculated into the final result. The offset shown in Fig. 37 is due to deductions for co-product allocation. Emissions during the agricultural phase therefore are the most significant contribution to the final reported value for GWP.

The GWP results for Study No. 7 (Bernesson et al.(317)) demonstrate how allocation method affects the final product. The range in Fig. 35 includes multiple scenarios for different allocation methods and facility sizes for WTT life-cycle. When allocation methods are used, the GWP between small and large scale facilities only change by about 10%; however, no allocation of by-products result in a 40% difference between the small and large scale facility. The largest amount of CO_2 equivalent emissions results from small-scale facilities with no allocation of co-products, and the smallest amount results when the expanded allocation method is used with large-scale systems. Using the expanded allocation method halves the GHG emissions compared to no allocation. The relative value in Fig. 36 relates the results from the large-scale production facility with physical allocation of co-products after comparison to MK1 diesel oil. The comparison shows a 44% reduction in GHG emissions. Although the comparison is made for slightly different units, it is clear that if no allocation method is used, the results would show little benefit in GHG emissions relative to diesel oil, and may in fact result in a dis-benefit. The main contributions to total GWP are agriculture and combustion (Fig. 37). The offset for co-products is already included in the values provided, so does not appear as a separate bar segment in Fig. 37. This study concludes that large-scale facilities provide the best GWP and energy benefits, and that physical allocation methods provide the best-defined inputs. However, this does not take into consideration changes in environmental impacts from displacing other products as the expanded allocation method does. Small changes in assumptions for the expanded method can drastically affect the results.

Study No. 16 (Edwards et al.(301)) compares biodiesel from sunflower and rapeseed oil. As was found with the ER results, sunflower oil also provides greater GWP benefits compared to rapeseed oil. The range of results for each is based on a variety of assumptions for uses of co-products, and from production using methanol or ethanol for rapeseed. An updated report for this study was published in November, 2008. The updates include additional biodiesel pathways that were not discussed in the original paper. The breakdown for RME when using glycerol as a chemical is shown in Fig. 37 to allow for comparison with a similar breakdown of RME from Study No. 7. This figure shows that the GWP contribution from combustion is offset by the carbon neutral principle. However, offsets from co-product allocation are included in the calculations in the fuel production phase, resulting in a negative GWP contribution by the fuel production phase. Therefore, the main contributions to GWP are from agricultural activities. Thus, total GWP shows a 45% benefit relative to conventional diesel.

Studies No. 11 (Gartner [(327)]) and 39 (Kalnes [(321)]) were identified as critical studies including GWP for biodiesel from hydro-proccessing.

The range of values reported in Fig. 35 for Study No. 11 are for rapeseed as a feedstock from different origins (produced locally on either set-aside land or natural land or imported from overseas) and for different locations for the production facility (the facility at Poorvoo, Finland, or for a location in Europe with average EU conditions). The report does not give a relative diesel value, but states that1.2-2.5 tons of CO_2 equivalent emissions per ton of NExBTL are saved relative to petroleum diesel. These values, with the total CO_2 equivalent emissions from each scenario, were used to estimate a relative diesel value of approximately 84 g CO_2 equivalent emissions per MJ of fuel, which was used to calculate the relative benefit in Fig. 36 and is reported in Fig. 37. Figure 37 shows the breakdown for the Poorvoo scenarios with rapeseed growth on set-aside land, although the contributions from each stage are not significantly different for the other scenarios. The offsets to GWP are from both the CO_2 uptake from the growth of the feedstock and from co-product allocation (including the use of biogas to power the facility). However, no combustion analysis was included in the study. If GHG emissions from combustion were included, it is likely that the total GWP of the fuel would increase, resulting in a lesser benefit compared to the reference fuel than the 70% figure shown here.

Study No. 39 includes scenarios for different feedstocks (rapeseed, palm oil and tallow) for production of both biodiesel and renewable diesel (from the EcoFining process). The range of values for palm oil in Fig. 35 includes only a high and low value that include the use of biogas or not. Figure 35 shows that the production of renewable diesel has a greater GWP benefit than biodiesel for all feedstocks. Tallow has the lowest GWP because it is considered a waste product from the rendering plant; therefore, it has smaller GHG inputs (i.e. it doesn’t require agricultural inputs for cultivation), resulting in a 95% decrease in GWP relative to conventional diesel when renewable diesel is produced. Figure 37 shows the breakdown for production of both biodiesel and renewable diesel from rapeseed. The offsets for each are already included in the calculations for total GWP, so are not included here as a separate bar. There is no GWP contribution for combustion for renewable diesel because the authors assume that all CO_2 emissions are offset from plant growth since all carbon is from renewable oils. There is a small contribution for biodiesel combustion, however, because there is some methanol derived CO_2, which is of fossil origin. The amount of CO_2 produced during oil production is larger for biodiesel than for renewable diesel, but the amount of GWP resulting from fuel manufacturing is slightly higher for renewable diesel. Renewable diesel, however, has a lower GWP than biodiesel for all feedstocks. Rapeseed results in the highest amount of emissions from agriculture of the three feedstocks because of larger N_2O emissions. Palm oil has the largest GWP of the three feedstocks due to higher amounts of energy required during oil production. This can be reduced, however, if the resulting biogas is used to power the facility.

Additional details on other studies included in the above figures are presented in Appendix VI-1 and VI-2.

8.2.3 Other Common Impact Categories

In addition to GWP and energy requirements, other ecological or resource impacts are often assessed using LCA methodologies. Some of these other categories that are occasionally included in biodiesel LCA studies are discussed briefly below, along with a description of results from the studies in which they were included.

8.2.3.1 Water Resources

Biodiesel production requires water during both growth of the feedstock and during the esterification process. Although water is an important resource, it is not frequently included in biodiesel LCA, likely because of the many uncertainties and regional specificities of water use for biofuel feedstocks. Additionally, it is believed that increased agricultural production of biofuels will not substantially increase the national water-use, although it may have local impacts on already stressed water resources. (321) Only two of the literature sources we reviewed explicitly included water use. Sheehan et al. (Study No. 1 (307)) found that water use from soybean-derived biodiesel is three times higher than petroleum diesel. However, they also found that wastewater generation is roughly 5 times higher for petroleum diesel than for biodiesel (0.175 L/MJ compared to 0.037 L/MJ, respectively), which has implications for additional environmental impacts. Another U.S. study by Kreider et al. (Study No. 24 (320)) found that biodiesel production requires about 25 L of water/MJ of fuel, while conventional diesel only requires 0.018 L/MJ.

8.2.3.2 Eutrophication

Eutrophication occurs as a result of excess nutrients (phosphorous and/or nitrogen) applied to increase agricultural yields which runoff into water supplies. In a nutrient-rich environment, plants such as algae grow and decay at a more rapid rate and can cause reductions in water quality or can cause hypoxia or dead zones, such as those that exist in Chesapeake Bay or the Gulf of Mexico. (321) The eutrophication potential (EUP) is commonly measured in agricultural LCAs and is sometimes included in biodiesel LCAs. The EUP for biodiesel from vegetable oils increases relative to conventional diesel (Bernesson, (317) Edwards, (301) and Hansson (323)). Ahlgren et al. (332) found that biodiesel produced from organic crop growth reduces EUP compared to conventional diesel. Additionally, using waste products such as waste vegetable oil shows an EUP benefit relative to conventional diesel (Niederl(318)).

8.2.3.3 Acidification

The acidification potential (ACP) also is increased slightly for biofuels. Acidification results when nitrogen, sulfur oxides, and ammonia that are released as a result of fertilization during plant growth are oxidized in the atmosphere to form acids. This can lead to “acid rain” which lowers the pH of soils and water. Since these types of emissions are only associated with agricultural activities, biodiesel fuels generally show an increase in ACP compared to petroleum diesel. (331,317,301,323) Again, use of waste vegetable oils and organic cropping methods can reduce these effects. (318,332)

8.2.3.4 Photochemical Ozone Creation Potential

A handful of studies included additional environmental impact categories. Although Photochemical Ozone Creation Potential (POCP) is an important environmental impact, it is rarely assessed. POCP, which relates to smog formation, increases due to ozone formation from NOx and hydrocarbon emissions from incomplete combustion. In three studies, it has been reported that biodiesel shows a small POCP benefit relative to diesel fuel.(331,317,318) However, considering the variability of results in the biodiesel emissions literature (see Section 7 above), a definitive conclusion about POCP benefits cannot be reached.

8.2.3.4 Other Impact Categories

Additional LCA impact categories include abiotic depletion, ozone layer depletion, human toxicity, waste, fresh water aquatoxicity, and habitat disruption. These categories were rarely reported in the literature. A small benefit for abiotic depeletion for biodiesel was reported by Niederl (318). An increase in ozone layer depletion for biodiesel relative to conventional diesel was reported by Gartner.(331) Harding et al.(333) reported values for abiotic depletion, ozone layer depletion, human toxicity and aquatoxicity, but did not relate them to a reference fuel. A recent report for the California Environmental Protection Agency summarized numerous environmental issues associated with the transport and fate of biodiesel, though most of those issues were not addressed on a life-cycle basis.(334)

9. Summary and Conclusions

Presently, there is considerable interest in the broad topic of biodistillates. Numerous facets of this topic constitute active and growing areas of investigation within the research, policy, and regulatory communities. Our review of the biodistillate literature (primarily technical literature) revealed rapidly increasing numbers of papers and reports over the past few years. Given below are brief summaries and major conclusions from individual sections of our review.

9.1 Policy Drivers

For reasons of energy security, sustainability, diversity, and climate change mitigation, many countries and regions have developed policies to promote greater production and use of biodistillate fuels. In the U.S., the dominant policy driver is the Energy Independence and Security Act of 2007, which requires 0.5 bg/y of biodiesel by 2009, and 1.0 bg/y by 2012. This larger amount represents about 2.5% of total U.S. on-road diesel fuel usage. European Union Directives currently require 2.0% biofuels content in all transportation fuels, ramping up to 5.75% by 2010.

Numerous other countries have also implemented policies encouraging (or requiring) increased biodistillate usage. Some of the most aggressive actions have been taken by China, India, and Brazil. However, unlike the U.S. situation, it appears that the biodistillate goals of many countries are not realistic, and will not be achieved within the projected time timeframe. Existing policy-based goals forecast total biodistillate usage (in the U.S., Europe, China, India, and Brazil) of about 23 bg/y in 2020. Based upon our assessment of the situation, we forecast a much lower usage of about 7 bg/y in 2020.

9.2 Biodiesel Volumes and Feedstocks

Growth in biodiesel production has been dramatic in recent years, especially in Europe and the U.S. Global production has increased from approximately 0.5 bg/y in 2005 to 2.5 bg/y in 2007. While numerous triglyceride feedstocks have been investigated as potential feedstocks for biodiesel production, only a few are in widespread commercial use. The dominant feedstock in the U.S. is soybean oil, with far lesser amounts of other seed oils, used cooking oils, and animal fats being used. In Europe, the dominant feedstock is rapeseed oil.

Biodiesel production capacity has grown much faster than actual production volumes. Excess capacity has become a serious problem within the biodiesel industry. Current production in the U.S. and Europe is well below 50% of capacity. This is driven mainly by limited availability and high costs of current feedstocks. Consequently, there is tremendous interest in developing alternative feedstocks, particularly those that do not have concurrent uses as food. Two of these so-called, 2nd generation feedstocks that are receiving great attention are jatropha and microalgae. It is likely that commercially produced biodistillates from these feedstocks will begin to appear in the marketplace within the next 5 years.

With its principal feedstocks being agriculturally-produced materials, the biodiesel industry has traditionally been viewed as an extension of agriculture. Until very recently, most biodiesel manufacturing plants have been small (< 5 mg/y) and located in crop-producing regions. The industry is now undergoing a significant change, with introduction of much larger manufacturing plants (> 20 mg/y) located near ports with access to world-wide feedstocks. Major energy and fuel companies, such as BP, Chevron, ConocoPhillips, Marathon, and Shell are now beginning to participate in the biodiesel activities. Additionally, production and use of renewable diesel (produced via hydroprocessing of triglyceride feedstocks) are becoming more common.

In most locations, the predominant use of biodiesel is as a low-concentration blend with petroleum diesel. Concentrations of 2% (B2), 5% (B5) and 20% (B20) are most common. Only in Germany and Austria is use of neat biodiesel (B100) commonly employed as a transportation fuel.

9.3 Biodistillate Production Technologies

Due to their high viscosity levels (and other related problems), raw vegetable oils are generally not suitable for use as a fuel in a diesel engine. Much lower viscosities result from transesterifying these oils with alcohols to produce esters. Mainly for reasons of cost, methanol is the preferred alcohol. The resulting fatty acid methyl esters (FAME) are the principal constituents of biodiesel. Typical biodiesel production conditions involve a large excess of methanol, use of hydroxide or alkoxide homogeneous catalyst, mild heating (50-60 °C), gravity separation, water washing, and distillation. However, numerous operational variations of these parameters are possible (and are employed). Certain feedstocks, such as used cooking oils and animal fats, are more difficult to handle, and may require additional processing steps.

The literature contains numerous reports of studies investigating improvements in the production of biodiesel. Most commonly discussed are uses of alcohols other than methanol, co-solvents, heterogeneous catalysts, supercritical methanol conditions, and ultrasonic or microwave heating. While many of these improvements have been demonstrated on a laboratory scale, none of them is in common commercial usage.

The transesterification route for biodiesel production unavoidably leads to co-production of glycerol. The presence of glycerol in biodiesel leads to performance problems. Hence, it is critical to remove glycerol to achieve acceptable, on-spec product. This adds processing complexity and cost, and results in a co-product stream having little value.

Hydroprocessing of triglycerides is an alternative route to biodistillates that does not involve alcohols or glycerol production. Unlike biodiesel, which consists of methyl esters, hydroprocessed triglycerides produce hydrocarbons that are virtually identical to those found in petroleum diesel. This hydroprocessed fuel is generally known as renewable diesel, as opposed to biodiesel. Production of renewable diesel is most conveniently accomplished within an integrated petroleum refinery.

While still in the R&D stage, there is also interest in other thermal processing routes to biodistillates, primarily through pyrolysis. Triglycerides can be pyrolyzed (or thermally cracked) to produce biodistillates, but of greater long-term interest is treatment of lignocellulosic materials. Although considerable work is being done in these areas, no commercial applications are in use today.

9.4 Fuel Properties and Specifications

The properties of biodiesel fuel are largely dictated by the chemical composition of the fatty acid methyl esters comprising the fuel. Because various triglyceride feedstocks differ substantially in their composition, the properties of the resulting biodiesel fuels also vary. Two of the most important chemical parameters affecting the overall fuel properties are carbon chain length and degree of unsaturation (carbon-carbon double bonds) within the FAME molecules.

Biodiesel typically contains about 11% oxygen, in the form of methyl esters. As a consequence, it has lower mass energy content than petroleum diesel – by about 10%. However, due to its somewhat higher specific gravity, biodiesel's volumetric energy content is only about 5-6% lower than that of petroleum diesel. Renewable diesel, containing no oxygen, has a mass energy content very similar to petroleum diesel. However, the volumetric energy content of renewable diesel is considerably lower than that of petroleum diesel (due to its lower specific gravity) and is similar to the volumetric energy content of biodiesel.

Standard specifications for biodiesel fuel have been developed, and are continuing to evolve, in many countries. In the U.S., current biodiesel (B100) specifications are defined by ASTM D 6751-08; European specifications are defined by EN 14214. At present, the U.S. is the only country having specifications for biodiesel blends: ASTM D 7467-08 applies to B6-B20 blends. In other countries (and in the U.S. until very recently), biodiesel blends are acceptable provided both the biodiesel component and the petroleum diesel component comply with their respective individual standards. In most countries (including the U.S.), biodiesel blends of 5% and lower must comply with the specifications established for conventional diesel fuel.

Biodiesel fuel standards include numerous different specifications and test methods, many of which are meant to ensure that the transesterification reaction and product clean-up steps were performed satisfactorily. For example, specifications for water content, viscosity, flash point, methanol content, sulfated ash, acid number, glycerine content, and others are meant to ensure high purity FAME product. The European standards include explicit specifications for various metrics of FAME unsaturation, such as iodine number and concentration of linolenic acid methyl ester. ASTM standards do not include these tests, but do incorporate an oxidative stability test (the Rancimat Test) that may be regarded as a surrogate test for unsaturation. Ensuring full compliance with biodiesel standard specifications requires extensive laboratory testing, which is not practical for many small producers. Nevertheless, it is important for every producer to conduct a subset of most critical product quality tests on each fuel batch, with more extensive outside testing done periodically.

Adhering to established quality control/quality assurance (QC/QA) measures is critical to ensuring satisfactory biodiesel quality in the marketplace. In the U.S., the BQ-9000 Quality Management System was recently developed to define acceptable QC/QA measures. BQ-9000 includes separate sets of requirements for B100 producers and B100 marketers. While still quite new, it appears that voluntary participation in the BQ-9000 Quality Management System is growing.

9.5 In-Use Handling and Performance of Biodiesel Fuels

All transportation fuels require proper handling and adherence to "good housekeeping practices" to ensure satisfactory quality in the field. However, with biodiesel, some extra precautions are warranted, due to this fuel's higher solvency, propensity to pick up water and disperse sediments, and inherent oxidative instability. Some reported field problems can be traced to poor handling and housekeeping practices.

Most in-use biodiesel is produced by blending B100 and petroleum diesel. Various methods of blending are commonly employed, but in-line blending at a fuel terminal is the preferred approach, as this provides the best control and most accurate blend compositions. Recent surveys of in-use biodiesel have shown significant inaccuracies of blending, with some reported B20 blends actually containing much more or much less than 20% biodiesel.

U.S. fuel quality surveys have also revealed problems with off-spec biodiesel in the marketplace, with poor oxidative stability being the greatest concern. The most recent surveys (conducted after the Rancimat Test method was included in ASTM D 6751) showed improved quality overall, with fuel manufactured by large producers (>1 bg/y) nearly always meeting all specifications. Fuel produced by small "Mom and Pop" operators continues to be a concern, as many of these producers do not have the tools or expertise to perform laboratory quality control tests.

Instability of biodiesel is a complex problem, with several contributing factors. No single laboratory test is able to assess all important degradation pathways, hence numerous tests have been developed and are used for different purposes. The degree and type of unsaturation within the FAME molecules are believed to be important determinants of instability. Antioxidant additives are useful for improving the stability of biodiesel, with synthetic materials generally being more effective than antioxidants naturally occurring in vegetable oils.

For many biodiesel users, low temperature operability is the greatest in-use concern, as this can lead to filter plugging and engine shutdown. Numerous laboratory tests have been developed to assess low temperature operability; the most common ones being cloud point (CP), pour point (PP), and low temperature filterability test (LTFT). In general, biodiesel has somewhat poorer low temperature operability than petroleum diesel, though the extent of the difference varies substantially based upon the unique chemical composition of the biodiesel in question. Visible wax formation, which defines CP, is first caused by crystallization of the least soluble species – namely, saturated, long-chain paraffins. Unsaturated FAME molecules are much less prone to crystallize. Hence, to some degree, there exists a tradeoff between fuel stability (enhanced by saturated FAME) and low temperature operability (diminished by saturated FAME). Low temperature operability of biodiesel can be improved by greater dilution with petroleum diesel, use of cold flow improver additives, and use of ethanol rather than methanol in the transesterification process.

While greatly reduced compared to raw vegetable oil, the viscosity of biodiesel is usually still higher than that of petroleum diesel. This can have adverse impacts with respect to fuel injection and atomization, particularly under low temperature conditions.

In general, biodiesel fuel provides excellent lubricity in fuel injection systems. This is due both to inherent properties of FAME itself, and to high lubricity trace constituents (such as free fatty acids) that are present as contaminants in the fuel. Use of low concentration biodiesel blends, such as B2, is an effective way to achieve satisfactory lubricity in today's ultra-low sulfur diesel (ULSD). By itself, ULSD can have quite poor lubricity, because the severe hydroprocessing used to achieve very low sulfur levels also removes naturally-occurring trace species having high lubricity. In the same way, renewable diesel, which is produced by hydroprocessing similar to that used for ULSD, also has poor lubricity. However, the lubricity of both ULSD and renewable diesel can be improved by means of fuel additives.

There have also been concerns about materials compatibility with biodiesel, as well as engine wear, corrosion, microbial growth, and other adverse impacts. While there is documented evidence supporting some of these claims, it is likely that in most cases, off-spec fuel and poor overall fuel housekeeping were also involved. (It is important to remember that the ASTM D 6751 standard specification for biodiesel did not include an oxidation stability test until 2007.)

While exceptions are possible, it appears that acceptable in-use handling and performance of biodiesel is best achieved by strict adherence to established fuel specifications and implementation of good fuel housekeeping practices. Additionally, to minimize concerns regarding fuel stability, viscosity, materials compatibility, and others, it is prudent to limit the biodiesel composition to B20 and below.

9.6 Exhaust Emissions Impacts

Reduction of exhaust emissions has been one of the drivers for biodiesel fuels for many years. Compared to conventional petroleum-derived diesel fuel, most literature reports indicate 10-20% reductions in CO, HC, and PM emissions when using B20 blends, with larger benefits at higher blend levels. Similar benefits are observed with both LD and HD engines/vehicles, though individual results vary widely from one study to the next. Although data are much more limited for renewable diesel cases, it appears that similar benefits in reduction of CO, HC, and PM are observed with these hydroprocessed fuels.

The fuel effects upon NOx emissions are much smaller, and difficult to discern. From use of B20 in HD engines, our assessment of the literature revealed a small NOx increase of 2.9% compared to reference diesel fuel. With B100 in HD engines, a NOx increase of 4.5% was determined. With LD engines, larger NOx increases were determined – 10.8% with B20; 15.3% with B100. However, it should be emphasized that the NOx results (and other emissions results) are highly variable from one study to the next, and even within a single study. This makes it extremely difficult to discern small fuel effects or trends with engine technology or model year. Because of this variability, we were unable to detect any consistent change in fuel effects upon emissions with changes in engine technology.

Given the caveats mentioned above, our assessment of biodistillate emissions effects are broadly consistent with preveious reviews – particularly for CO, HC, and PM. NOx effects remain confusing and controversial. Based upon our analysis, the established EPA view that use of biodiesel increases NOx emissions cannot be refuted. At the same time, many individual studies show a NOx decrease (or no effect) with use of biodiesel. Literature reports of NOx effects from renewable diesel are still quite sparce. However, the available information suggests that renewable diesel may provide a benefit over biodiesel in terms of NOx emissions. This area requires further investigation.

Much less information is available regarding non-criteria pollutant emissions from use of biodistillate fuels. Most mobile source air toxics (MSAT) data relate to formaldehyde and acetaldehyde. As with the criterial pollutants, these aldehyde results are highly variable, showing both increases and decreases compared to use of conventional diesel. Somewhat surprisingly, the majority of the results indicate a slight decrease in aldehyde emissions when using B20, and a larger decrease when using B100. A more substantial body of emissions data is necessary to confirm (or refute) these observations.

9.7 Life-Cycle and Land Use Impacts

Life-cycle assessments (LCA) of "well-to-wheels" energy inputs and GHG emissions are now recognized as important tools for understanding the relative benefits of biodistillate fuels compared to conventional fuels. However, LCA models are very data intensive, and require numerous inputs having high uncertainty. Some of the most critical inputs are in areas in areas that are most uncertain – such as assumed agricultural practices and their emissions, impacts attributed to co-products, and land use changes (LUC). Many LCA models include treatment of direct LUC, such as emissions resulting from conversion from one crop to another in the U.S. However, treatment of indirect LUC, such as conversion of pastureland in Brazil to soybean fields in response to U.S. fuel demand, is in its infancy. Although there are U.S. regulatory requirements to consider indirect effects in assessing the life-cycle impacts of biofuels, no standard methodology has been established to do so. Progress is being made in this direction by attempting to merge global economic models with LCA models.

Well-to-wheels LCA studies of energy inputs and GHG emissions are often separated into two parts: (1) well-to-tank and (2) tank-to-wheels. These two steps are sometimes referred to as upstream and downstream, or production and use. For conventional fuels, a considerable portion of the total life-cycle GHG emissions occurs during the tank-to-wheels stage, as the fuel is combusted to produce CO_2. For biofuels, this component is generally ignored, based on the assumption of carbon neutrality, meaning that the CO_2 emissions arise from combustion of a fuel whose carbon was recently extracted from the atmosphere. Consequently, for biofuels, well-to-tank and well-to-wheels GHG emissions are very similar.

Allocating some fraction of life-cycle energy inputs and GHG emissions to co-products is reasonable and necessary, but also constitutes a major area of disagreement among different LCA models and modelers. Of the various allocation approaches used, the "expanded allocation method" seems most realistic, in that it attempts to credit energy and emissions from the processes used to produce products now being replaced by biofuel co-products. However, this approach requires additional assumptions, and further convolutes the LCA methodology.

To some degree, LCA modeling suffers from the perception (and perhaps reality) that by proper tailoring of input assumptions and methodologies, the practitioner can derive any outcome that is desired. Because of this, direct comparison of life-cycle energy inputs and GHG emissions across different studies is often problematic. More instructive is comparison of the relative differences between biodistillates and conventional diesel fuel reported by different investigators.

Life-cycle energy results are typically reported as energy return on investment (EROI, or more simply, ER), meaning the heating value of the final biofuel divided by the total energy inputs involved in producing, distributing, and using the fuel. Typically, ER values for conventional diesel fuel are slightly under 1.0. Our analysis of 17 LCA studies gave an overall average ER value of about 3.1 for biodistillates, indicating substantial benefits for these fuels (both biodiesel and renewable diesel) in terms of life-cycle energy. However, the range of ER benefits is extremely large, depending upon assumptions and methodologies chosen. There are even a few cases where biodiesel scenarios gave lower ER values than the reference conventional fuel.

LCA results for GHG emissions are usually expressed in terms of relative global warming potential (GWP). This metric includes not only the effects of CO_2, but also of other GHG emissions that occur over the entire life-cycle. Emissions of N_2O are especially important, although there are significant uncertainties about the actual emissions levels of this potent greenhouse gas. In nearly every case in which comparisons are possible, the life-cycle GWP of biodistillate fuels is lower than that for conventional fuel. This is true for both biodiesel and renewable diesel fuels. However, as with ER, the reported GWP benefits of biodistillates vary widely from one study to the next. In most of the 20 studies we investigated, the GWP benefits of the biodistillate fuels ranged from 10% to 90%, with an overall average value of about 60%. There are a few exceptions, mainly due to assumptions of high N_2O emissions, where biodiesel scenarios showed overall GWP dis-benefits compared to conventional diesel.

Besides energy in puts and GWP, LCA analyses can be used to evaluate additional environmental impacts related to water resources, eutrophication, acidification, and other outcomes. While still a fairly immature area, these types of analyses are increasingly being investigated to give a more complete picture of biofuels' total life-cycle impacts.

10. Information Gaps and Recommendations

1. Many new triglyceride feedstocks are being investigated for 2nd Generation biodistillate production. The two currently receiving the greatest interest are microalgae and jatropha, though many others are also being explored, including castor oil, karanja, pongamia, soapnut oil, and others. Large scale production of these feedstocks raises issues about sustainability and environmental impacts. Additionally, the composition and properties of biodistillates (particularly biodiesel) produced from new triglyceride feedstocks would require investigation. As a point of illustration, castor oil is unique in containing significant amounts of ricinoleic acid, which is likely to impact the composition of biodistillates produced from it.

   Recommendation: CRC and its member companies should monitor developments in these areas, but no specific actions are recommended at this time.

2. Lignocellulosic materials are increasingly being investigated as feedstocks for production of transportation fuels, including biodistillates. While most activity has been directed towards production of alcohols or Fischer-Tropsch products, there is growing interest in thermal processes to produce pyrolysis oils that could be feedstocks for distillate fuels. Such pyrolyis-derived fuels raise concerns about product stability, handling, and blending. Additionally, the performance and emissions impacts of such fuels are largely unexplored.

   Recommendation: CRC and its member companies should monitor developments in these areas. Once pyrolysis oils are being used as feedstocks for fuel production, the properties and impacts of the derived biodistillate should be investigated.

3. Field surveys of biodistillate fuels have revealed problems with the quality of some fuels in the marketplace. The occurrence of "off-spec" fuels may be more common than is acceptable, particularly fuels produced and marketed by small operators. ASTM biodiesel standards have been developed or modified recently to address known problems in this area. For example, the Rancimat oxidative stability test was added to the standard specifications for B100 in 2007. In 2008, a new set of standard specifications was introduced (ASTM D 7467) for B6-B20 blends. No large-scale, systematic field survey of biodiesel fuel quality has been conducted since these new standards were introduced.

   Recommendation: CRC and its member companies should consider participating in a coordinated field survey project to evaluate the quality of biodiesel and biodiesel blends in the marketplace.

4. Accurate blending of biodistillates with conventional diesel is sometimes problematic, as indicated by analyses of fuels drawn from the marketplace. To promote public confidence and monitor compliance with renewable fuel standards, it is important to have a rapid, accurate, and inexpensive means of determining the biodiesel and renewable diesel contents in finished fuel blends.

Recommendation: CRC and its member companies should consider developing a real-time sensor to monitor both biodiesel and renewable diesel contents in finished biodistillate blends.

5. Exhaust emissions impacts of biodistillate fuels has been a subject of great interest. Based upon previous extensive testing, a consensus has arisen that in heavy-duty (HD) applications, use of biodiesel significantly reduces HC, CO, and PM emissions, but slightly increases NOx. To a first order approximation, these emissions effects are linear with biodiesel blend level. (The emissions effects are not as clear for LD applications, though they seem broadly consistent with HD.) However, individual HD studies report highly variable results. In addition, very little emissions work has been conducted using modern, low-emitting engines and biodiesel fuels that comply with today's ASTM standards.

   Recommendation: CRC and its member companies should monitor current emissions research (sponsored by CARB and others) investigating the emissions effects of typical biodistillate fuels in fairly modern HD engines. An additional test program may be considered (perhaps as an add-on to the ACES Program) in which biodistillate emissions effects are investigated in a 2010-certified HD engine. Differences in emissions between biodiesel and renewable diesel should be systematically investigated.

6. Compared to the criteria emissions (CO, HC, NOx, and PM) very little is known about the impacts of biodistillates upon mobile source air toxics (MSAT) emissions. Consisting of oxygenated species, it might be expected that carbonyl emissions would increase from use of biodiesel. However, the literature is not consistent on this point – some studies report an increase in carbonyls, while others do not.

   Recommendation: CRC and its member companies should consider sponsoring a carefully-controlled laboratory test program to investigate the effects of biodiesel and renewable diesel upon MSAT emissions from one or more modern diesel engines. Emisisons of carbonyls are of greatest concern, but impacts on other species – including aromatics, olefins, and PM – may also be of interest.

7. Questions have been raised in the past about the impacts of biodistillates upon engine performance and wear. Some studies (including those sponsored by CRC) have demonstrated problems, although most adverse effects are likely related to poor fuel housekeeping or use of off-spec fuels. No major studies in this area have been conducted using fuels meeting today's ASTM standard specifications.

   Recommendation: CRC and its member companies should consider sponsoring a carefully designed test program involving modern engines and fuel system materials to investigate possible adverse effects of biodistillates that (1) meet and (2) do not meet all applicable ASTM standard specifications. Field performance under realistic, low temperature conditions should also be considered.

8. LCA studies are becoming increasingly common for assessing the total energy inputs and environmental impacts of a particular fuel. Different LCA approaches, using a wide range of

input assumptions, can lead to dramatically different results. In particular, assumptions about land use changes and co-product allocation are extremely influential in determining the final LCA results.

Recommendation: CRC and its member companies should monitor developments in this area, and be prepared to critique LCA studies performed by other groups. To ensure reasonable assumptions and proper treatment of all fuels, CRC may wish to sponsor research in this area.

11. Acknowledgements

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12. List of Acronyms and Abbreviations

ACP	Acidification potential
API	American Petroleum Institute
ASTM	American Soc. for Testing and Materials International
B100	Neat (100%) biodiesel
B20	Blend of 20% biodiesel in petroleum diesel
BG/Y	Billion gallons per year
BHP	Brake horsepower
BOCLE	Ball on cylinder lubricity evaluator
BTL	Biomass-to-liquids
BOCLE	Ball on cylinder lubricity evaluator
BTU	British thermal unit
CARB	California Air Resources Board
CCI	Calculated cetane index
CEN	European Committee for Standardization
CFI	Cold flow improver
CFPP	Cold filter plugging point
CI	Compression ignition
CIDI	Compression ignition direct injection
CN	Cetane number
CO	Carbon monoxide
CO_2	Carbon dioxide
CP	Cloud point
CRC	Coordinating Research Council
DARPA	Defense Advanced Research Projects Agency
DI	Direct injection
DOE	U.S. Department of Energy
EBAMM	ERG Biofuel Analysis Meta-Model
EGR	Exhaust gas recirculation
EMA	Engine Manufacturers' Association
EN	European Norm
EPA	U.S. Environmental Protection Agency
EROI	Energy return on investment
EU	European Union
EUP	Eutrophication potential
FAEE	Fatty acid ethyl ester
FAME	Fatty acid methyl ester
FCC	Fluid catalytic cracking
FFA	Free fatty acid
FTD	Fischer Tropsch diesel
GHG	Greenhouse gas
GREET	Greenhouse gases, Regulated Emissions, and Energy use in Transportation model
GTL	Gas-to-liquids
GWP	Global Warming Potential
HDDV	Heavy-duty diesel vehicle
HEV	Hybrid electric vehicle
HFRR	High frequency reciprocating rig
HVO	Hydrotreated vegetable oil

ICE	Internal combustion engine
IDI	Indirect injection
IPCC	Intergovernmental Panel on Climate Change
LAD	Low aromatic diesel fuel
LCA	Life-cycle assessment
LCO	Light cycle oil
LDDV	Light-duty diesel vehicle
LTFT	Low temperature flow test
LUC	Land Use Change
MB/D	Million barrels per day
MG/Y	Million gallons per year
MMT/Y	Million metric tons per year
MSAT	Mobile source air toxic
NAAQS	National ambient air quality standard
NERD	Non-ester renewable diesel
N_2O	Nitrous oxide
NAAQS	National Ambient Air Quality Standards
NBB	National Biodiesel Board
NCWM	National Conference on Weights and Measures
NO	Nitric oxide
NO_2	Nitrogen dioxide
NOx	Oxides of nitrogen
NREL	National Renewable Energy Laboratory
O_3	Ozone
OSI	Oxidative Stability Index
PAH	Polycyclic aromatic hydrocarbon
PM	Particulate matter
PM_{10}	PM with diameter $\leq 10\ \mu m$
$PM_{2.5}$	PM with diameter $\leq 2.5\ \mu m$
POCP	Photochemical ozone creation potential
PP	Pour point
RME	Rapeseed methyl ester
ROW	Rest of world
SAE	Society of Automotive Engineers International
SCR	Selective catalytic reduction
SME	Soy methyl ester
SOx	Oxides of sulfur
SVO	Straight vegetable oil
TDP	Thermal de-polymerization
TTW	Tank-to-wheels
ULSD	Ultra-low sulfur diesel fuel
VGO	Vacuum gas oil
VOC	Volatile organic compound
WAP	Wax appearance point
WTE	Waste-to-energy
WTT	Well-to-tank
WTW	Well-to-wheels
WVO	Waste vegetable oil

13. Table of Conversion Factors

Land Area	1 Acre = 0.405 Hectares 1 Hectare = 10,000 m^2
Pressure	1 Atmosphere = 1.013 Bar 1 Atmosphere = .1013 MPa 1 Atmosphere = 14.7 PSI
Mass	1 Metric Tonne = 1000 kg = 2205 lb 1 U.S. Ton = .908 Metric Tonnes 1 lb. = .454 kg
Biomass Production	1 U.S. ton/acre = 2.242 Metric Tonnes/hectare
Volume	1 U.S. Gal. (liquid) = 3.785 Liters = 0.833 Imperial Gal. 1 m^3 = 264.172 U.S. Gallon (liquid)
Energy	1 kcal = 4.187 kJ 1 BTU = 1.055 kJ 1 BTU/lb. = 2.326 kJ/kg 1 BTU/Gal. = 0.279 kJ/L 1 Quad = 10^{15} BTU = 1.055 Exajoules
Power	1.0 Watt = 1.0 joule/sec = 3.413 BTU/hr 1.0 KW = 3413 BTU/hr = 1.341 horsepower 1.0 KW-hr = 3.6 MJ = 3413 BTU
Fuel Energy (Approximate, based on LHV)	1 Gal Gasoline = 115,000 BTU = 121 MJ 1 Gal Petroleum Diesel = 130,500 BTU = 137 MJ 1 Gal Biodiesel = 122,000 BTU = 128 MJ 1 Gal Ethanol = 75,700 BTU = 80 MJ

APPENDICES

Appendix I. Glossary of Fuel Terms

1st Generation Biofuels	Fuels produced from commonly available, edible food feedstocks via fermentation (such as grain to ethanol) or transesterification (such as vegetable oil to biodiesel).
2nd Generation Biofuels	Biofuels produced from non-food feedstocks (such as jatropha, algae, and lignocellulose) by any processing technology, or from edible feedstocks using advanced conversion processes (such as catalytic hydroprocessing).
Advanced Biofuel	Renewable fuel (other than ethanol from grain) that is derived from renewable biomass – particularly from lignocellulosic material.
Algal Fuel	Subset of biofuels, produced from algal lipids. Biodiesel is most common, but could also include renewable diesel.
Alternative Fuel	Any fuel produced from non-petroleum sources. Includes biofuels as well as liquid fuels produced from coal and natural gas.
Biodiesel	Fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oil or animal fats.
Biodistillate	Any mid-distillate fuel (diesel fuel, kerosene, jet fuel, or heating oil) produced from recently living plant or animal materials by a variety of processing technologies.
Biofuel	Fuel produced from recently living plants or animals. This includes gases, liquids, and solids produced via fermentation, digestion, enzymatic hydrolysis, thermal conversion, and other processes.
Biogas	Gas produced by biological breakdown of organic matter in the absence of oxygen. Generally arising from landfills or digestion of sewage material.
Biomass	Living or recently dead lignocellulosic plant matter that can be used as a fuel or fuel feedstock.
Cellulosic Fuel	Subset of biofuel, produced from lignocellulosic feedstocks.
Cetane Number	A measure of the ignition quality of a fuel based upon ignition delay in a compression ignition engine. The higher the cetane number, the shorter the ignition delay, and the better the ignition quality.
Clean Fuels	Ill-defined, colloquial term having variable meanings. Often used in regulatory language.
Cloud Point	Temperature at which a fuel sample first shows a cloud or haze of crystals when it is cooled under standard test conditions as defined in ASTM D2500.
Conventional Biofuel	Ethanol produced via fermentation of sugars derived from corn, sugar cane, or other edible feedstock.
Conventional Fuels	Any fuel produced from petroleum sources.
Fatty Acids	Any of the saturated or unsaturated mono-carboxylic acids that occur naturally in the form of mono-, di-, or tri-acylglycerides in animal fats and vegetable oils.
Fischer-Tropsch Diesel	Diesel fuel produced via gasification of organic feedstocks, followed by Fischer-Tropsch process to convert synthesis gas into non-aromatic, liquid hydrocarbons.
Fossil Fuel	Fuel produced from fossil resources – including coal, petroleum, and natural gas.

Gasification	Process involving high temperature thermal reaction of carbonaceous materials under reduced oxygen conditions to produce synthesis gas (mainly CO and H_2)
Glycerol (Glycerine)	By-product of biodiesel synthesis, arising from transesterification reaction of triglyceride feedstocks.
Green Diesel	Non-fossil hydrocarbon fuel produced by catalytic hydroprocessing of triglycerides from vegetable oils or animal fats. Synonymous with Renewable Diesel.
Hydroprocessing	Range of refinery processes involving catalytic treatment of feedstocks in the presence of hydrogen.
Pour Point	The lowest temperature at which a fuel will just flow when tested under standard conditions as defined in ASTM D97.
Pyrolysis	Process involving moderate temperature thermal reaction of carbonaceous materials under oxygen-free conditions to produce pyrolysis oil, gases, and char.
Pyrolysis Oil	Liquid produced via thermal treatment of organic solids in the absence of oxygen. With cellulosic feedstocks, the resulting oils are highly oxygenated.
Rancimet Test	Oxidative stability test procedure (EW14112) applied to biodiesel fuel. Based upon detection of secondary oxidation products from reaction of biodiesel with oxygen at elevated temperature.
Renewable Diesel	Non-fossil hydrocarbon fuel produced by catalytic hydroprocessing of triglycerides from vegetable oils or animal fats. Synonymous with Green Diesel.
Renewable Fuel	Gas, liquid, or solid fuel produced from modern biologic feedstocks (plants and animals) that can be replenished.
Synthesis Gas (syngas)	Principally carbon monoxide and hydrogen, produced via high temperature treatment of organic material from fossil or renewable sources.
Synthetic Fuel	Liquid fuel, produced from non-petroleum resources, generally via gasification and subsequent reaction of the synthesis gas.
Thermal Depolymerization	Process involving heat and pressure to decompose long-chain organic polymer structures into shorter-chain hydrocarbons that are useful as fuels or chemicals.
Transesterification	Chemical process involving reaction of triglycerides with an alcohol (usually methanol) to produce biodiesel.
Triacylglycerides (also called triglycerides)	Chemical constituents of animal fats and vegetable oils. Consist of fatty acid esters of glycerol.
Yellow Grease	Recovered vegetable oil and animal fats that have been used in cooking operations. Also called used cooking oil.

Appendix II. Biodistillate Bibliography

Reference	Pub Type	Year	Biofuel Feed-Stock	Fuel Prod. Tech.	Fuel Props. and Specs	Vehicle Emissi-ons	Fuel handling and Perform.	Life-Cycle Analysis	Econ.	Policy
A Preliminary Roadmap for the Development of Biomass in California;CEC-500-2006-095-D; California Energy Commission: Dec, 06.	Report	2006						x		x
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Abreu, F. R.; Alves, M. B.; Macedo, C. C. S.; Zara, L. F.; Suarez, P. A. Z. New multi-phase catalytic systems based on tin compounds active for vegetable oil transesterificaton reaction. Journal of Molecular Catalysts. Vol. 227, pp.263-267. 2005	Journal	2005		x						
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Activities and Accomplishments in Model Year 2007;State & Alternative Fuel Provider Fleet Programs/EPAct Fleet Information & Regulations; DOE. 08.	Report	2008								x
Adams, T. N.; Appel, B. S.; Einfeldt, C. T.; Freiss, J. H. Depolymerization Process of Conversion of Organic and Non-Organic Waste Materials into Useful Products. May 3, 2007.	Patent	2007		x						
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Reference	Pub Type	Year	Biofuel Feed-Stock	Fuel Prod. Tech.	Fuel Props. and Specs	Vehicle Emissi-ons	Fuel handling and Perform.	Life-Cycle Analysis	Econ.	Policy
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Agarwal, D. and Agarwal, A. K.. Performance and emissions characteristics of Jatropha oil (preheated and blends) in a direct injection compression ignition engine. Applied Thermal Engineering 27[13], 2314-2323. 2007.	Journal	2007	x		x		x		x	
Agarwal, D., Kumar, L., and Agarwal, A. K., Performance evaluation of a vegetable oil fuelled compression ignition engine, *Renewable Energy*, Vol. 33, No. 6, 2008, pp. 1147-1156.	Journal	2008	x		x		x		x	
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Ahouissoussi, N. B. C.; Wetzstein, M. E. A comparative cost analysis of biodiesel, compressed natural gas, methanol, and diesel for transit bus systems. Resource and Energy Economics 1998, 20 (1), 1-15.	Journal	1998							x	
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Alleman, T. L. and McCormick, R. L., "Analysis of Coconut-Derived Biodiesel and Conventional Diesel Fuel Samples from the Philippines," NREL/MP-540-38643, 2006.	Report	2006			x		x			
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Reference	Pub Type	Year	Biofuel Feed-Stock	Fuel Prod. Tech.	Fuel Props. and Specs	Vehicle Emissi-ons	Fuel handling and Perform.	Life-Cycle Analysis	Econ.	Policy
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Bhusnoor, S. S., Babu, M. K. G., and Subrahmanyam, J. P., "Characterization and Lubricity Testing (SRV Wear Tester) of Diesel and Diesel Biodiesel (LOME) Blends," *SAE International*, 2008, SAE 2008-28-0042.	Paper	2008			x	x	x			
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Reference	Pub Type	Year	Biofuel Feed-Stock	Fuel Prod. Tech.	Fuel Props. and Specs	Vehicle Emissi-ons	Fuel handling and Perform.	Life-Cycle Analysis	Econ.	Policy
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Reference	**Pub Type**	**Year**	**Biofuel Feed-Stock**	**Fuel Prod. Tech.**	**Fuel Props. and Specs**	**Vehicle Emissi-ons**	**Fuel handling and Perform.**	**Life-Cycle Analysis**	**Econ.**	**Policy**
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Chiu, C. W.; Dasari, M. A.; Sutterlin, W. R.; Suppes, G. J. Removal of residual catalyst from simulated biodiesel's crude glycerol for glycerol hydrogenolysis to propylene glycol. Industrial & Engineering Chemistry Research 2006, 45 (2), 791-795	Journal	2006		x	x					

Reference	Pub Type	Year	Biofuel Feed-Stock	Fuel Prod. Tech.	Fuel Props. and Specs	Vehicle Emissi-ons	Fuel handling and Perform.	Life-Cycle Analysis	Econ.	Policy
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Reference	Pub Type	Year	Biofuel Feed-Stock	Fuel Prod. Tech.	Fuel Props. and Specs	Vehicle Emissi-ons	Fuel handling and Perform.	Life-Cycle Analysis	Econ.	Policy
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Di Serio, M., Tesser, R., Pengmei, L., and Santacesaria, E., "Heterogeneous catalysts for biodiesel production," *Energy & Fuels*, Vol. 22, 2008, pp. 207-217.	Journal	2008		x						
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Reference	Pub Type	Year	Biofuel Feed-Stock	Fuel Prod. Tech.	Fuel Props. and Specs	Vehicle Emissi-ons	Fuel handling and Perform.	Life-Cycle Analysis	Econ.	Policy
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Reference	Pub Type	Year	Biofuel Feed-Stock	Fuel Prod. Tech.	Fuel Props. and Specs	Vehicle Emissi-ons	Fuel handling and Perform.	Life-Cycle Analysis	Econ.	Policy
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Reference	Pub Type	Year	Biofuel Feed-Stock	Fuel Prod. Tech.	Fuel Props. and Specs	Vehicle Emissi-ons	Fuel handling and Perform.	Life-Cycle Analysis	Econ.	Policy
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Reference	Pub Type	Year	Biofuel Feed-Stock	Fuel Prod. Tech.	Fuel Props. and Specs	Vehicle Emissi-ons	Fuel handling and Perform.	Life-Cycle Analysis	Econ.	Policy
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Fang, H. L.; McCormick, R. L. Spectroscopic Study of Biodiesel Degradation Pathways. SAE International 2006, 2006-01-3300.	Paper	2006					x			
Fang,H.L; Alleman,T.L.; McCormick,R.L. "Quantification of Biodiesel Content in Fuels and Lubricants by FTIR and NMR Spectroscopy," *SAE International*, 2006, 2006-01-3301.	Paper	2006			x		x			
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Fargione, J.; Hill, J.; Tilman, D.; Polasky, S.; Hawthorne, P. Land clearing and the biofuel carbon debt. Science 2008, 319, 1235-1237.	Journal	2008						x		
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Feng, J.; Yuan, M. L.; Chen, H.; Li, X. J. Study and applications of catalytic hydrogenolysis of glycerol. Progress in Chemistry 2007, 19 (5), 651-658.	Journal	2007		x						
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Fernando, S., Hall, C., and Jha, S., "NOx reduction from biodiesel fuels," *Energy & Fuels*, Vol. 20, No. 1, 2006, pp. 376-382.	Journal	2006				x				
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Ferreira, D. A. C.; Meneghetti, M. R.; Meneghetti, S. M. P.; Wolf, C. R. Methanolysis of soybean oil in the presence of tin(IV) complexes. *Applied Catalysis A-General* 2007, 317 (1), 58-61.	Journal	2007		x						

Reference	Pub Type	Year	Biofuel Feed-Stock	Fuel Prod. Tech.	Fuel Props. and Specs	Vehicle Emissi-ons	Fuel handling and Perform.	Life-Cycle Analysis	Econ.	Policy
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Fischer, J. Biodiesel Quality Management: The AGQM Story. In The Biodiesel Handbook, Knothe, G., Van Gerpen, J., Krahl, J., Eds.; AOCS Press, Urbana, IL 61802: 2005; pp 204-210.	Book Chapter	2005		x		x				
Fleming, J.S., Stanciulescu, V., Reilly-Roe, P. Policy considerations derived from transportation fuel life cycle assessment. SAE 2007-01-1606 (2007).	Paper	2007						x		x
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Reference	Pub Type	Year	Biofuel Feed-Stock	Fuel Prod. Tech.	Fuel Props. and Specs	Vehicle Emissi-ons	Fuel handling and Perform.	Life-Cycle Analysis	Econ.	Policy
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Gartner, S. O.; Reinhardt, G. A. Environmental Implications of Biodiesel (Life-Cycle Assessment). In The Biodiesel Handbook, Knothe, G., Van Gerpen, J., Krahl, J., Eds.; AOCS Press, Urbana, IL 61802: 2005; pp 219-230.	Book Chapter	2005						x		
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Geller, D. P., Adams, T. T., Goodrum, J. W., and Pendergrass, J., "Storage stability of poultry fat and diesel fuel mixtures: Specific gravity and viscosity," *Fuel*, Vol. 87, 2008, pp. 92-102.	Journal	2008					x			
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Georgogianni, K. G., Kontominas, M. G., Tegou, E., Avlonitis, D., and Gergis, V., "Biodiesel production: Reaction and process parameters of alkali-catalyzed transesterification of waste frying oils," *Energy & Fuels*, Vol. 21, 2007, pp. 3023-3027.	Journal	2007		x	x					
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Reference	Pub Type	Year	Biofuel Feed-Stock	Fuel Prod. Tech.	Fuel Props. and Specs	Vehicle Emissi-ons	Fuel handling and Perform.	Life-Cycle Analysis	Econ.	Policy
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Hanh, H. D.; Dong, N. T.; Starvarache, C.; Okitsu, K.; Maeda, Y.; Nishimura, R. Methanolysis of triolein by low frequency ultrasonic irradiation. Energy Conversion and Management 2008, 49276-280	Journal	2008		x						
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Reference	Pub Type	Year	Biofuel Feed-Stock	Fuel Prod. Tech.	Fuel Props. and Specs	Vehicle Emissi-ons	Fuel handling and Perform.	Life-Cycle Analysis	Econ.	Policy
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Reference	Pub Type	Year	Biofuel Feed-Stock	Fuel Prod. Tech.	Fuel Props. and Specs	Vehicle Emissi-ons	Fuel handling and Perform.	Life-Cycle Analysis	Econ.	Policy
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Reference	Pub Type	Year	Biofuel Feed-Stock	Fuel Prod. Tech.	Fuel Props. and Specs	Vehicle Emissi-ons	Fuel handling and Perform.	Life-Cycle Analysis	Econ.	Policy
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Reference	Pub Type	Year	Biofuel Feed-Stock	Fuel Prod. Tech.	Fuel Props. and Specs	Vehicle Emissi-ons	Fuel handling and Perform.	Life-Cycle Analysis	Econ.	Policy
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Reference	Pub Type	Year	Biofuel Feed-Stock	Fuel Prod. Tech.	Fuel Props. and Specs	Vehicle Emissi-ons	Fuel handling and Perform.	Life-Cycle Analysis	Econ.	Policy
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Reference	Pub Type	Year	Biofuel Feed-Stock	Fuel Prod. Tech.	Fuel Props. and Specs	Vehicle Emissi-ons	Fuel handling and Perform.	Life-Cycle Analysis	Econ.	Policy
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Reference	Pub Type	Year	Biofuel Feed-Stock	Fuel Prod. Tech.	Fuel Props. and Specs	Vehicle Emissi-ons	Fuel handling and Perform.	Life-Cycle Analysis	Econ.	Policy
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Reference	Pub Type	Year	Biofuel Feed-Stock	Fuel Prod. Tech.	Fuel Props. and Specs	Vehicle Emissi-ons	Fuel handling and Perform.	Life-Cycle Analysis	Econ.	Policy
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Reference	Pub Type	Year	Biofuel Feed-Stock	Fuel Prod. Tech.	Fuel Props. and Specs	Vehicle Emissi-ons	Fuel handling and Perform.	Life-Cycle Analysis	Econ.	Policy
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Reference	Pub Type	Year	Biofuel Feed-Stock	Fuel Prod. Tech.	Fuel Props. and Specs	Vehicle Emissi-ons	Fuel handling and Perform.	Life-Cycle Analysis	Econ.	Policy
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Reference	Pub Type	Year	Biofuel Feed-Stock	Fuel Prod. Tech.	Fuel Props. and Specs	Vehicle Emissi-ons	Fuel handling and Perform.	Life-Cycle Analysis	Econ.	Policy
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Reference	Pub Type	Year	Biofuel Feed-Stock	Fuel Prod. Tech.	Fuel Props. and Specs	Vehicle Emissi-ons	Fuel handling and Perform.	Life-Cycle Analysis	Econ.	Policy
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Ramadhas, A. S.; Jayaraj, S.; Muraleedharan, C. Characterization and effect of using rubber seed oil as fuel in the compression ignition engines. *Renewable Energy* 2005, 30 (5), 795-803.	Journal	2005			x		x			
Ramadhas, A. S.; Muraleedharan, C.; Jayaraj, S. Performance and emission evaluation of a diesel engine fueled with methyl esters of rubber seed oil. *Renewable Energy* 2005, 30 (12), 1789-1800	Journal	2005		x	x	x				
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Reksowardojo, I. K.; Lubis, I. H.; Manggala, S. A.; Brodjonegoro, T. P.; Soerawidjaya, T. H.; Arismunandar, W. Performance and Exhaust Gas Emissions of Using Biodiesel Fuel from Physic Nut (Jatropha Curcas L.) Oil on a Direct Injection Diesel Engine (DI). SAE International 2007, JSAE 20077278 (SAE 2007-01-2025).	Paper	2007				x	x			
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Reference	Pub Type	Year	Biofuel Feed-Stock	Fuel Prod. Tech.	Fuel Props. and Specs	Vehicle Emissi-ons	Fuel handling and Perform.	Life-Cycle Analysis	Econ.	Policy
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Reference	Pub Type	Year	Biofuel Feed-Stock	Fuel Prod. Tech.	Fuel Props. and Specs	Vehicle Emissi-ons	Fuel handling and Perform.	Life-Cycle Analysis	Econ.	Policy
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Zhang, Y. and Boehman, A. L., "Impact of biodiesel on NOx emissions in a common rail direct injection diesel engine," *Energy & Fuels*, Vol. 21, No. 4, 2007, pp. 2003-2012.	Journal	2007				x				
Zhang, Y.; Dube, M. A.; McLean, D. D.; Kates, M. Biodiesel production from waste cooking oil: 1. Process design and technological assessment. *Bioresources Technol.* 2003, 89, 1-16.	Journal	2003		x						
Zheng, M., Mulenga, M. C., Reader, G. T., Wang, M. P., Ting, D. S. K., and Tjong, J., "Biodiesel engine performance and emissions in low temperature combustion," *Fuel*, Vol. 87, No. 6, 2008, pp. 714-722.	Journal	2008				x	x			
Zheng, M.; Skelton, R. L.; Mackley, M. R. Biodiesel reaction screening using oscillatory flow meso reactors. Process Safety and Environmental Protection 2007, 85, 365-371.	Paper	2008				x	x			
Zhou, C. H. C.; Beltramini, J. N.; Fan, Y. X.; Lu, G. Q. M. Chemoselective catalytic conversion of glycerol as a biorenewable source to valuable commodity chemicals. Chemical Society Reviews 2008, 37 (3), 527-549.	Journal	2008		x						
Zhou, H., Lu, H. F., and Liang, B., "Solubility of multicomponent systems in the biodiesel production by transesterification of Jatropha curcas L. oil with methanol," *Journal of Chemical and Engineering Data*, Vol. 51, No. 3, 2006, pp. 1130-1135.	Journal	2006		x						
Zhu, L. Y.; Zong, M. H.; Wu, H. Efficient lipid production with Trichosporon fermentans and its use for biodiesel preparation. Bioresource Technology 2008, 99 (16), 7881-7885.	Journal	2008			x					

Reference	Pub Type	Year	Biofuel Feed-Stock	Fuel Prod. Tech.	Fuel Props. and Specs	Vehicle Emissi-ons	Fuel handling and Perform.	Life-Cycle Analysis	Econ.	Policy
Zygarlicke, C. J.; Schmidt, D. D.; Olson, E. S.; Leroux, K. M.; Wocken, C. A.; Auick, T. A.; Williams, K. D. EERC Center for BIomass Utilization 2005; U.S. DOE. DOE/GO/13055-1; Jul 28, 2008.	Report	2005								

Appendix III. Algae Players

Company	Location	Focus	Type	Facility	Other Notes	Website
A2BE Carbon Capture	Boulder, CO	Deploy algae growth technology on a global industrial scale	Closed photo-bioreactor "algae water beds" for growing green micro algae	Commissioning a prototype facility in 2008 Algae oils will be processed via transesterification	Patent pending on their algae growth system	www.algaeatwork.com
AG Energy (also known as Infinifuel)	Dayton, NV	Researching growing systems using geothermal heat	Geothermally heated growing ponds	300 acre facility in Wabuska, NV	No active production reported	www.agenergycorp.com
Algae Link	Netherlands	Algae production equipment	Photo-bioreactors and green houses	Small scale (2-4 kg) pilot plant for sale	Working with Air France KLMSA to develop algae oil to be used as a jet fuel	www.algaelink.com
Algal Biomass Association		Non-profit organization dedicated to the advancement of algal biomass production technologies				www.algalbiomass.org/
Algenol Biofuels		Direct production of ethanol from algae			First commercial project expected in 2009 in Mexico	www.algenolbiofuels.com
Aquaflow Bionomic	New Zealand	Developing methods of harvesting algae and producing biodiesel	Open oxidation ponds of standard effluent management systems	Demo plant at Marlborough Sewage plant: 60 ha of open ponds		www.aquaflowgroup.com
Aquatic Energy	Lake Charles, LA	Development, construction and operation of algal growth ponds using their own process	Process system using open ponds	2 acre pilot plant 250 ha commercial plant in planning stages		www.aquaticenergy.com
Aurora BioFuels Inc	Alameda, CA	Researching methods to produce biodiesel from algal oil	Process system using open ponds			www.aurorabiofuels.com
Bionavitas	Washington State	Developing technology for high volume production growth of microalgae	Photo-bioreactors		Startup facility with plans commercialize within 4 years	www.bionavitas.com
Bodega Algae	Jamaica Plain, MA	Improved methods of introducing light and nutrients to promote algae growth	Experimental photobioreactors			www.bodegaalgae.com
Cellana	Hawaii	Building a algae growth and oil extraction facility to produce biodiesel	Open-air ponds	Kona Demonstration Facility is 25 ha Plans to scale facility to 1000 ha in 2 years and 20,000 ha if successful	Started with Shell and HR Petroleum	www.cellana.com

Company	Location	Focus	Type	Facility	Other Notes	Website
Chevron	San Ramon, CA	Funding research to develop algae strains and to research bio-oil reforming			Partnership with NREL, focusing on transportation fuels	www.chevron.com
Circle Biodiesel and Ethanol Corporation	San Marcos, CA	Sells and installs biodiesel plants and biodiesel processers	Commercial photo-bioreactor and harvesting systems available for algae production	None	$195k system processes 1 gallon of algal oil per minute	None
Community Fuels	Encinitas, CA	One R&D topic is to address key issues in commercial scale production of biodiesel from algae				www.communityfuels.com
DARPA		Funding algae research to develop military jet fuel				www.darpa.mil
Diversified Energy	Gilbert, AZ	Development and commercialization of algae growth systems (DEC-XLR Simgae™)	Photo-bioreactors (Algae Biotape™)	Currently conducting concept demonstrations at their labs and at a dairy farm in Casa Grande, AZ	Project with XL Renewables Biorefinery. $25k-35k per acre, 40-60 tons dry algae per acre w/ oil content 10-40%	www.diversified-energy.com
Energy Farms						
Enhanced Biofuels & Technologies	London and India	Using algae growth to reduce CO2 emissions from flue gases	Combination of photo-bioreactors and open raceway ponds	None noted		www.ebtplc.com
General Atomics	Carlsbad, NM	Develop improved processes for growing algae and extracting oil	Outdoor ponds for salt-water microalgae	Research scale plant in NM	Partnership with Center for Excellence of Hazardous Materials Management (CEHMM) and Texas Agrilife	www.ga.com
General Electric					Participating in DARPA-funded project	
Genifuel	Baltimore, MD	Gasification of algal biomass	Micro algae (including cyanobacteria)			genifuel.com
Global Green Solutions	Vancouver, BC	Developing a high density vertical bioreactor (HDVB) to produce algae with supercritical oil extraction	Photo-bioreactors	Proof of concept (using chlorella algae)	Joint project with Valcent	www.globalgreensoluctionsinc.com
Green Fuel	Cambridge, MA	Developing and selling systems to recycle CO2 from smokestack, fermentation, and geothermal gases via algae growth	Not stated	"Has successfully installed systems at gas, coal, and oil burning facilities" Facility at Redhawk Power Plant in AZ w/ APS	Working with IGV to deploy bioreactor technology	www.greenfuelonline.com

Company	Location	Focus	Type	Facility	Other Notes	Website
Green Shift		No mention of algae on webpage--just ethanol and biodiesel from corn				www.greenshift.com
Green Star Products	Chula Vista, CA	Research on algae growth formula Montana Micronutrient Booster (MMB) Focused more on algae farming		Working to develop a high production facility	Moving to a new lab facility in Utah	www.greenstarusa.com
Honeywell UOP		Developing processing technology to convert algal oils to transportation fuels			Participating in DARPA-funded project	www.uop.com
HR BioPetroleum	San Diego, CA	Pairing algae production with industrial processes to reduce CO2 emissions	Coupled close-cultured bioreactors and open ponds in two-stage process	Kona Demonstration Facility--2ha validation facility in Hawaii (with Shell and Cellana)	Looking toward commercial-scale algae growth and marketing final product	www.hrbp.com
IGV	Germany	Have commercially available photobioreactors	Photobioreactors	Existing facilities used to produce algae for cosmetics	Working with GreenFuel to deploy bioreactor technology to accelerate commercialization of biofuels from algae	www.igv-gmbh.de
Imperium Renewables	Seattle, WA	Agreement with solazyme to provide algal oil for their biodiesel facility in Seattle		Biodiesel facility in Seattle	Doesn't make or research algae	www.imperiumrenewables.com
Inventure Chemical	Seattle, WA	Algae-specific biofuel conversion processes (patent pending process)	A variety of algae species can be used, ranging from 1-10 micron and fresh- or salt-water	A commercial prototype algae biofuel processing facility in Seattle is producing biodiesel and ethanol from algae sourced from facilities in Israel, Arizona, and Australia		www.inventurechem.com
Kent SeaTech Corp	San Diego, CA	Fish hatchery and aquaculture company			No mention of algae on website, however, working on algae REDUCTION for Salton Sea	www.kentseatech.com
Kwikpower	UK	Licensed algae production technology developed at NREL (Advanced Biofuels Technology)	A novel strain of microalgae developed by Dr Arthur Nonomura at UC Berkeley		No website found, article at:	http://www.greencarcongress.com/2006/06/kwikpower_acqui.html

Company	Location	Focus	Type	Facility	Other Notes	Website
LiveFuels Inc	Menlo Park, CA	A national alliance of labs and scientists working on algae to biofuels			Partnership with Sandia, NREL and DOE among other private labs	www.livefuels.com
Menova Energy	Canada	Solar energy solution company	Developed a photobioreactor	Proposed pilot project	Partnering with Trident Exploration to produce algae from processing of petroleum products	www.power-spar.com
MidContinental Chemical Inc		Biodiesel facility, no mention of algae research				www.mcchemical.com
National Algae Association	The Woodlands, TX	National trade association for the algae industry				www.nationalalgaeassociation.com
National Renewable Energy Lab (NREL)	Golden, CO	Federally funded research organization investigating algae-to-fuels technologies				www.nrel.gov
Neptune Industry	Florida	Fish farm and aquaculture	"Floating sock" in a rock quarry fed with fish waste	Projected yields of 10,000 gallons/acre	Florida farm to Fuel grant	
Old Dominion University	Virginia	Algae growth for wastewater treatment	algae at municipal sewage treatment plants		No specific website, article found at:	http://www.odu.edu/oduhome/news/spotlight111.shtml
Oregon State Univ Sustainable Technologies Lab	Corvallis, OR		Experimental photobioreactors			
Organic Fuels	Houston, TX	Sponsored research on extraction of oil from algae (University of Texas, Austin)				www.organicfuels.com
Originoil	Los Angeles, CA	Algae cultivation and oil extraction (patent pending technology)	Photo-bioreactor with Quantum Fracturing™ (water, CO2 and other nutrients are fractured at high pressure and injected into system) Extraction via proprietary catalysts	None mentioned		www.originoil.com
PetroAlgae	Melbourne, FL	Commercializing technologies to grow and harvest oil from algae	Natural strains of micro-algae developed by University of Arizona Cultivated in photo-bioreactors	R&D site at Fellsmere, FL	Plan on 1 year to commercial	www.petroalgae.com

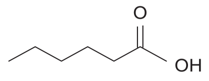
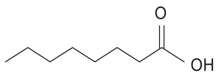
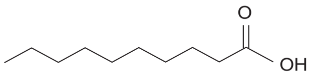
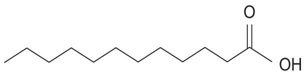
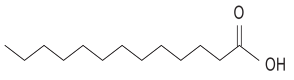
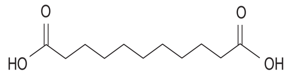
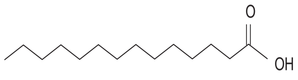
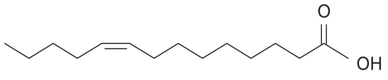
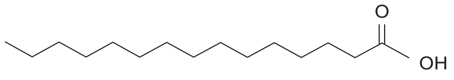
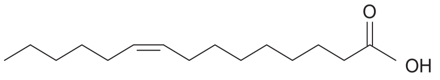
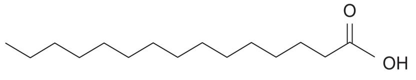
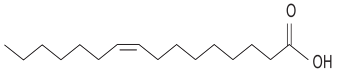
Company	Location	Focus	Type	Facility	Other Notes	Website
PetroSun BioFuels Refining	Arizona	Operations include oil and gas exploration, development, production, oilfield tubular sales and algae-to-algal oil alternative biofuel production	Open growing ponds	1100 acres of growing ponds at developing facility in Rio Hondo, TX	Approved plans for a pilot plant to produce algae at a waste water treatment plant in AZ. Planning on building a commercial farm system in Queensland, Australia with Icon Energy. Also engaged in negotiations to build facility in New South Wales, Australia.	www.petrosuninc.com
Sapphire Energy	San Diego	Developing a platform that produces "green crude" and biohydrocarbon fuels from a modified algae	Photobioreactors		Renewable 91 octane gasoline, not biodiesel. Also working with Imperium Renewables on jet fuel.	www.sapphireenergy.com/
SeaAg Inc						No webpage
Shell						http://www.shell.com/home/content/responsible_energy/energy_for_the_future/biofuels/biofuels_22032008.html
Solazyme	South San Francisco, CA	Conducts research to synthetically evolve marine microbes to produce a variety of valuable products using proprietary genetic engineering method	Microbial fermentation process that allows algae to produce oil quickly and efficiently, without sunlight Process can utilize waste glycerol and many cellulosic materials		SoladieselRD™ passed ASTM D-975 specifications.	www.solazyme.com
Solix Biofuels	Fort Collins, CO	Designing and building photobioreactors that can produce algae on a large scale Researching different types of algae	Photobioreactors	Planning on building test reactor that will utilize CO2 from New Belgium Brewing Co	http://www.popsci.com/node/10164	www.solixbiofuels.com
Targeted Growth		No mention of algae on webpage				www.targetedgrowth.com
Texas Agrilife Research	Texas	Phased R&D program for developing promising algae strains, algae production systems, and algae oil separation systems	Microalgae	Initial demonstration facility could be scaled to 2,000 acres	$4M research contract with General Atomics.	www.agriliferesearch.tamu.edu

Appendix III (cont.)

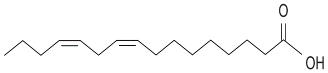
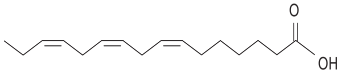
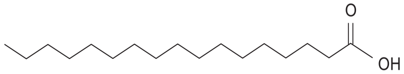
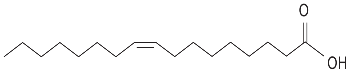
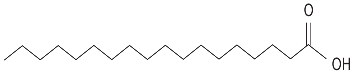
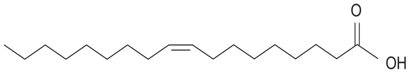
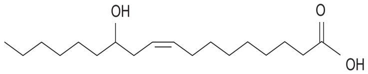
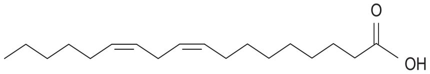
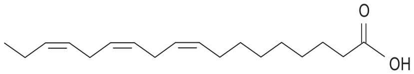
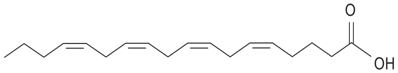
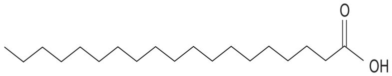
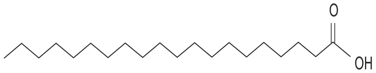
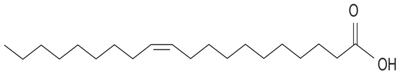
Company	Location	Focus	Type	Facility	Other Notes	Website
Texas Clean Fuels						no web page, maybe an initiative
Trident Exploration	Canada	Natural gas exploration and development company focused on Natural Gas from coal	Developed a photobioreactor	Proposed pilot project	Partnering with Menova Energy to produce algae from processing of petroleum products.	www.tridentexploration.ca
University of Minnesota, Center for Biorefining	Minnesota	Developing ways to grow mass quantities of algae, identifying promising strains, and exploring options for treating residues	Algae is grown in sewage plant discharge			/biorefining.cfans.umn.edu
University of New Hampshire Biodiesel Group	New Hampshire	Investigating redesigning waste water treatment plants to use raceway ponds to grow algae for biodiesel extraction	Open raceway ponds		Also investigating using algae mush as a fertilizer	www.unh.edu/p2/biodiesel/
University of North Dakota--Energy and Environmental Research Center	Grand Forks, ND	EERC has a biomass utilization research program which includes all types of feedstocks			Research CO2 sequestration with switchgrass and algae.	www.undeerc.org/programareas/renewableenergy
University of Texas	Texas	Provides nearly 3000 strains of algae to the community	Researching cyanobacteria for biofuels in photobioreactors	Lab-scale		www.utex.org
US Sustainable Energy	Texas	Biodiesel producer and supplier	Testing biodiesel production from algae oil supplied by Green Star	Under negotiations to install photobioreactors from Green Star		www.ussec.us
Valcent Products	Vancouver, BC El Paso, TX	Researches and develops life-enhancing products	High-Density Vertical Photo-bioreactor (HDVP)	Research facility in El Paso, TX	Working with Global Green Solutions	www.valcent.net
Xcel Energy	Minnesota	Utility provider, funding algae research	Utility			www.xcelenergy.com
XL Renewables	Phoenix, AZ	Algae biomass production technology	Developed XL super trough liner for open algae ponds	Algae Development Center on 25 acres in Casa Grande, AZ to test production system design and operation, algae variety development, and system optimization		www.xldairygroup.com

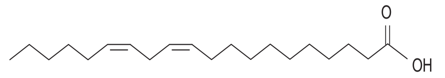
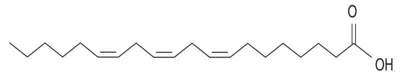
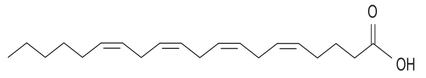
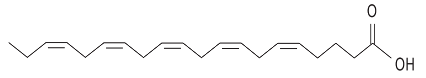
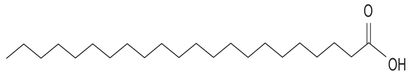
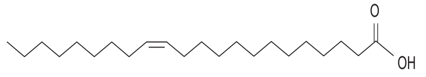
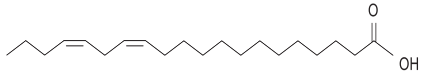
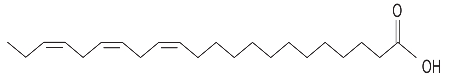
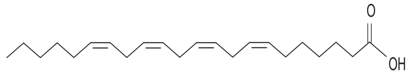
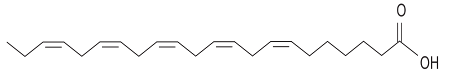
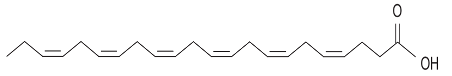
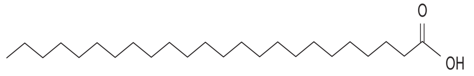
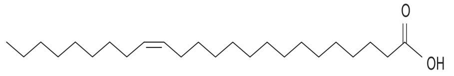
Appendix IV. Composition and Properties of Biodiesel Fuel and its Precursors

Appendix IV-1. Fatty Acid Precursors to Biodistillates

Common Name	Formal Name	CAS. No.	Abbreviation	Molecular Formula	Molecular Weight	Molecular Structure
Caproic Acid	Hexanoic Acid	142-62-1	6:0	$C_6H_{12}O_2$	116.16	
Caprylic Acid	Octanoic Acid	124-07-2	8:0	$C_8H_{16}O_2$	144.22	
Capric Acid	Decanoic Acid	334-48-5	10:0	$C_{10}H_{20}O_2$	172.27	
Lauric Acid	Dodecanoic Acid	143-07-7	12:0	$C_{12}H_{24}O_2$	200.32	
Tridecylic Acid	Tridecanoic Acid	638-53-9	13:0	$C_{13}H_{26}O_2$	214.35	
Brassylic Acid	1,11-Undecane-dicarboxylic Acid	505-52-2	13:0	$C_{13}H_{24}O_4$	244.33	
Myristic Acid	Tetradecanoic Acid	544-63-8	14:0	$C_{14}H_{28}O_2$	228.38	
Myristoleic Acid	cis-9-Tetradece-noic Acid	544-64-9	14:1	$C_{14}H_{26}O_2$	226.26	
Pentadecanoic Acid	Pentadecanoic Acid	1002-84-2	15:0	$C_{15}H_{30}O_2$	242.40	
Pentadecenoic Acid	cis-9-Pentadecenoic Acid		15:1	$C_{15}H_{28}O_2$	240.28	
Palmitic Acid	Hexadecanoic Acid	57-10-3	16:0	$C_{16}H_{32}O_2$	256.43	
Palmitoleic Acid	cis-9-Hexadecenoic Acid	373-49-9	16:1	$C_{16}H_{30}O_2$	254.42	

Appendix IV-1 (cont.)

Common Name	Formal Name	CAS. No.	Abbreviation	Molecular Formula	Molecular Weight	Molecular Structure
Hexadecadienoic Acid	cis-9,12-Hexadecadienoic Acid		16:2	$C_{16}H_{28}O_2$	252.40	
Hexadecatrienoic Acid	cis-7,10,13-Hexadecatrienoic Acid		16:3	$C_{16}H_{26}O_2$	250.38	
Margaric Acid	Heptadecanoic Acid	506-12-7	17:0	$C_{17}H_{34}O_2$	270.46	
Heptadecenoic Acid	cis-9-Heptadecenoic Acid		17:1	$C_{17}H_{32}O_2$	268.44	
Stearic Acid	Octadecanoic Acid	57-11-4	18:0	$C_{18}H_{36}O_2$	284.48	
Oleic Acid	cis-9-Octadecenoic Acid	112-80-1	18:1	$C_{18}H_{34}O_2$	282.47	
Ricinoleic Acid	12-Hydroxy-*cis*-9-Octadecenoic Acid	141-22-0	18:1	$C_{18}H_{34}O_3$	298.46	
Linoleic Acid	cis-9,12-Octadecadienoic Acid	60-33-3	18:2	$C_{18}H_{32}O_2$	280.46	
Linolenic Acid	cis-9,12,15-Octadecatrienoic Acid	463-40-1	18:3	$C_{18}H_{30}O_2$	278.44	
Stearidonic Acid	cis-5,8,11,14-Octadecatetraenoic Acid	20290-75-9	18:4	$C_{18}H_{28}O_2$	276.40	
Nonadecylic Acid	Nonadecanoic Acid	646-30-0	19:0	$C_{19}H_{38}O_2$	298.51	
Arachidic Acid	Eicosanoic Acid	506-30-9	20:0	$C_{20}H_{40}O_2$	312.54	
Gondoic Acid	cis-11-Eicosenoic Acid	5561-99-9	20:1	$C_{20}H_{38}O_2$	310.53	

Common Name	Formal Name	CAS. No.	Abbreviation	Molecular Formula	Molecular Weight	Molecular Structure
Auricolic Acid	cis-11,14-Eicosadienoic Acid	2091-39-6	20:2	$C_{20}H_{36}O_2$	308.51	
Eicosatrienoic Acid	cis-8,11,14-Eicosatrienoic Acid	1783-84-2	20:3	$C_{20}H_{34}O_2$	306.49	
Arachidonic Acid	cis-5,8,11,14-Eicosatetraenoic Acid	506-32-1	20:4	$C_{20}H_{32}O_2$	304.48	
Eicosapentaenoic Acid	cis-5,8,11,14,17-Eicosapentaenoic Acid	10417-94-4	20:5	$C_{20}H_{30}O_2$	302.46	
Behenic Acid	Docosanoic Acid	112-85-6	22:0	$C_{22}H_{44}O_2$	340.60	
Erucic Acid	cis-13-Docosenoic Acid	112-86-7	22:1	$C_{22}H_{42}O_2$	338.58	
Docosadienoic Acid	cis-13,16-Docosadienoic Acid	17735-98-7	22:2	$C_{22}H_{40}O_2$	336.56	
Docosatrienoic Acid	cis-13,16,19-Docosatrienoic Acid	28845-86-5	22:3	$C_{22}H_{38}O_2$	334.54	
Adrenic Acid	cis-7,10,13,16-Docosatetraenoic Acid	122068-08-0	22:4	$C_{22}H_{36}O_2$	332.52	
Docosapentaenoic Acid	cis-7,10,13,16,19-Docosapentaenoic Acid	2006-01-1	22:5	$C_{22}H_{34}O_2$	330.50	
Docosahexaenoic Acid	cis-4,7,10,13,16,19-Docosahexaenoic Acid	6217-54-5	22:6	$C_{22}H_{32}O_2$	328.49	
Lignoceric Acid	Tetracosanoic Acid	557-59-5	24:0	$C_{24}H_{48}O_2$	368.65	
Nervonic Acid	cis-15-Tetracosenoic Acid	506-37-6	24:1	$C_{24}H_{46}O_2$	366.63	

Appendix IV-2. Compositional Profiles of Triglycerides (wt.%)

Page 1 of 5

Fatty Acid		Almond Kernel	Andiroba	Babassu	Bay Laurel leaf	Camelina	Canola	Castor Oil	Caycuma	Cocoa Butter	Coconut Oil	Corn Oil	Cotton-seed Oil
Common Name	Abbrev.												
Capriotic	6:0										.4 - .5		
Caprylic	8:0			2.6 - 7.3							.7 - 9.8		
Capric	10:0			1.2 - 7.6							.6 - 9.7	3.9	
Lauric	12:0			40 - 48							44.6 - 54.1		
Tridecylic	13:0												
Myristic	14:0			11 - 27							13 - 20.6	.1 - 2	0 - 2
Myristoleic	14:1												
Pentadanoic	15:0												
Pentadecenoic	15:1												
Palmitic	16:0	6.5	27	5.2 - 11	25.9	5.4	1.5 - 6	.7 - 1.1		26	6.1 - 10.5	7 - 13	11.7- 28
Palmitoleic	16:1	1.4	1		0.3						0.1	.2 - 1.6	
Hexadecadienoic	16:2												
Hexadecatrienoic	16:3												
Heptadecanoic	17:0											.1 [2]	
Heptadecenoic	17:1												
Stearic	18:0	70.7	7	1.8 - 7.4	3.1	2.6	1 - 2.5	.9 - 3.1	2.5	34	1 - 3.8	1 - 5	.9 - 5
Oleic	18:1	20	49	9 - 20	10.8	14.3	52 - 66	2.8 - 4.9	50.2	35	5 - 8.8	19 - 49	13 - 35
Ricinoleic	18:1							90.2 [1]					
Linoleic	18:2		16	1.4 - 6.6	11.3	14.3	16.1 - 31	1.3 - 4.4	40.6	3	.4 - 2.7	39 - 62.5	40 - 58
Linolenic	18:3				17.6	38.4	6.4 - 14.1	0.2	6.7		.1 - .3	0 - 3	trace
Stearidonic	18:4												
Arachidic	20:0					0.3		0.2			0.1	.4 - .6	
Gondoic	20:1					16.8		0.4					
Auricolic	20:2												
Eicosatrienoic	20:3												
Arachidonic	20:4												
Eicosapentaenoic	20:5												
Behenic	22:0					1.4							
Erucic	22:1					2.9	1 - 2						
Adrenic	22:4												
Clupanodonic	22:5												
Docosahexaenoic	22:6												
Lignoceric	24:0												
Nervonic	24:1												
References													

Appendix IV-2 (cont.)

Fatty Acid		Crambe	Cumaru	Cuphea	Cynara	Epoxy Oils	Ethiopian Mustard	Hazelnut Kernel	Jatropha	Karanja	Lesquerella	Linseed	Mahua
Common Name	**Abbrev.**												
Capriotic	6:0												
Caprylic	8:0			.2 - 73									
Capric	10:0			5.3 - 95.3									
Lauric	12:0			.2 - 81.4					0.3				
Tridecylic	13:0												
Myristic	14:0			.2 - 67.9	.1				.1				
Myristoleic	14:1												
Pentadanoic	15:0												
Pentadecenoic	15:1												
Palmitic	16:0	2	23		11 - 14	2.8 - 4.1	5.3 - 5.4	4.9	12 - 17	3.7 - 11.7	1 - 5.8	4 - 7	16.0 - 37
Palmitoleic	16:1				0.1			0.2	.4 - 1.4		.5 - 1.4	0.3	
Hexadecadienoic	16:2												
Hexadecatrienoic	16:3												
Heptadecanoic	17:0												
Heptadecenoic	17:1												
Stearic	18:0	1	7		3 - 3.7	1.1 - 2.6	0.2	2.6	5.4 - 9.7	2.4 - 8.9	1.5 - 5.4	2 - 5	18.6 - 25.1
Oleic	18:1	19	37		25	4.0 - 20.7	10 - 43.2	83.6	37 - 63	44.5 - 71.3	11.8 - 27	21 - 40	32 - 51
Ricinoleic	18:1												
Linoleic	18:2	9	29		56 - 59.9	9.2 - 13.7	24.6 - 36	8.5	19 - 41	10.8 - 18.3	3 - 7.6	5 - 40	8.9 - 18
Linolenic	18:3	7				.1 -. 4	15.2 - 16.5	0.2	0.8	2.7	.9 - 13.1	25 - 60	0 - 1
Stearidonic	18:4												
Arachidic	20:0	2			0.4					3.4	0.8		0 - 3.3
Gondoic	20:1				0.2						56.3		
Auricolic	20:2										3.5		
Eicosatrienoic	20:3												
Arachidonic	20:4												
Eicosapentaenoic	20:5												
Behenic	22:0	1											
Erucic	22:1	59					43.6						
Adrenic	22:4												
Clupanodonic	22:5												
Docosahexaenoic	22:6												
Lignoceric	24:0	1								1.1 - 3.5			
Nervonic	24:1												
References													

Appendix IV-2 (cont.)

Fatty Acid		Microalgae	Milkweed Oil	Neem	Olive	Palm Kernel Oil	Palm Oil	Peanut	Piqui	Polanga	Poppy Seed	Rape Seed	Rice Bran
Common Name	Abbrev.												
Capriotic	6:0					0.2							
Caprylic	8:0					3.3 - 4.0	0.1	.1					
Capric	10:0				7.3	3 - 4.3	0.1					0.6	
Lauric	12:0	0.0 – 7.4			0 - 1.3	48.4 - 50.8	.3 - 2.4	0.7				trace	
Tridecylic	13:0						1.0[1]						
Myristic	14:0	0.22 – 18.8		.2 - .3	7 - 20	15 - 17.4	.5 - 47.5	.4				.1 - 1.5	.4 - .6
Myristoleic	14:1	0.1 - 15											
Pentadanoic	15:0												
Pentadecenoic	15:1												
Palmitic	16:0	2.9 – 50.9	5.9	13.6 - 16.2	.5 - 11	8 - 9.1	3.5 - 48.8	6 - 13.7	40	12.0	12.6	1 - 7.3	11.7 - 16.5
Palmitoleic	16:1	0.1 – 39.3	6.8		0.3 - .46		.2 - 1.8				0.1	0.1 -.3	0.3
Hexadecadienoic	16:2	1.1 – 7.5											
Hexadecatrienoic	16:3	1.1 – 11.7											
Heptadecanoic	17:0						.1[1]					.1[4]	
Heptadecenoic	17:1												
Stearic	18:0	0.3 - 11.4	2.3	14.4 - 24.1	1.8 - 84.5	2.1 - 2.7	1.7 - 53	2 - 8.9	2	13	4	0 - 3.5	1.7 - 2.5
Oleic	18:1	0.2 – 38.7	34.8	49.1 - 61.9	3.5 - 84	11.9 - 15.1	6 - 52	36.4 - 65	47	34	22.3	8 - 73	39.2 - 43.7
Ricinoleic	18:1												
Linoleic	18:2	0.6 – 31.2	48.7	2.3 - 15.8	5.8 - 17.6	2.1 - 2.4	5 - 14	13 - 47.8	4	38.3	60.2	9.5 - 35.2	26.4 - 35.1
Linolenic	18:3	0.1 – 25.2	1.2		trace - .6	0.1	.2 - .6	.5 - 29.2		0.3	0.5	.4 - 60	1.1
Stearidonic	18:4	0.4 – 30.7											
Arachidic	20:0	0.3 - 22.6	0.2				0.3	1 - 4				.7 - 7.4	.4 - .6
Gondoic	20:1	0.3 – 0.4			0.3			1.2				1 - 12.1	0.4
Auricolic	20:2											0.6	
Eicosatrienoic	20:3												
Arachidonic	20:4	0.2 – 8.7											
Eicosapentaenoic	20:5	0.9 – 88.2											
Behenic	22:0	8.4						2 - 3				.4 - 2.1	
Erucic	22:1							.1 - .2				.4 - 60	
Adrenic	22:4												
Clupanodonic	22:5	22.7 – 34.3											
Docosahexaenoic	22:6	0.1 – 9.9											
Lignoceric	24:0	<15						1				0.2	.4 - .9
Nervonic	24:1											.2 -34.8	
References													

Appendix IV-2 (cont.)

Fatty Acid		Rubber Seed Oil	Safflower	Sal	Sesame	Soapnut Oil	Soybean Oil	Spring Mustard	Sunflower Oil	Sunola	Tucum oil	Vann	Walnut Kernel
Common Name	**Abbrev.**												
Capriotic	6:0												
Caprylic	8:0										1.9	2.5 - 3.9	
Capric	10:0										2.1	.7 - 5.1	
Lauric	12:0						trace				52.5	35.6 - 49.6	
Tridecylic	13:0												
Myristic	14:0		.1				.1 -.3		.2		25.0	26.4 - 50.8	
Myristoleic	14:1												
Pentadanoic	15:0												
Pentadecenoic	15:1												
Palmitic	16:0	10.2 - 11	4.8 - 10.6	4.5 - 8.6	7.2 - 13	4.7	2.3 - 13	2.4 - 4.2	3 - 8	3	7.5		7.2
Palmitoleic	16:1					.4	.1 - .3		0.1				0.2
Hexadecadienoic	16:2												
Hexadecatrienoic	16:3												
Heptadecanoic	17:0						11.4[6]						
Heptadecenoic	17:1												
Stearic	18:0	8.7 - 12	1.2 - 4.8	34.2 - 44.8	4 - 7.7	1.5	2 - 27.2	1 - 3	1 - 6.5	4.4	0.5	5 - 8.3	1.9
Oleic	18:1	17 - 24.6	8.8 - 74.4	34.2 - 44.8	35 - 53	52.6	16.7 - 84	11.2 - 64.5	11.6 - 43	88.2	8.4	2.1 - 2.2	18.5
Ricinoleic	18:1												
Linoleic	18:2	35 - 39.6	19.7 - 83.8	2.7	30 - 48	4.7	1.6 - 57.1	9.2 - 30.2	44 -77.9	4.3	2.1		56
Linolenic	18:3	16.3 - 24				2	1.2 - 11	4.2 - 12.9	0 - 8.2	0.1			16.2
Stearidonic	18:4												
Arachidic	20:0	1		6.3 - 12.2		7	0.2		.3 - 4			2.2 - 4.7	
Gondoic	20:1					23.9	.3 - .32	2.6 - 16.6	0.3				
Auricolic	20:2												
Eicosatrienoic	20:3												
Arachidonic	20:4												
Eicosapentaenoic	20:5												
Behenic	22:0					1.5	.1 - .4		.8 - 1				
Erucic	22:1					1.1	0 - .3	1.1 - 50.7					
Adrenic	22:4												
Clupanodonic	22:5												
Docosahexaenoic	22:6												
Lignoceric	24:0					.5			0.3				
Nervonic	24:1						trace						
References													

Fatty Acid		Wheat Grain	Yellow Grease	Animal Fats					
Common Name	Abbrev.			Butter	Hog Lard	Beef Tallow	Fish Oil *	Chicken and Turkey	Sheep
Capriotic	6:0								
Caprylic	8:0			5.5					
Capric	10:0			3	0.1				
Lauric	12:0		trace	3.6	0.1	.1 - .1	0.4	0.1	
Tridecylic	13:0						.2		
Myristic	14:0		trace - 2.4	7 - 11.6	1 - 2	2.1 - 8	10.3	.8 - 1	3
Myristoleic	14:1					.9	.2	.2	
Pentadanoic	15:0				.1	.5	1	.1	
Pentadecenoic	15:1						.1		
Palmitic	16:0	20.6	11.9 - 23.2	24 - 33.4	24 - 30	23.3 - 37	20.8	20 - 25.3	21
Palmitoleic	16:1	1	trace - 4.6		2 - 3.3	.1 - 5	12.7	6 - 7.2	2
Hexadecadienoic	16:2						1.9		
Hexadecatrienoic	16:3						2.3		
Heptadecanoic	17:0				.4	1-1.5	.8	.1	
Heptadecenoic	17:1				.2	.8	.3	.1	
Stearic	18:0	1.1	1.6 - 13.4	10 - 13	12 - 18	9.5 - 34.2	3.3	6 - 6.5	25
Oleic	18:1	16.6	31.3 - 80.3	28 - 31	40 - 50	14 - 50	9.8	37.7 - 40	34
Ricinoleic	18:1								
Linoleic	18:2	56	.6 - 50.8	1 - 3.1	7 - 13	1.5 - 50	1.6	17 - 24	5
Linolenic	18:3	2.9	0 - 1.3	.2 - .5	0 - 1	0 - .7	1.9	.8 - 2	3
Stearidonic	18:4						2.5		
Arachidic	20:0		.1 - 1.1		.2 - .5	.2 - 1.2	0.2	0.2	
Gondoic	20:1		.2 - 1.3		0.7	.3 - .51	1.3	0.3	
Auricolic	20:2				0.1		0.4		
Eicosatrienoic	20:3						0.4		
Arachidonic	20:4						2.3		
Eicosapentaenoic	20:5						12.5		
Behenic	22:0		.3 - .8		0.2	.1 - .1	0.2		
Erucic	22:1		trace		0.1	.1 - .1	0.3		
Adrenic	22:4						0.3		
Clupanodonic	22:5						2.5		
Docosahexaenoic	22:6						7.1		
Lignoceric	24:0						0.1		
Nervonic	24:1		0 - .2		trace	trace	0.3		
References									

* Fish Oil contains some odd fatty acids not listed

Appendix IV-3. Typical Properties of Vegetable Oils and Animal Fats

Page 1 of 2

Name	Sulfur Content, ppm ^{u}	Viscosity @ 40° C, mm^2/s^a	Cloud Point, °C ^{p}	Flash Point, °C ^{q}	Pour Point, $°C^b$	Cetane $No.^c$	Lower Heating Value, MJ/kg ^{Ta}	Specific $Gravity^e$	References
Vegetable Oils									
Ailanthus		30.2		240			37.04^a		
Babassu		30.3	20	150		38.0			
Bay Laurel		23.2		226			36.95^a		
Beech		34.6		242			37.22^a		
Beechnut		38.0		260			37.42^a		
Canola		30.2	-2 - 13	270 - 290	-9	49.4	37.62	0.88	
Castor		239 297		260 - 310	-32		39.50^a		
Caycuma					63		39.68		
Coconut		27.0		231			36.13^a		
Corn		34.9 - 35.4	-1	259 - 277	-40	37.6	37.13 – 37.28	0.91	
Cottonseed	8 - 10	33.5 - 50.0	2	110 - 251	-15 - -5	42 - 57	38.80 – 40.36	.86 - .91	
Crambe		53.6	10	274 - 284	-12	44.6	39.83 – 40.50		
Ethiopian Mustard		33.8 - 118.8		212 - 245			37.20^a		
Ground Nut			23				36.01		
Hazelnut		24.0 - 31.0		180 - 230	-15	52.6	$36.97 – 39.75^a$		
Jatropha	21.5	18.2 - 49.9		174 - 240		45.0	38.50 – 39.78	0.92	
Karanja	7.1	27.8 - 69.9	0	205 - 232	-3 - 6	37.5 - 39	34.00 – 42.49	0.91	
Linseed	8 - 10	22.1 - 39.8	2	108 - 241	-15 - -4	34.6	39.30 – 39.75	.865 - .903	
Mahua	8.2	24.6 - 37.2		238 - 260	12 - 15	43.5 - 53	36.00 – 40.00	0.90	
Neem		33.9				51.0	39.60		
Olive		29.8		231			37.13^a		
Palm Oil		24.1 - 39.6	31	228-267		42.0	37.36^a		
Palm Kernel		31.1		264			36.28^a		
Peanut		39.6	13	271	-7	41.8	37.42^a		
Polanga		72.0		221			39.25	0.90	

Appendix IV-3 (cont.)

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Name	Sulfur Content, ppm [u]	Viscosity @ 40° C, mm^2/s[a]	Cloud Point, °C [p]	Flash Point, °C [q]	Pour Point, °C[b]	Cetane No.[c]	Lower Heating Value, MJ/kg [Ta]	Specific Gravity[e]	References
Vegetable Oils									
Poppy Seed		42.4		265			36.57 – 37.35[a]		
Rape Seed		37.0- 37.3	-4	246 - 258	-32	37.6	37.60 – 39.52	0.88	
Rape Seed			8	191			36.38[a]		
Rice Bran		44.5					39.50	0.92	
Rubber Seed		66.2	14	198	-1		37.50	0.91	
Safflower		31.3 - 41.2	18	260 - 275	-7	41.3	37.13 – 37.40[a]		
Sesame		35.5	-4	260	-9	40.2	36.95[a]		
Soybean	0	28.0 - 32.6	-4 - 12	141 - 254	-12 - 0	37.6 - 57.6	37.42 – 39.60	0.88	
Spruce		35.6		240			37.20[a]		
Sunflower		33.9	7	274	-15 - -8	37.1	39.60		
Sunflower			-1	187	-8	49.4	36.57[a]		
Tobacco Seed		27.7 - 101							
Used Cooking Oil		35.3	3 - 14	147 - 177	11	63.2			
Vann	18	44.6		254	36				
Walnut		36.8		251					
Yellow Grease	2 - 40		-7 - 13	83 - 284	-4	45 - 64	37.20 – 39.55		
Animal Fats/Oils									
Beef Tallow		51.2		201			40.06		
Poultry Fat			4 - 15	113 - 134					
Algae Oils									
							36.00		

Footnotes:

[a] Higher heating values were reported in the literature. Values shown here were reduced by 6% to estimate lower heating values

Appendix IV-4. Typical Properties of Biodiesel (FAME) and Renewable Diesel

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Feedstock	Sulfur Content, ppm [u]	Viscosity @ 40° C, mm^2/s [a]	Cloud Point, °C [p]	Pour Point, °C [b]	Flash Point, °C [q]	Cetane No. [c]	Lower Heating Value, MJ/kg [f]	Specific Gravity [e]	References
FAME									
B Carinata		4.9	-9	-6	163	56.9	39.55		
Babassu	5	3.6	4		112 - 127	63.0	31.80	0.88	
Canola		3.9	-2	-6	146	52.9	40.00		
Castor		13.8			120				
Coconut		2.7		-5		57.0	35.22		
Corn		3.6 - 4.5	-3	-3	111 - 154	65.0	38.48 – 41.14		
Cottonseed		3.8		-4	110 - 182	45.5 - 51.2	41.18		
Crambe		5.1			190		41.98		
Cyrana		3.6	-1		175	48.6 - 59	37.20		
Hazelnut		3.6 - 5.4			152 - 183	55.0	37.23 – 41.12	0.88	
Jatropha	3 - 100	3 - 5.7	4	3	130 - 180	36.7 - 58.4	38.45 – 41.00	0.86	
Karanja	3 - 30	4.2 - 5.7	-2 - 24	-6 - 14	141-170	48 - 55.1	36.72 – 37.43		
Linseed	50	2.8 - 5.0	-4	-14 - -5	142 - 192	30.0	37.00 – 39.75	0.89	
Mahua	164.8	4.0 - 5.0		6 - 15	120 - 208	65.4	37.00		
Microalgae		5.2		‘-12	115		38.54	0.87	
Mustard		4.1			169		41.30		
Olive	1	4.2 - 4.6	-2	-3	174 - 210	51 - 61	37.29 – 41.35		
Palm Oil	40	2.9 - 5.6	-47	-35	162 - 168	54.6 - 66.5	33.50 – 37.10	0.88	
Peanut		4.9	5		176	54.0	33.60	0.88	
Polanga		4.9	13	4	140		38.66		
Pongamia	1	4.5 - 5.5	13	13 - 15	125 - 171	52.8 - 61.4	36.01 – 41.30	0.88	
Rape Seed	1-5	4.5 - 5.0	-30 - 2	-1	111 - 153	49 - 54.7	32.10 – 39.83		
Rice Bran		4.5 – 5.3	-4 – 9	-3 - -2	152 – 265	51.6 – 63.8	37.70 – 42.20	.88 - .88	
Rubber Seed		4.7 – 5.8	4	-8 - -4	130 – 174		36.50 – 38.90	.87 - .93	
Safflower	11	4.1 – 4.3	-5 - -2	-6 - -8	176	49.8 – 52.3	40.06 – 45.21	0.88	
Vann	1200	3.3		3	130				
Sesame		3.0			145		40.90		
Soy Oil	20	4.0 – 5.1	-25 – 2	-36 – 0	114 – 288	47.4 – 59.0	37.10 – 39.72	.88 - .89	
Sunflower		4.2 – 4.6	0 – 3		164 – 183	47 – 56.4	33.50 – 37.40	86	
Tallow		5.0	12 – 16	9 – 13	96 – 188	61.8	37.54 – 39.97		
Tobacco Seed		3.5 – 5.2					44.63		
Walnut		4.1			170	59.9	41.32		

Appendix IV-4 (cont.)

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Feedstock	Sulfur Content, ppm u	Viscosity @ 40° C, mm2/sa	Cloud Point, °C p	Pour Point, °Cb	Flash Point, °C q	Cetane No.c	Lower Heating Value, kJ/kg T	Specific Gravity	References
Renewable Diesel									
Hydrotreated Vegetable Oil (HVO)		2.9 - 3.5	-25 - -5			80 - 99			
Green Diesel	1		-10 - 20			70 - 90	44.00	0.78	
NExBTL	0	2.9 - 3.5	-5 - -30			84 - 99	44.00	0.77 - .79	

Footnotes:

a Higher heating values were reported in the literature. Values shown here were reduced by 6% to estimate lower heating values

Appendix V. Exhaust Emissions from Biodistillates

Reference	Model Year	Fuel	Engine	Test	Test Cycle	Emission Control System	Nox	PM	HC	CO	CO_2
Ilkilic, C. The effect of sunflower oil methyl ester and diesel fuel blend on the performance of a diesel engine. Energy Sources Part A-Recovery Utilization and Environmental Effects 2008, 30 (19), 1761-1770.		B75 Sunflower	Test Engine	Engine Dyno.	Constant Speeds		900 - 1300 (ppm)			650 - 2750 (ppm)	7 - 8 (%)
Ilkilic, C. The effect of sunflower oil methyl ester and diesel fuel blend on the performance of a diesel engine. Energy Sources Part A-Recovery Utilization and Environmental Effects 2008, 30 (19), 1761-1770.		Diesel	Test Engine	Engine Dyno.	Constant Speeds		1100 - 1600 (ppm)			1300 - 4000 (ppm)	7 - 11 (%)
Lapuerta, M.; Herreros, J. M.; Lyons, L. L.; Garcia-Contreras, R.; Briceno, Y. Effect of the alcohol type used in the production of waste cooking oil biodiesel on diesel performance and emissions. Fuel 2008, 87 (15-16), 3161-3169		B70 Waste Cooking Oil	LD	Chassis Dyno.	European Driving Cycle (C,F,G,H,U10)	EGR only	4.5 - 5.5 (g/kWh)	.06 - .07 (g/kWh)	.08 - .33 (g/kWh)		
Lapuerta, M.; Herreros, J. M.; Lyons, L. L.; Garcia-Contreras, R.; Briceno, Y. Effect of the alcohol type used in the production of waste cooking oil biodiesel on diesel performance and emissions. Fuel 2008, 87 (15-16), 3161-3169		B100 Waste Cooking Oil	LD	Chassis Dyno.	European Driving Cycle (C,F,G,H,U10)	EGR only	4.3 - 5.3 (g/kWh)	.05 - .06 (g/kWh)	.03 - .08 (g/kWh)		
Lapuerta, M.; Herreros, J. M.; Lyons, L. L.; Garcia-Contreras, R.; Briceno, Y. Effect of the alcohol type used in the production of waste cooking oil biodiesel on diesel performance and emissions. Fuel 2008, 87 (15-16), 3161-3169		B30 Waste Cooking Oil	LD	Chassis Dyno.	European Driving Cycle (C,F,G,H,U10)	EGR only	4 - 5.7 (g/kWh)	.06 - 1.0 (g/kWh)			
Lapuerta, M.; Herreros, J. M.; Lyons, L. L.; Garcia-Contreras, R.; Briceno, Y. Effect of the alcohol type used in the production of waste cooking oil biodiesel on diesel performance and emissions. Fuel 2008, 87 (15-16), 3161-3169		Diesel	LD	Chassis Dyno.	European Driving Cycle (C,F,G,H,U10)	EGR only	4 - 5.7 (g/kWh)	0.07 - 0.14 (g/kWh)	0.06 - 0.40 (g/kWh)		
Bennett, M.; Volckens, J.; Stanglmaier, R.; McNichol, A. P.; Ellenson, W. D.; Lewis, C. W. Biodiesel effects on particulate radiocarbon (C-14) emissions from a diesel engine. Journal of Aerosol Science 2008, 39 (8), 667-678.		B20 Soy	HD	Off-Road	Constant Load and Speed	US Tier 2 emissions guidelines	584 (ppm)	0.04 - 0.06 (g/kWh)	130 (ppm)	81.4 (ppm)	8.25 (%)

Reference	Model Year	Fuel	Engine	Test	Test Cycle	Emission Control System	Nox	PM	HC	CO	CO_2
Bennett, M.; Volckens, J.; Stanglmaier, R.; McNichol, A. P.; Ellenson, W. D.; Lewis, C. W. Biodiesel effects on particulate radiocarbon (C-14) emissions from a diesel engine. Journal of Aerosol Science 2008, 39 (8), 667-678.		B29 Soy	HD	Off-Road	Constant Load and Speed	US Tier 2 emissions guidelines	551(ppm)	.03 - .04 (g/kWh)	104 (ppm)	83.3 (ppm)	8.05 (%)
Bennett, M.; Volckens, J.; Stanglmaier, R.; McNichol, A. P.; Ellenson, W. D.; Lewis, C. W. Biodiesel effects on particulate radiocarbon (C-14) emissions from a diesel engine. Journal of Aerosol Science 2008, 39 (8), 667-678.		B83 Soy	HD	Off-Road	Constant Load and Speed	US Tier 2 emissions guidelines	596 (ppm)	.02 - .04 (g/kWh)	64.3 (ppm)	80.2 (ppm)	8.3 (%)
Bennett, M.; Volckens, J.; Stanglmaier, R.; McNichol, A. P.; Ellenson, W. D.; Lewis, C. W. Biodiesel effects on particulate radiocarbon (C-14) emissions from a diesel engine. Journal of Aerosol Science 2008, 39 (8), 667-678.		Diesel	HD	Off-Road	Constant Load and Speed	US Tier 2 emissions guidelines	575 - 583 (ppm)		120 - 132 (ppm)	87 - 93 (ppm)	8.16 (%)
Zervas, E. Regulated and non-regulated pollutants emitted from two aliphatic and a commercial diesel fuel. Fuel 2008, 87 (7), 1141-1147.		B100	LD		New European Driving Cycle	Diesel Oxidation Catalyst	.38 - .42 (g/km)	.03 - .04 (g/km)	.10 - .25 (g/km)	.08 - .32 (g/km)	
Altun, S.; Bulut, H.; Oner, C. The comparison of engine performance and exhaust emission characteristics of sesame oil-diesel fuel mixture with diesel fuel in a direct injection diesel engine. Renewable Energy 2008, 33 (8), 1791-1795.		B50 Sesame	Test Engine	Engine Dyno.	Constant Speeds		175 - 800 (ppm)			150 - 250 (ppm)	
Altun, S.; Bulut, H.; Oner, C. The comparison of engine performance and exhaust emission characteristics of sesame oil-diesel fuel mixture with diesel fuel in a direct injection diesel engine. Renewable Energy 2008, 33 (8), 1791-1795.		Diesel	Test Engine	Engine Dyno.	Constant Speeds		350 - 780 (ppm)			350 - 600 (ppm)	
Suh, H. K.; Roh, H. G.; Lee, C. S. spray and combustion characteristics of biodiesel/diesel blended fuel in a direct injection common-rail diesel engine. Journal of Engineering for Gas Turbines and Power-Transactions of the Asme 2008, 130 (3).		B20 Soy	LD	Engine Dyno.	Constant Speed		25 - 375 (ppm)		50 - 80 (ppm)	.05 - .55 (%)	

Reference	Model Year	Fuel	Engine	Test	Test Cycle	Emission Control System	Nox	PM	HC	CO	CO_2
Suh, H. K.; Roh, H. G.; Lee, C. S. spray and combustion characteristics of biodiesel/diesel blended fuel in a direct injection common-rail diesel engine. Journal of Engineering for Gas Turbines and Power-Transactions of the Asme 2008, 130 (3).		Diesel	LD	Engine Dyno.	Constant Speed		25 - 250 (ppm)		75 - 150 (ppm)	0.05 - 0.18 (%)	
Arai, M.; Saito, T.; Furuhata, T. Effect of biodiesel fuel on direct injection diesel engine performance. Journal of Propulsion and Power 2008, 24 (3), 603-608.		B20 Palm Oil	Test Engine	Engine Dyno.	Constant speed with excess air ratios		1000 - 1400 (ppm)	.5 - 1.2 (g/kWh)		~0 (ppm)	6 - 10
Ballesteros, R.; Hernandez, J. J.; Lyons, L. L.; Cabanas, B.; Tapia, A. Speciation of the semivolatile hydrocarbon engine emissions from sunflower biodiesel. Fuel 2008, 87 (10-11), 1835-1843.		B100 Sunflower	LD	Chassis Dyno.	European Emission Directive 70/220 (Extra Urban and Urban mode)	Fixed EGR		.03 - .24 (g/kWh)	.002 - .07 (g/kWh)		
Cheng, C. H.; Cheung, C. S.; Chan, T. L.; Lee, S. C.; Yao, C. D.; Tsang, K. S. Comparison of emissions of a direct injection diesel engine operating on biodiesel with emulsified and fumigated methanol. Fuel 2008, 87 (10-11), 1870-1879.		B100 Waste Cooking Oil	MD	Engine Dyno.	Constant speed with differing loads		6.4 - 11.8 (g/kWh)	$.5x10^4$ - $4x10^4$ (ug/m^3)	. 5 - 5 (g/kWh)	1 - 17 (g/kWh)	750 - 1800 (g/kWh)
Cheng, C. H.; Cheung, C. S.; Chan, T. L.; Lee, S. C.; Yao, C. D.; Tsang, K. S. Comparison of emissions of a direct injection diesel engine operating on biodiesel with emulsified and fumigated methanol. Fuel 2008, 87 (10-11), 1870-1879.		Diesel	MD	Engine Dyno.	Constant speed with differing loads		5.8 - 11.2 (g/kWh)	$.7x10^4$ - $8.3x10^4$ (ug/m^3)	2 - 8 (g/kWh)	2 - 20 (g/kWh)	800 - 1800 (g/kWh)
Banapurmath, N. R.; Tewari, P. G.; Hosmath, R. S. Performance and emission characteristics of a DI compression ignition engine operated on Honge, Jatropha and sesame oil methyl esters. Renewable Energy 2008, 33 (9), 1982-1988.		B100 Pongamia	Test Engine	Engine Dyno.	Constant Speed		100 - 1050 (ppm)		27 - 82 (ppm)	.06 - .32 (%)	
Banapurmath, N. R.; Tewari, P. G.; Hosmath, R. S. Performance and emission characteristics of a DI compression ignition engine operated on Honge, Jatropha and sesame oil methyl esters. Renewable Energy 2008, 33 (9), 1982-1988.		B100 Jatropha	Test Engine	Engine Dyno.	Constant Speed		140 - 1000 (ppm)		25 - 87 (ppm)	.07 - .4 (%)	

Reference	Model Year	Fuel	Engine	Test	Test Cycle	Emission Control System	Nox	PM	HC	CO	CO_2
Banapurmath, N. R.; Tewari, P. G.; Hosmath, R. S. Performance and emission characteristics of a DI compression ignition engine operated on Honge, Jatropha and sesame oil methyl esters. Renewable Energy 2008, 33 (9), 1982-1988.		B100 Sesame	Test Engine	Engine Dyno.	Constant Speed		120 - 1070 (ppm)		22 - 77 (ppm)	.05 - .28 (%)	
Banapurmath, N. R.; Tewari, P. G.; Hosmath, R. S. Experimental investigations of a four-stroke single cylinder direct injection diesel engine operated on dual fuel mode with producer gas as inducted fuel and Honge oil and its methyl ester (HOME) as injected fuels. Renewable Energy 2008, 33 (9), 2007-2018.		B100 Honge Oil	Test Engine	Engine Dyno.	Constant Speed		900 - 550 (ppm)			.42 - .85 (%)	
Banapurmath, N. R.; Tewari, P. G.; Hosmath, R. S. Experimental investigations of a four-stroke single cylinder direct injection diesel engine operated on dual fuel mode with producer gas as inducted fuel and Honge oil and its methyl ester (HOME) as injected fuels. Renewable Energy 2008, 33 (9), 2007-2018.		Diesel	Test Engine	Engine Dyno.	Constant Speed		110 - 1250 (ppm)		18 - 65 (ppm)	0.04 - 0.19 (%)	
Sureshkumar, K.; Velraj, R.; Ganesan, R. Performance and exhaust emission characteristics of a CI engine fueled with Pongamia pinnata methyl ester (PPME) and its blends with diesel. Renewable Energy 2008, 33 (10), 2294-2302.		B20 Pongamia	Test Engine	Generator w/ rheostat	Constant Speed with varying load		85 - 220 (ppm)		1 (ppm)	.01 - .03 (% vol.)	1.9 - 3.0 (% vol.)
Sureshkumar, K.; Velraj, R.; Ganesan, R. Performance and exhaust emission characteristics of a CI engine fueled with Pongamia pinnata methyl ester (PPME) and its blends with diesel. Renewable Energy 2008, 33 (10), 2294-2302.		B40 Pongamia	Test Engine	Generator w/ rheostat	Constant Speed with varying load		50 - 160 (ppm)			0.02 (% vol.)	.9 - 1.5 (% vol.)
Sureshkumar, K.; Velraj, R.; Ganesan, R. Performance and exhaust emission characteristics of a CI engine fueled with Pongamia pinnata methyl ester (PPME) and its blends with diesel. Renewable Energy 2008, 33 (10), 2294-2302.		B60 Pongamia	Test Engine	Generator w/ rheostat	Constant Speed with varying load		48 - 150 (ppm)				0.5 - 0.7 (% vol.)
Sureshkumar, K.; Velraj, R.; Ganesan, R. Performance and exhaust emission characteristics of a CI engine fueled with Pongamia pinnata methyl ester (PPME) and its blends with diesel. Renewable Energy 2008, 33 (10), 2294-2302.		B80 Pongamia	Test Engine	Generator w/ rheostat	Constant Speed with varying load		50 - 165 (ppm)			.006 - .01 (% vol.)	1.6 - 2.[illegible] (% vol.)

Reference	Model Year	Fuel	Engine	Test	Test Cycle	Emission Control System	Nox	PM	HC	CO	CO_2
Sureshkumar, K.; Velraj, R.; Ganesan, R. Performance and exhaust emission characteristics of a CI engine fueled with Pongamia pinnata methyl ester (PPME) and its blends with diesel. Renewable Energy 2008, 33 (10), 2294-2302.		B100 Pongamia	Test Engine	Generator w/ rheostat	Constant Speed with varying load		75 - 190 (ppm)			.007 - .01 (% vol.)	1.6 - 2.[illegible] (% vol.)
Sureshkumar, K.; Velraj, R.; Ganesan, R. Performance and exhaust emission characteristics of a CI engine fueled with Pongamia pinnata methyl ester (PPME) and its blends with diesel. Renewable Energy 2008, 33 (10), 2294-2302.		Diesel	Test Engine	Generator w/ rheostat	Constant Speed with varying load		75 - 240 (ppm)		1 - 2 (ppm)	0.02 (% vol.)	0.5 - 2.7 (% vol.)
Kim, M. Y.; Yoon, S. H.; Hwang, J. W.; Lee, C. S. Characteristics of Particulate Emissions of Compression Ignition Engine Fueled With Biodiesel Derived From Soybean. ASME Internal Combusion Engine Division 2007 Fall Technical Conference 2007, ICEF2007-1715, 1-7.		B100 Soybean	Test Engine	Engine Dyno.	Constant Speed		2.0 - 8.0 (g/kWh)		.13 - .15 (g/kWh)	2.3 - 3.5 (g/kWh)	
Kim, M. Y.; Yoon, S. H.; Hwang, J. W.; Lee, C. S. Characteristics of Particulate Emissions of Compression Ignition Engine Fueled With Biodiesel Derived From Soybean. ASME Internal Combusion Engine Division 2007 Fall Technical Conference 2007, ICEF2007-1715, 1-7.		Diesel	Test Engine	Engine Dyno.	Constant Speed		2.0 - 8.0 (g/kWh)		0.13 - 0.15 (g/kWh)	2.0 - 3.5 (g/kWh)	
Zhang, X.; Wang, H.; Li, L.; Wu, Z.; Hu, Z.; Zhao, H.; Yang, W. Characteristics of Particulates and Exhaust Gases Emissions of DI Diesel Engine Employing Common Rail Fuel System Fueled with Bio-diesel Blends. SAE International 2008, 2008-01-1834.		B10 Waste Cooking Oil	LD	Chassis Dyno.	Constant Speeds with varying loads	EGR and Diesel Oxidation Catalyst	180 - 780 ($x10^{-6}$)			2.3 - 9.2 ($x10^{-6}$)	.038 - .078
Zhang, X.; Wang, H.; Li, L.; Wu, Z.; Hu, Z.; Zhao, H.; Yang, W. Characteristics of Particulates and Exhaust Gases Emissions of DI Diesel Engine Employing Common Rail Fuel System Fueled with Bio-diesel Blends. SAE International 2008, 2008-01-1834.		B20 Waste Coooking Oil	LD	Chassis Dyno.	Constant Speeds with varying loads	EGR and Diesel Oxidation Catalyst	180 - 775 ($x10^{-6}$)			2.3 - 8.2 ($x10^{-6}$)	.038 - .078
Zhang, X.; Wang, H.; Li, L.; Wu, Z.; Hu, Z.; Zhao, H.; Yang, W. Characteristics of Particulates and Exhaust Gases Emissions of DI Diesel Engine Employing Common Rail Fuel System Fueled with Bio-diesel Blends. SAE International 2008, 2008-01-1834.		B40 Waste Cooking Oil	LD	Chassis Dyno.	Constant Speeds with varying loads	EGR and Diesel Oxidation Catalyst	180 - 800 ($x10^{-6}$)			2.0 - 5.0 ($x10^{-6}$)	.038 - .078

Reference	Model Year	Fuel	Engine	Test	Test Cycle	Emission Control System	Nox	PM	HC	CO	CO_2
Zhang, X.; Wang, H.; Li, L.; Wu, Z.; Hu, Z.; Zhao, H.; Yang, W. Characteristics of Particulates and Exhaust Gases Emissions of DI Diesel Engine Employing Common Rail Fuel System Fueled with Bio-diesel Blends. SAE International 2008, 2008-01-1834.		B60 Waste Cooking Oil	LD	Chassis Dyno.	Constant Speeds with varying loads	EGR and Diesel Oxidation Catalyst	180 - 810 ($x10^{-6}$)			1.9 - 4.2 ($x10^{-6}$)	.038 - .078
Zhang, X.; Wang, H.; Li, L.; Wu, Z.; Hu, Z.; Zhao, H.; Yang, W. Characteristics of Particulates and Exhaust Gases Emissions of DI Diesel Engine Employing Common Rail Fuel System Fueled with Bio-diesel Blends. SAE International 2008, 2008-01-1834.		B100 Waste Cooking Oil	LD	Chassis Dyno.	Constant Speeds with varying loads	EGR and Diesel Oxidation Catalyst	180 - 1050 ($x10^{-6}$)			1.8 - 3.2 ($x10^{-6}$)	.038 - .081
Lea-Langton, A.; Li, H.; Andrews, G. E. Comparison of Particulate PAH Emissions for Diesel, Biodiesel adn Cooking Oil using a Heavy Duty DI Diesel Engine. SAE International 2008, 2008-01-1811.	1999	B100 Waste Cooking Oil	HD	Generator	Steady State	Oxidation Catalyst (Euro 2)	6.5 - 8.0 (g/kWh)	.025 - .07 (g/kWh)	.25 - 0.6 (g/kWh)	0.2 - 1.6 (g/kWh)	
Lea-Langton, A.; Li, H.; Andrews, G. E. Comparison of Particulate PAH Emissions for Diesel, Biodiesel adn Cooking Oil using a Heavy Duty DI Diesel Engine. SAE International 2008, 2008-01-1811.	1999	B100 Rapeseed	HD	Generator	Steady State	Oxidation Catalyst (Euro 2)	7.8 - 8.0 (g/kWh)	.022 - .07 (g/kWh)	.28 - 0.8 (g/kWh)	0.8 - 3.0 (g/kWh)	
Lea-Langton, A.; Li, H.; Andrews, G. E. Comparison of Particulate PAH Emissions for Diesel, Biodiesel adn Cooking Oil using a Heavy Duty DI Diesel Engine. SAE International 2008, 2008-01-1811.	1999	B100 Rapeseed	HD	Generator	Steady State	Oxidation Catalyst (Euro 2)	6.0 - 8.1 (g/kWh)		.55 - 1.2 (g/kWh)	2.2 - 6.5 (g/kWh)	
Savvidis, D.; Triandafyllis, J.; Grammatikis, V.; Gkatzianis, G.; Pecqueur, M. A New Volvo V70 2.5 and an Old Ford Escort 1.6 Were Tested and Compared on a Chassis Dynamometer, Using the Same Blends of Frying Biodiesel and Neat Diesel. SAE International 2008, 2008-01-1576.	1986	B10 Frying Oil	LD	Chassis Dyno.	Constant Speeds, Different Gears	No ECU, EURO 1	320 - 370 (ppm)				10.5 (% vol.)
Savvidis, D.; Triandafyllis, J.; Grammatikis, V.; Gkatzianis, G.; Pecqueur, M. A New Volvo V70 2.5 and an Old Ford Escort 1.6 Were Tested and Compared on a Chassis Dynamometer, Using the Same Blends of Frying Biodiesel and Neat Diesel. SAE International 2008, 2008-01-1576.	1986	B20 Frying Oil	LD	Chassis Dyno.	Constant Speeds, Different Gears	No ECU, EURO 1	300 - 380 (ppm)				10.4 - 11 (% vol.)

Reference	Model Year	Fuel	Engine	Test	Test Cycle	Emission Control System	Nox	PM	HC	CO	CO_2
Savvidis, D.; Triandafyllis, J.; Grammatikis, V.; Gkatzianis, G.; Pecqueur, M. A New Volvo V70 2.5 and an Old Ford Escort 1.6 Were Tested and Compared on a Chassis Dynamometer, Using the Same Blends of Frying Biodiesel and Neat Diesel. SAE International 2008, 2008-01-1576.	1986	B30 Frying Oil	LD	Chassis Dyno.	Constant Speeds, Different Gears	No ECU, EURO 1	305 - 400 (ppm)				10.1 - 10.5 (% vol.)
Savvidis, D.; Triandafyllis, J.; Grammatikis, V.; Gkatzianis, G.; Pecqueur, M. A New Volvo V70 2.5 and an Old Ford Escort 1.6 Were Tested and Compared on a Chassis Dynamometer, Using the Same Blends of Frying Biodiesel and Neat Diesel. SAE International 2008, 2008-01-1576.	1986	B40 Frying Oil	LD	Chassis Dyno.	Constant Speeds, Different Gears	No ECU, EURO 1	300 - 380 (ppm)				10.1 - 10.5 (% vol.)
Savvidis, D.; Triandafyllis, J.; Grammatikis, V.; Gkatzianis, G.; Pecqueur, M. A New Volvo V70 2.5 and an Old Ford Escort 1.6 Were Tested and Compared on a Chassis Dynamometer, Using the Same Blends of Frying Biodiesel and Neat Diesel. SAE International 2008, 2008-01-1576.	1986	B50 Frying Oil	LD	Chassis Dyno.	Constant Speeds, Different Gears	No ECU, EURO 1	300 - 390 (ppm)				9.9 - 10.7 (% vol.)
Savvidis, D.; Triandafyllis, J.; Grammatikis, V.; Gkatzianis, G.; Pecqueur, M. A New Volvo V70 2.5 and an Old Ford Escort 1.6 Were Tested and Compared on a Chassis Dynamometer, Using the Same Blends of Frying Biodiesel and Neat Diesel. SAE International 2008, 2008-01-1576.	1986	B100 Frying Oil	LD	Chassis Dyno.	Constant Speeds, Different Gears	No ECU, EURO 1	310 - 400 (ppm)				10.2 - 10.6 (% vol.)
Savvidis, D.; Triandafyllis, J.; Grammatikis, V.; Gkatzianis, G.; Pecqueur, M. A New Volvo V70 2.5 and an Old Ford Escort 1.6 Were Tested and Compared on a Chassis Dynamometer, Using the Same Blends of Frying Biodiesel and Neat Diesel. SAE International 2008, 2008-01-1576.	2003	B10 Frying Oil	LD	Chassis Dyno.	Constant Speeds, Different Gears	ECU, EGR	530 - 790 (ppm)				11.5 - 11.7 (% vol.)
Savvidis, D.; Triandafyllis, J.; Grammatikis, V.; Gkatzianis, G.; Pecqueur, M. A New Volvo V70 2.5 and an Old Ford Escort 1.6 Were Tested and Compared on a Chassis Dynamometer, Using the Same Blends of Frying Biodiesel and Neat Diesel. SAE International 2008, 2008-01-1576.	2003	B20 Frying Oil	LD	Chassis Dyno.	Constant Speeds, Different Gears	ECU, EGR	590 - 800 (ppm)				11.4 - 11.6 (% vol.)

Reference	Model Year	Fuel	Engine	Test	Test Cycle	Emission Control System	Nox	PM	HC	CO	CO_2
Savvidis, D.; Triandafyllis, J.; Grammatikis, V.; Gkatzianis, G.; Pecqueur, M. A New Volvo V70 2.5 and an Old Ford Escort 1.6 Were Tested and Compared on a Chassis Dynamometer, Using the Same Blends of Frying Biodiesel and Neat Diesel. SAE International 2008, 2008-01-1576.	2003	B30 Frying Oil	LD	Chassis Dyno.	Constant Speeds, Different Gears	ECU, EGR	615 - 810 (ppm)				11.4 - 11.6 (% vol.)
Savvidis, D.; Triandafyllis, J.; Grammatikis, V.; Gkatzianis, G.; Pecqueur, M. A New Volvo V70 2.5 and an Old Ford Escort 1.6 Were Tested and Compared on a Chassis Dynamometer, Using the Same Blends of Frying Biodiesel and Neat Diesel. SAE International 2008, 2008-01-1576.	2003	B40 Frying Oil	LD	Chassis Dyno.	Constant Speeds, Different Gears	ECU, EGR	640 - 820 (ppm)				11.4 - 11.5 (% vol.)
Savvidis, D.; Triandafyllis, J.; Grammatikis, V.; Gkatzianis, G.; Pecqueur, M. A New Volvo V70 2.5 and an Old Ford Escort 1.6 Were Tested and Compared on a Chassis Dynamometer, Using the Same Blends of Frying Biodiesel and Neat Diesel. SAE International 2008, 2008-01-1576.	2003	B50 Frying Oil	LD	Chassis Dyno.	Constant Speeds, Different Gears	ECU, EGR	680 - 820 (ppm)				11.5 - 11.6 (% vol.)
Savvidis, D.; Triandafyllis, J.; Grammatikis, V.; Gkatzianis, G.; Pecqueur, M. A New Volvo V70 2.5 and an Old Ford Escort 1.6 Were Tested and Compared on a Chassis Dynamometer, Using the Same Blends of Frying Biodiesel and Neat Diesel. SAE International 2008, 2008-01-1576.	2003	B100 Frying Oil	LD	Chassis Dyno.	Constant Speeds, Different Gears	ECU, EGR	690 - 850 (ppm)				11.5 - 11.6 (% vol.)
Savvidis, D.; Triandafyllis, J.; Grammatikis, V.; Gkatzianis, G.; Pecqueur, M. A New Volvo V70 2.5 and an Old Ford Escort 1.6 Were Tested and Compared on a Chassis Dynamometer, Using the Same Blends of Frying Biodiesel and Neat Diesel. SAE International 2008, 2008-01-1576.	2003	Diesel	LD	Chassis Dyno.	Constant Speeds, Different Gears	ECU, EGR	500 - 660 (ppm)				11.8 - 12 (% vol.)
Savvidis, D.; Triandafyllis, J.; Grammatikis, V.; Gkatzianis, G.; Pecqueur, M. A New Volvo V70 2.5 and an Old Ford Escort 1.6 Were Tested and Compared on a Chassis Dynamometer, Using the Same Blends of Frying Biodiesel and Neat Diesel. SAE International 2008, 2008-01-1576.	1986	Diesel	LD	Chassis Dyno.	Constant Speeds, Different Gears	No ECU, EURO 1	300 - 360 (ppm)				10.7 - 11.2 (% vol.)

Reference	Model Year	Fuel	Engine	Test	Test Cycle	Emission Control System	Nox	PM	HC	CO	CO_2
Sivaprakasam, S.; Saravanan, C. G. Optimization of the transesterification process for biodiesel production and use of biodiesel in a compression ignition engine. Energy & Fuels 2007, 21, 2998-3003.		B100 Jatropha	LD	Engine Dyno.	Various Brake Power		445 - 515 (ppm)				
Sivaprakasam, S.; Saravanan, C. G. Optimization of the transesterification process for biodiesel production and use of biodiesel in a compression ignition engine. Energy & Fuels 2007, 21, 2998-3003.		B60 Jatropha	LD	Engine Dyno.	Various Brake Power		175 - 500 (ppm)				
Sivaprakasam, S.; Saravanan, C. G. Optimization of the transesterification process for biodiesel production and use of biodiesel in a compression ignition engine. Energy & Fuels 2007, 21, 2998-3003.		B20 Jatropha	LD	Engine Dyno.	Various Brake Power		150 - 460 (ppm)				
Sivaprakasam, S.; Saravanan, C. G. Optimization of the transesterification process for biodiesel production and use of biodiesel in a compression ignition engine. Energy & Fuels 2007, 21, 2998-3003.		Diesel	LD	Engine Dyno.	Various Brake Power		120 - 530 (ppm)				
McCormick, R. L.; Alvarez, J. R.; Graboski, M. S.; Tyson, K. S.; Vertin, K. Fuel Additive and Blending Approaches to Reducing NOx Emissions from Biodiesel. SAE Technical Paper Series 2002, 2002-01-1658.	1991	B20 Soybean Oil	HD		Constant Speeds	CA Code of Reg. Title 13 section 2282	4.3 (g-bhp-h)	0.146 (g-bhp-h)	.005 (g-bhp-h)	3.6 (g-bhp-h)	
McCormick, R. L.; Alvarez, J. R.; Graboski, M. S.; Tyson, K. S.; Vertin, K. Fuel Additive and Blending Approaches to Reducing NOx Emissions from Biodiesel. SAE Technical Paper Series 2002, 2002-01-1658.	1991	B80 Soybean	HD		Constant Speeds	CA Code of Reg. Title 13 section 2282	5.1 (g-bhp-h)	.078 (g-bhp-h)	.006 (g-bhp-h)	3.0 (g-bhp-h)	
Kerihuel; Kumar, M. S.; Bellettre, J.; Tazerout, M. Investigations on a CI Engine Using Animal Fat and its Emulsions With Water and Methanol as Fuel. SAE International 2005, 2005-01-1729.		B100 Animal Fat	Test Engine	Engine Dyno.	Differing Loads				.19 - 0.8 (g/kWh)	1.0 - 26 (g/kWh)	7.0 - 18.5 (g/kWh)
Kass, M. D.; Lewis, S. A.; Swartz, M. M.; Huff, S. P.; Lee, D. W.; Wagner, R. M.; Storey, J. M. E. Utilizing Water-Emulsification to Reduce NOx and Particulate Emissions Associated with Biodiesel; 07.		86.5% B100, 10% Water, 3.5% surfactant	LD		Fixed speed with varying EGR	Dual EGR	0.4 - 7.1 (g/hp-h)	2.0 - 6.0 (g/hp-h)	0.4 - 0.6 (g/hp-h)	1.3 - 3.6 (g/hp-h)	5.6 - 10 (g/hp-h)

Reference	Model Year	Fuel	Engine	Test	Test Cycle	Emission Control System	Nox	PM	HC	CO	CO_2
Kass, M. D.; Lewis, S. A.; Swartz, M. M.; Huff, S. P.; Lee, D. W.; Wagner, R. M.; Storey, J. M. E. Utilizing Water-Emulsification to Reduce NOx and Particulate Emissions Associated with Biodiesel; 07.		B100 Soybean Oil	LD		Fixed speed with varying EGR	Dual EGR	0.7 - 6.8 (g/hp-h)	2.0 - 7.0 (g/hp-h)	0.1 - 0.2 (g/hp-h)	0.8 - 2.0 (g/hp-h)	6.0 - 104 (g/hp-h)
McCormick, R. L.; Williams, A.; Ireland, J.; Brimhall, M.; Hayes, R. R. Effects of Biodiesel Blends on Vehicle Emissions;NREL/MP-540-40554; Oct 1, 06.	2003	B20	HD	Chassis Dyno.	Steady State		7.22 - 7.96 (g/mile)	.17 - .18 (g/mile)	.03 - .20 (g/mile)	.12 - 3.2 (g/mile)	
McCormick, R. L.; Williams, A.; Ireland, J.; Brimhall, M.; Hayes, R. R. Effects of Biodiesel Blends on Vehicle Emissions;NREL/MP-540-40554; Oct 1, 06.	2003	Diesel	HD	Chassis Dyno.	Steady State		6.99 - 7.75 (g/mile)	0.239 - 0.2538 (g/mile)	0.138 - 0.228 (g/mile)	3.66 - 4.05 (g/mile)	
McCormick, R. L.; Williams, A.; Ireland, J.; Brimhall, M.; Hayes, R. R. Effects of Biodiesel Blends on Vehicle Emissions;NREL/MP-540-40554; Oct 1, 06.	2000	B20	HD	Chassis Dyno.	Steady State		23.1 - 30.3 (g/mile)	.36 - 1.48 (g/mile)	.17 - .45 (g/mile)	7.58 - 24.49 (g/mile)	
McCormick, R. L.; Williams, A.; Ireland, J.; Brimhall, M.; Hayes, R. R. Effects of Biodiesel Blends on Vehicle Emissions;NREL/MP-540-40554; Oct 1, 06.	2000	Diesel	HD	Chassis Dyno.	Steady State		22.27 - 29.65 (g/mile)	0.4826 - 1.83 (g/mile)	0.20 - 0.536 (g/mile)	8.14 - 27.41 (g/mile)	
McCormick, R. L.; Williams, A.; Ireland, J.; Brimhall, M.; Hayes, R. R. Effects of Biodiesel Blends on Vehicle Emissions;NREL/MP-540-40554; Oct 1, 06.	2004	B20	HD	Chassis Dyno.	Steady State		9.79 - 10.39 (g/mile)	.20 - .53 (g/mile)	.30 - .43 (g/mile)	5.72 - 6.93 (g/mile)	
McCormick, R. L.; Williams, A.; Ireland, J.; Brimhall, M.; Hayes, R. R. Effects of Biodiesel Blends on Vehicle Emissions;NREL/MP-540-40554; Oct 1, 06.	2004	Diesel	HD	Chassis Dyno.	Steady State		9.78 - 9.85 (g/mile)	0.193 - 0.695 (g/mile)	0.373 - 0.439 (g/mile)	5.22 - 8.95 (g/mile)	
McCormick, R. L.; Williams, A.; Ireland, J.; Brimhall, M.; Hayes, R. R. Effects of Biodiesel Blends on Vehicle Emissions;NREL/MP-540-40554; Oct 1, 06.	2006	B20	HD	Chassis Dyno.	Steady State		7.64 - 9.14 (g/mile)	.0012 - .0017 (g/mile)	.021 - .031 (g/mile)	.06 - .12 (g/mile)	
McCormick, R. L.; Williams, A.; Ireland, J.; Brimhall, M.; Hayes, R. R. Effects of Biodiesel Blends on Vehicle Emissions;NREL/MP-540-40554; Oct 1, 06.	2006	Diesel	HD	Chassis Dyno.	Steady State		7.70 - 8.93 (g/mile)	0.0009 - 0.0014 (g/mile)	0.023 (g/mile)	0.10 - 0.15 (g/mile)	
McCormick, R. L.; Williams, A.; Ireland, J.; Brimhall, M.; Hayes, R. R. Effects of Biodiesel Blends on Vehicle Emissions;NREL/MP-540-40554; Oct 1, 06.	2005	B20	HD	Chassis Dyno.	Steady State		6.9 - 11.0 (g/mile)	.14 - .21 (g/mile)	.45 - .99 (g/mile)	1.82 - 4.22 (g/mile)	

Reference	Model Year	Fuel	Engine	Test	Test Cycle	Emission Control System	Nox	PM	HC	CO	CO$_2$
McCormick, R. L.; Williams, A.; Ireland, J.; Brimhall, M.; Hayes, R. R. Effects of Biodiesel Blends on Vehicle Emissions;NREL/MP-540-40554; Oct 1, 06.	2005	Diesel	HD	Chassis Dyno.	Steady State		6.75 - 11.04 (g/mile)	0.2163 - 0.299 (g/mile)	0.515 - 1.192 (g/mile)	2.13 - 4.98 (g/mile)	
McCormick, R. L.; Williams, A.; Ireland, J.; Brimhall, M.; Hayes, R. R. Effects of Biodiesel Blends on Vehicle Emissions;NREL/MP-540-40554; Oct 1, 06.	2000	B20	HD	Chassis Dyno.	Steady State		18.65 (g/mile)	0.23 (g/mile)	.63 (g/mile)	2.63 (g/mile)	
McCormick, R. L.; Williams, A.; Ireland, J.; Brimhall, M.; Hayes, R. R. Effects of Biodiesel Blends on Vehicle Emissions;NREL/MP-540-40554; Oct 1, 06.	2000	Diesel	HD	Chassis Dyno.	Steady State		19.80 (g/mile)	0.274 (g/mile)	0.871 (g/mile)	3.60 (g/mile)	
McCormick, R. L.; Williams, A.; Ireland, J.; Brimhall, M.; Hayes, R. R. Effects of Biodiesel Blends on Vehicle Emissions;NREL/MP-540-40554; Oct 1, 06.	2000	B20	HD	Chassis Dyno.	Steady State		18.67 (g/mile)	.22 (g/mile)	.57 (g/mile)	2.73 (g/mile)	
McCormick, R. L.; Williams, A.; Ireland, J.; Brimhall, M.; Hayes, R. R. Effects of Biodiesel Blends on Vehicle Emissions;NREL/MP-540-40554; Oct 1, 06.	2000	Diesel	HD	Chassis Dyno.	Steady State		19.44 (g/mile)	0.321 (g/mile)	0.794 (g/mile)	3.43 (g/mile)	
McCormick, R. L.; Williams, A.; Ireland, J.; Brimhall, M.; Hayes, R. R. Effects of Biodiesel Blends on Vehicle Emissions;NREL/MP-540-40554; Oct 1, 06.	2000	B20	HD	Chassis Dyno.	Steady State		19.04 - 19.7 (g/mile)	.24 (g/mile)	.592 - .66 (g/mile)	2.48 - 2.7 (g/mile)	
McCormick, R. L.; Williams, A.; Ireland, J.; Brimhall, M.; Hayes, R. R. Effects of Biodiesel Blends on Vehicle Emissions;NREL/MP-540-40554; Oct 1, 06.	2000	Diesel	HD	Chassis Dyno.	Steady State		19.78 (g/mile)	0.3079 (g/mile)	0.824 (g/mile)	3.04 (g/mile)	
McCormick, R. L.; Williams, A.; Ireland, J.; Brimhall, M.; Hayes, R. R. Effects of Biodiesel Blends on Vehicle Emissions;NREL/MP-540-40554; Oct 1, 06.	2000	B20	HD	Chassis Dyno.	Steady State		6.75 - 29.65 (g/mile)	0.0014 - 1.83 (g/mile)	0.023 - 1.192 (g/mile)	0.10 - 27.41 (g/mile)	
McCormick, R. L.; Williams, A.; Ireland, J.; Brimhall, M.; Hayes, R. R. Effects of Biodiesel Blends on Vehicle Emissions;NREL/MP-540-40554; Oct 1, 06.	2000	Diesel	HD	Chassis Dyno.	Steady State		20.24 (g/mile)	0.281 (g/mile)	0.824 (g/mile)	3.07 (g/mile)	
Guo, H.; Shenghua, L.; Longbao, Z.; Dayong, J. Study on Ethylene Glycol Monomethyl Ether Peanut Oil Monoester as a Novel Biodiesel. SAE International 2008, 2008-01-1575.		B100 Peanut Oil Monoester	Test Engine	Engine Dyno.	Steady State		350 - 1400 (x10^{-6})		3 - 7 (x10^{-6})	.01 - .17 (%vol.)	

Reference	Model Year	Fuel	Engine	Test	Test Cycle	Emission Control System	Nox	PM	HC	CO	CO_2
Guo, H.; Shenghua, L.; Longbao, Z.; Dayong, J. Study on Ethylene Glycol Monomethyl Ether Peanut Oil Monoester as a Novel Biodiesel. SAE International 2008, 2008-01-1575.		B50 Peanut Oil Monoester	Test Engine	Engine Dyno.	Steady State		350 - 1300 ($x10^{-6}$)		5.5 - 9.5 ($x10^{-6}$)	.01 - 0.2 (% vol.)	
Guo, H.; Shenghua, L.; Longbao, Z.; Dayong, J. Study on Ethylene Glycol Monomethyl Ether Peanut Oil Monoester as a Novel Biodiesel. SAE International 2008, 2008-01-1575.		Diesel	Test Engine	Engine Dyno.	Steady State		375 - 1550 (ppm)		7 - 13 (ppm)	0.02 - 0.23 (% vol.)	
Saanum, I.; Bysveen, M.; Hustad, J. E. Study of Particulate Matter-,NOx-and Hydrocarbon Emissions from a Diesel Engine Fueled with Diesel Oil and Biodiesel with Fumigation of Hydrogen, Methane and Propane. SAE International 2008, 2008-01-1809.	1995	B80 Rapeseed	MD		Varying Load	EURO 2	10 - 13.5 (g/kWh)	.04 - .12 (g/kWh)	0.3 - 5.5 (g/kWh)		
Fanick, E. R. Diesel Fuel Keeping Pace with Diesel Engine Technology. SAE International 2008, 2008-01-1808.		B100 Linseed	HD		Steady State		4.9 - 5.1 (g/hp-hr)	.05 - .08 (g/hp-hr)		.04 - 1.3 (g/hp-hr)	
Fanick, E. R. Diesel Fuel Keeping Pace with Diesel Engine Technology. SAE International 2008, 2008-01-1808.		B20 Linseed	HD		Steady State		4.7 - 4.9 (g/hp-hr)	.09 - .11 (g/hp-hr)		0.7 - 1.6 (g/hp-hr)	
Fanick, E. R. Diesel Fuel Keeping Pace with Diesel Engine Technology. SAE International 2008, 2008-01-1808.		Diesel	HD		Steady State		4.6 - 4.7 (g/hp-hr)	0.1 - 0.125 (g/hp-hr)		0.75 - 2.05 (g/hp-hr)	
Williams, A.; McCormick, R. L.; Hayes, R.; Ireland, J. Biodiesel Effects on Diesel Particle Filter Performance;NREL/TP-540-39606; Mar, 06.	2002	B20 Soybean Oil	HD	Engine Dyno.	Steady State	EGR/ Diesel Oxidation Catalyst (CCRT)	2.15 - 2.18 (g/bhp-hr)	.001 - .002 (g/bhp-hr)	0.001 (g/bhp-hr)	0.01 (g/bhp-hr)	
Williams, A.; McCormick, R. L.; Hayes, R.; Ireland, J. Biodiesel Effects on Diesel Particle Filter Performance;NREL/TP-540-39606; Mar, 06.	2002	B20 Soybean Oil	HD	Engine Dyno.	Steady State	EGR	2.13 - 2.23 (g/bhp-hr)	.061 - .074 (g/bhp-hr)	.13 - .17 (g/bhp-hr)	.99 - 1.14 (g/bhp-hr)	
Williams, A.; McCormick, R. L.; Hayes, R.; Ireland, J. Biodiesel Effects on Diesel Particle Filter Performance;NREL/TP-540-39606; Mar, 06.	2002	Diesel	HD	Engine Dyno.	Steady State	EGR	2.05 (g/bhp-hr)	0.0859 (g/bhp-hr)	0.172 (g/bhp-hr)	1.19 (g/bhp-hr)	
McCormick, R. L.; Alleman, T. L. Impact of Biodiesel Fuel on Pollutant Emissions from Diesel Engines; NREL: 07.	1991	B100	HD		Steady State, varying iodine number		5.7 - 7.3 (g/kWh)	0.7 - 2.5 (g/kWh)			
McCormick, R. L.; Alleman, T. L. Impact of Biodiesel Fuel on Pollutant Emissions from Diesel Engines; NREL: 07.	1991	B20	HD		Steady State, varying iodine number		1 % change	-12 % change	-20 % change	-12 % change	

Reference	Model Year	Fuel	Engine	Test	Test Cycle	Emission Control System	Nox	PM	HC	CO	CO_2
McCormick, R. L.; Alleman, T. L. Impact of Biodiesel Fuel on Pollutant Emissions from Diesel Engines; NREL: 07.	1991	B100	HD		Steady State, varying iodine number		10 % change	-48 % change	-67 % change	-48 % change	
Mazzoleni, C.; Kuhns, H. D.; Moosmüller, H.; Witt, J.; Nussbaum, N. J.; Chang, M.-C. O.; Parthasarathy, G.; Kumar, S.; Nathagoundenpalayam, K.; Nikolich, G.; Watson, J. G. A case study of real-world tailpipe emissions for school buses using a 20% biodiesel blend. Science of the Total Environment 385, 146-159. 2007.	1983-2004	B20	HD	On Road	Steady state		20 - 36 (g/kg)	1.1 - 2.1 (g/kg)	1.6 - 5.0 (g/kg)	17 - 40 (g/kg)	
Kim, M. Y.; Yoon, S. H.; Hwang, J. W.; Lee, C. S. Characteristics of Particulate Emissions of Compression Ignition Engine Fueled With Biodiesel Derived From Soybean. ASME Internal Combustion Engine Division 2007 Fall Technical Conference 2007, ICEF2007-1715, 1-7.		B100 Soybean Oil	Test Engine	Engine Dyno.	Constant Speeds		3 - 8 (g/kWh)		.05 - .06 (g/kWh)	.5 - 2.0 (g/kWh)	
Mbarawa, M. Performance, emission and economic assessment of clove stem oil-diesel blended fuels as alternative fuels for diesel engines. Renewable Energy 2008, 33 (5), 871-882.		B25 Clove Stem Oil	LD	Engine Dyno.	Constant Speeds		200 - 260 (ppm)		7 - 55 (ppm)	0.9 - 1.4 %	10.3 - 12.5 %
Mbarawa, M. Performance, emission and economic assessment of clove stem oil-diesel blended fuels as alternative fuels for diesel engines. Renewable Energy 2008, 33 (5), 871-882.		B50 Clove Stem Oil	LD	Engine Dyno.	Constant Speeds		310 - 460 (ppm)		6 - 52 (ppm)	.45 - 1.15 %	11.4 - 13.8 %
Mbarawa, M. Performance, emission and economic assessment of clove stem oil-diesel blended fuels as alternative fuels for diesel engines. Renewable Energy 2008, 33 (5), 871-882.		Diesel	LD	Engine Dyno.	Constant Speeds		310 - 450 (ppm)		13 - 72 (ppm)	0.9 - 1.55 (%)	11.4 - 13.8 (%)
Durbin, T. D.; Norbeck, J. M. The Effects of Biodiesel Blends and ARCO EC-Diesel on Emissions from Light Heavy-Duty Diesel Vehicles; CE-CERT: 02.	1983-1993	B20 Soy Gold (Soybean Oil)	HD	Chassis Dyno.	Steady State		1.9 - 10 (g/mi)	160 - 960 (mg/mi.)	.15 - 1.3 (g/mi)	.9 - 7.7 (g/mi.)	
Durbin, T. D.; Norbeck, J. M. The Effects of Biodiesel Blends and ARCO EC-Diesel on Emissions from Light Heavy-Duty Diesel Vehicles; CE-CERT: 02.	1983-1993	B20 OXyG B-60 (Yellow Grease)	HD	Chassis Dyno.	Steady State		2.0 - 9.2 (g/mi.)	170 - 640 (mg/mi)	.15 - 1.0 (g/mi.)	0.8 - 6.0 (g/mi.)	

Reference	Model Year	Fuel	Engine	Test	Test Cycle	Emission Control System	Nox	PM	HC	CO	CO_2
Durbin, T. D.; Norbeck, J. M. The Effects of Biodiesel Blends and ARCO EC-Diesel on Emissions from Light Heavy-Duty Diesel Vehicles; CE-CERT: 02.	1983-1993	Diesel	HD	Chassis Dyno.	Steady State		2 - 8.7 (g/mi.)	125 - 600 (g/mile)	0.10 - 1.30 (g/mile)	0.70 - 7.50 (g/mile)	
Sheehan, J.; Camobreco, V.; Duffield, J.; Graboski, M.; Shapouri, H. An Overview of Biodiesel and Petroleum Diesel Life Cycles;NREL/TP-580-24772; NREL: May, 98.		B20 Soybean Oil	HD	On Road	Steady State		4.9 (g/bhp-h)	.07 (g/bhp-h)	.09 (g/bhp-h)	1.1(g/bhp-h)	520 (g/bhp-h)
Sheehan, J.; Camobreco, V.; Duffield, J.; Graboski, M.; Shapouri, H. An Overview of Biodiesel and Petroleum Diesel Life Cycles;NREL/TP-580-24772; NREL: May, 98.		B100 Soybean Oil	HD	On Road	Steady State		5.2 (g/bhp-h)	.03 (g/bhp-h)	.06 (g/bhp-h)	543 (g/bhp-h)	130 (g/bhp-h)
Sheehan, J.; Camobreco, V.; Duffield, J.; Graboski, M.; Shapouri, H. An Overview of Biodiesel and Petroleum Diesel Life Cycles;NREL/TP-580-24772; NREL: May, 98.		Diesel	HD	On Road	Steady State		4.8 (g/bhp-h)	0.08 (g/bhp-h)	0.1 (g/bhp-h)	1.2 (g/bhp-h)	633 (g/bhp-h)
Murillo, S.; Miguez, J. L.; Porteiro, J.; Granada, E.; Moran, J. C. Performance and exhaust emissions in the use of biodiesel in outboard diesel engines. Fuel 2007, 86 (12-13), 1765-1771.		B30 Waste Coooking Oil	outboard engine	Engine Dyno.	Constant Speeds		5.5 - 13.2 (g/kWh)			8.0 - 14.4 (g/kWh)	
Murillo, S.; Miguez, J. L.; Porteiro, J.; Granada, E.; Moran, J. C. Performance and exhaust emissions in the use of biodiesel in outboard diesel engines. Fuel 2007, 86 (12-13), 1765-1771.		B100 Waste Coooking Oil	outboard engine	Engine Dyno.	Constant Speeds		6.1 - 15.2 (g/kWh)			8.0 - 13.0 (g/kWh)	
Murillo, S.; Miguez, J. L.; Porteiro, J.; Granada, E.; Moran, J. C. Performance and exhaust emissions in the use of biodiesel in outboard diesel engines. Fuel 2007, 86 (12-13), 1765-1771.		Diesel	outboard engine	Engine Dyno.	Constant Speeds		5 - 13.7 (g/kWh)			8 - 15.5 (g/kWh)	
Wang, W. G.; Lyons, D. W.; Clark, N. N.; Gautam, M.; Norton, P. M. Emissions from nine heavy trucks fueled by diesel and biodiesel blend without engine modification. Environmental Science & Technology 34[6], 933-939. 2000.		B35 Soybean Oil	HD	Chassis Dyno.	Truck Cylce/Mile Route Cycle		20 - 260 (ppm)	0.2 - 2.1 (g/mi.)	9 - 13 (ppm)	10 - 210 (ppm)	
Durbin, T. D.; Collins, J. R.; Norbeck, J. M.; Smith, M. R. Effects of biodiesel, biodiesel blends, and a synthetic diesel on emissions from light heavy-duty diesel vehicles. Environmental Science & Technology 34[3], 349-355. 2000.	1988	B100	HD	Chassis Dyno.	Federal Test Procedure	None	6.3 (g/mi)	425 (mg/mi)	.32 (g/mi)	1.35 (g/mi)	

Reference	Model Year	Fuel	Engine	Test	Test Cycle	Emission Control System	Nox	PM	HC	CO	CO_2
Durbin, T. D.; Collins, J. R.; Norbeck, J. M.; Smith, M. R. Effects of biodiesel, biodiesel blends, and a synthetic diesel on emissions from light heavy-duty diesel vehicles. Environmental Science & Technology 34[3], 349-355. 2000.	1988	B20	HD	Chassis Dyno.	Federal Test Procedure	None	7.0 (g/mi)	400 (mg/mi)	.33 (g/mi)	1.30 (g/mi)	
Durbin, T. D.; Collins, J. R.; Norbeck, J. M.; Smith, M. R. Effects of biodiesel, biodiesel blends, and a synthetic diesel on emissions from light heavy-duty diesel vehicles. Environmental Science & Technology 34[3], 349-355. 2000.	1990	B100	HD	Chassis Dyno.	Federal Test Procedure	None	6.3 (g/mi)	480 (mg/mi)	1.12 (g/mi)	2.20 (g/mi)	
Durbin, T. D.; Collins, J. R.; Norbeck, J. M.; Smith, M. R. Effects of biodiesel, biodiesel blends, and a synthetic diesel on emissions from light heavy-duty diesel vehicles. Environmental Science & Technology 34[3], 349-355. 2000.	1990	B20	HD	Chassis Dyno.	Federal Test Procedure	None	7.0 (g/mi)	850 (mg/mi)	.73 (g/mi)	2.25 (g/mi)	
Durbin, T. D.; Collins, J. R.; Norbeck, J. M.; Smith, M. R. Effects of biodiesel, biodiesel blends, and a synthetic diesel on emissions from light heavy-duty diesel vehicles. Environmental Science & Technology 34[3], 349-355. 2000.	1995	B100	HD	Chassis Dyno.	Federal Test Procedure	Oxidation Catalyst	6.2 (g/mi)	110 (mg/mi)	.50 (g/mi)	1.90 (g/mi)	
Durbin, T. D.; Collins, J. R.; Norbeck, J. M.; Smith, M. R. Effects of biodiesel, biodiesel blends, and a synthetic diesel on emissions from light heavy-duty diesel vehicles. Environmental Science & Technology 34[3], 349-355. 2000.	1995	B20	HD	Chassis Dyno.	Federal Test Procedure	Oxidation Catalyst	6.5 (g/mi)	120 (mg/mi)	.22 (g/mi)	1.75 (g/mi)	
Durbin, T. D.; Collins, J. R.; Norbeck, J. M.; Smith, M. R. Effects of biodiesel, biodiesel blends, and a synthetic diesel on emissions from light heavy-duty diesel vehicles. Environmental Science & Technology 34[3], 349-355. 2000.	1996	B100	HD	Chassis Dyno.	Federal Test Procedure	Oxidation Catalyst	8.5 (g/mi)	75 (mg/mi)	.33 (g/mi)	1.60 (g/mi)	
Durbin, T. D.; Collins, J. R.; Norbeck, J. M.; Smith, M. R. Effects of biodiesel, biodiesel blends, and a synthetic diesel on emissions from light heavy-duty diesel vehicles. Environmental Science & Technology 34[3], 349-355. 2000.	1996	B20	HD	Chassis Dyno.	Federal Test Procedure	Oxidation Catalyst	8.4 (g/mi)	80 (mg/mi)	.28 (g/mi)	1.62 (g/mi)	
Durbin, T. D.; Collins, J. R.; Norbeck, J. M.; Smith, M. R. Effects of biodiesel, biodiesel blends, and a synthetic diesel on emissions from light heavy-duty diesel vehicles. Environmental Science & Technology 34[3], 349-355. 2000.	1988 - 1996	Diesel	HD	Chassis Dyno.	Federal Test Procedure	Oxidation Catalyst	6.25 - 8.25 (g/mi)	75 - 350 (mg/mi)	0.35 - 0.92 (g/mile)	1.45 - 2.25 (g/mi.)	

Reference	Model Year	Fuel	Engine	Test	Test Cycle	Emission Control System	Nox	PM	HC	CO	CO_2
Tsolakis, A. Effects on particle size distribution from the diesel engine operating on RME-biodiesel with EGR. Energy & Fuels 2006, 20 (4), 1418-1424.		B100 Rapeseed Oil	Test Engine	Engine Dyno.	3 Different Engine Operating Conditions	EGR	580 - 920 (ppm)				
Tsolakis, A. Effects on particle size distribution from the diesel engine operating on RME-biodiesel with EGR. Energy & Fuels 2006, 20 (4), 1418-1424.		Diesel	Test Engine	Engine Dyno.	3 Different Engine Operating Conditions	EGR	200 - 700 (ppm)				
Kegl, B. Experimental investigation of optimal timing of the diesel engine injection pump using biodiesel fuel. Energy & Fuels 2006, 20 (4), 1460-1470.		B100 Rapeseed	HD	Engine Dyno.	Constant Speeds	Direct Injection M system	800 - 2750 (ppm)		50 - 100 (ppm)	150 - 600 (ppm)	
Kegl, B. Experimental investigation of optimal timing of the diesel engine injection pump using biodiesel fuel. Energy & Fuels 2006, 20 (4), 1460-1470.		Diesel	HD	Engine Dyno.	Constant Speeds	Direct Injection M system	800 - 1700 (ppm)		50 - 100 (ppm)	100 - 700 (ppm)	
Agarwal, D.; Sinha, S.; Agarwal, A. K. Experimental investigation of control of NOx emissions in biodiesel-fueled compression ignition engine. Renewable Energy 2006, 31 (14), 2356-2369.		B10 Rice Bran Oil	LD	Genset	Constant Speeds with varying EGR %	EGR	50 - 155 (ppm)		850 - 3100 (ppm)	200 - 730 (ppm)	
Agarwal, D.; Sinha, S.; Agarwal, A. K. Experimental investigation of control of NOx emissions in biodiesel-fueled compression ignition engine. Renewable Energy 2006, 31 (14), 2356-2369.		Diesel	LD	Genset	Constant Speeds with varying EGR %	EGR	65 - 200 (ppm)		1200 - 3000 (ppm)	175 - 625 (ppm)	
Leung, D. Y. C.; Luo, Y.; Chan, T. L. Optimization of exhaust emissions of a diesel engine fuelled with biodiesel. Energy & Fuels 2006, 20 (3), 1015-1023.			Test Engine		Varyinig Engine settings		450 - 1150 (ppm)		107 - 130 (ppm)		
Zheng, M.; Mulenga, M. C.; Reader, G. T.; Wang, M. P.; Ting, D. S. K.; Tjong, J. Biodiesel engine performance and emissions in low temperature combustion. Fuel 2008, 87 (6), 714-722.		B100 Soy Bean Oil	Test Engine	Engine Dyno.	Steady Shot	EGR	8.0 (g/kWh)		0.1 (g/kWh)	2.3 (g/kWh)	
Zheng, M.; Mulenga, M. C.; Reader, G. T.; Wang, M. P.; Ting, D. S. K.; Tjong, J. Biodiesel engine performance and emissions in low temperature combustion. Fuel 2008, 87 (6), 714-722.		B100 Canola	Test Engine	Engine Dyno.	Steady Shot	EGR	3.3 (g/kWh)		0.2 (g/kWh)	3.0 (g/kWh)	
Zheng, M.; Mulenga, M. C.; Reader, G. T.; Wang, M. P.; Ting, D. S. K.; Tjong, J. Biodiesel engine performance and emissions in low temperature combustion. Fuel 2008, 87 (6), 714-722.		B100 Yellow Grease	Test Engine	Engine Dyno.	Steady Shot	EGR	3.8 (g/kWh)		0.2 (g/kWh)	2.2 (g/kWh)	

Reference	Model Year	Fuel	Engine	Test	Test Cycle	Emission Control System	Nox	PM	HC	CO	CO_2
Zheng, M.; Mulenga, M. C.; Reader, G. T.; Wang, M. P.; Ting, D. S. K.; Tjong, J. Biodiesel engine performance and emissions in low temperature combustion. Fuel 2008, 87 (6), 714-722.		Diesel	Test Engine	Engine Dyno.	Steady Shot	EGR	3.7 (g/kWh)		0.4 (g/kWh)	4.25 (g/kWh)	
Hribernik, A.; Kegl, B. Influence of biodiesel fuel on the combustion and emission formation in a direct injection (DI) diesel engine. Energy & Fuels 2007, 21 (3), 1760-1767.		B100	LD turbo	Engine Dyno.	Constant Speeds		6.1 - 7.1 (g/kWh)		0.9 - 1.3 (g/kWh)	0.5 - 4.0 (g/kWh)	
Hribernik, A.; Kegl, B. Influence of biodiesel fuel on the combustion and emission formation in a direct injection (DI) diesel engine. Energy & Fuels 2007, 21 (3), 1760-1767.		B100	MD	Engine Dyno.	Constant Speeds		6.6 - 12.6 (g/kWh)		0.1 - 0.2 (g/kWh)	0.6 - 1.6 (g/kWh)	
Hribernik, A.; Kegl, B. Influence of biodiesel fuel on the combustion and emission formation in a direct injection (DI) diesel engine. Energy & Fuels 2007, 21 (3), 1760-1767.		Diesel	MD	Engine Dyno.	Constant Speeds		6.6 - 12.6 (g/kWh)		0.2 - 2.2 (g/kWh)	0.5 - 2.1 (g/kWh)	
Zhang, Y.; Boehman, A. L. Impact of biodiesel on NOx emissions in a common rail direct injection diesel engine. Energy & Fuels 2007, 21 (4), 2003-2012.		B20	LD		Low load and High load	EGR	2.8 - 5.8 (g/kWh)				
Zhang, Y.; Boehman, A. L. Impact of biodiesel on NOx emissions in a common rail direct injection diesel engine. Energy & Fuels 2007, 21 (4), 2003-2012.		B40	LD		Low load and High load	EGR	2.7 - 6.4 (g/kWh)				
Lu, X. C.; Ma, J. J.; Ji, L. B.; Huang, Z. Experimental study on the combustion characteristics and emissions of biodiesel fueled compression ignition engines with premixed dimethoxymethane. Lu, X. C.; Ma, J. J.; Ji, L. B.; Huang, Z. Experimental study on the combustion characteristics and emissions of biodiesel fueled compression ignition engines with premixed dimethoxymethane. .		B100 Soy Bean Oil with Dimethoxy methane	Test Engine	Engine Dyno.	Vary DMM %	EGR	40 - 550 (ppm)		50 - 160 (ppm)	0.02 - 0.32 (%)	
Kegl, B. NOx and particulate matter (PM) emissions reduction potential by biodiesel usage. Energy & Fuels 2007, 21, 3310-3316.		B100 Soy Bean Oil	HD	Engine Dyno.	13 modes of European stationary cycle test		75 - 2400 (ppm)		30 - 110 (ppm)	120 - 810 (ppm)	
Kegl, B. NOx and particulate matter (PM) emissions reduction potential by biodiesel usage. Energy & Fuels 2007, 21, 3310-3316.		Diesel	HD	Engine Dyno.	13 modes of European stationary cycle test		125 - 2200 (ppm)		42 - 160 (ppm)	170 - 800 (ppm)	

Reference	Model Year	Fuel	Engine	Test	Test Cycle	Emission Control System	Nox	PM	HC	CO	CO_2
Ozkan, M. Comparative study of the effect of biodiesel and diesel fuel on a compression ignition engine's performance, emissions, and its cycle by cycle variations. Energy & Fuels 2007, 21, 3627-3636.		B100	LD	Engine Dyno.	Constant Speeds		360 - 650 (ppm)		0.8 - 3.0 (ppm)	.02 - .03 (% vol.)	10.8 - 12.4 (% vol.)
Ozkan, M. Comparative study of the effect of biodiesel and diesel fuel on a compression ignition engine's performance, emissions, and its cycle by cycle variations. Energy & Fuels 2007, 21, 3627-3636.		Diesel	LD	Engine Dyno.	Constant Speeds		230 - 575 (% vol.)		0.5 - 2.3 (% vol.)	0.07 - 0.10 (% vol.)	12 - 14 (% vol.)
Lu, X.; Ma, J.; Ji, L.; Huang, Z. Simultaneous reduction of NOx emission and smoke opacity of biodiesel-fueled engines by port injection of ethanol. Fuel 2007, 87, 1289-1296.		B100 and Ethanol	Test Engine	Engine Dyno.	Constant Speed varying Ethanol %		30 - 550 (ppm)		230 - 500 (ppm)	.08 - 0.3 (%)	
Lin, Y. C.; Lee, C. F.; Fang, T. Characterization of particle size distribution from diesel engines fueled with palm-biodiesel blends and paraffinic fuel blends LIN2008. Atmos. Environ. 2008, 42 (6), 1133-1143.		B20 Palm Oil	HD	Engine Dyno.	Steady State			1.07 (mgm^3)	2.2 (ppm)	24.8 (ppm)	6980 (ppm)
Lin, Y. C.; Lee, C. F.; Fang, T. Characterization of particle size distribution from diesel engines fueled with palm-biodiesel blends and paraffinic fuel blends LIN2008. Atmos. Environ. 2008, 42 (6), 1133-1143.		B100 Palm Oil	HD	Engine Dyno.	Steady State			1.37 (mgm^3)	4.7 (ppm)	29.1 (ppm)	6570 (ppm)
Lin, Y. C.; Lee, C. F.; Fang, T. Characterization of particle size distribution from diesel engines fueled with palm-biodiesel blends and paraffinic fuel blends LIN2008. Atmos. Environ. 2008, 42 (6), 1133-1143.		Diesel	HD	Engine Dyno.	Steady State		49 (ppm)	1.23 mg/m^3	4.8 (ppm)	27.0 (ppm)	6650 (ppm)
Muncrief, R. L.; Rooks, C. W.; Cruz, M.; Harold, M. P. Combining biodiesel and exhaust gas recirculation for reduction in NOx and particulate emissions. Energy & Fuels 2008, 22 (2), 1285-1296.	1999	B20 Cottonseed Oil	HD	Chassis Dyno.	On Road SAE J1263	EGR and DPF	13.9 (g/mi.)	0.53 (g/mi.)	0.02 (g/mi.)	0.18 (g/mi.)	2461 (g/mi.)
Muncrief, R. L.; Rooks, C. W.; Cruz, M.; Harold, M. P. Combining biodiesel and exhaust gas recirculation for reduction in NOx and particulate emissions. Energy & Fuels 2008, 22 (2), 1285-1296.	1999	B50 Cottonseed Oil	HD	Chassis Dyno.	On Road SAE J1263	EGR and DPF	13.1 (g/mi.)	0.34 (g/mi.)	0.02 (g/mi.)	0.13 (g/mi.)	2452 (g/mi.)
Muncrief, R. L.; Rooks, C. W.; Cruz, M.; Harold, M. P. Combining biodiesel and exhaust gas recirculation for reduction in NOx and particulate emissions. Energy & Fuels 2008, 22 (2), 1285-1296.	1999	B100 Cottonseed Oil	HD	Chassis Dyno.	On Road SAE J1263	EGR and DPF	11.9 (g/mi.)	0.22 (g/mi.)	0.03 (g/mi.)	0.22 (g/mi.)	2460 (g/mi.)

Reference	Model Year	Fuel	Engine	Test	Test Cycle	Emission Control System	Nox	PM	HC	CO	CO_2
Muncrief, R. L.; Rooks, C. W.; Cruz, M.; Harold, M. P. Combining biodiesel and exhaust gas recirculation for reduction in NOx and particulate emissions. Energy & Fuels 2008, 22 (2), 1285-1296.	1999	B100 Soy Bean Oil	HD	Chassis Dyno.	On Road SAE J1263	EGR and DPF	14.2 (g/mi.)	0.21 (g/mi.)	0.03 (g/mi.)	0.21 (g/mi.)	2464 (g/mi.)
Muncrief, R. L.; Rooks, C. W.; Cruz, M.; Harold, M. P. Combining biodiesel and exhaust gas recirculation for reduction in NOx and particulate emissions. Energy & Fuels 2008, 22 (2), 1285-1296.	1999	B20 Cottonseed Oil	HD	Chassis Dyno.	On Road SAE J1263	None	18.0 (g/mi.)	0.30 (g/mi.)	0.03 (g/mi.)	0.19 (g/mi.)	2444 (g/mi.)
Muncrief, R. L.; Rooks, C. W.; Cruz, M.; Harold, M. P. Combining biodiesel and exhaust gas recirculation for reduction in NOx and particulate emissions. Energy & Fuels 2008, 22 (2), 1285-1296.	1999	B50 Cottonseed Oil	HD	Chassis Dyno.	On Road SAE J1263	None	16.8 (g/mi.)	0.21 (g/mi.)	0.03 (g/mi.)	0.13 (g/mi.)	2382 (g/mi.)
Muncrief, R. L.; Rooks, C. W.; Cruz, M.; Harold, M. P. Combining biodiesel and exhaust gas recirculation for reduction in NOx and particulate emissions. Energy & Fuels 2008, 22 (2), 1285-1296.	1999	B100 Cottonseed Oil	HD	Chassis Dyno.	On Road SAE J1263	None	16.2 (g/mi.)	0.15 (g/mi.)	0.03 (g/mi.)	0.14 (g/mi.)	2443 (g/mi.)
Muncrief, R. L.; Rooks, C. W.; Cruz, M.; Harold, M. P. Combining biodiesel and exhaust gas recirculation for reduction in NOx and particulate emissions. Energy & Fuels 2008, 22 (2), 1285-1296.	1999	B100 Soy Bean Oil	HD	Chassis Dyno.	On Road SAE J1263	None	18.7 (g/mi.)	0.14 (g/mi.)	0.03 (g/mi.)	0.13 (g/mi.)	2452 (g/mi.)
Muncrief, R. L.; Rooks, C. W.; Cruz, M.; Harold, M. P. Combining biodiesel and exhaust gas recirculation for reduction in NOx and particulate emissions. Energy & Fuels 2008, 22 (2), 1285-1296.	1999	Diesel	HD	Chassis Dyno.	On Road SAE J1263	None	18.7 (g/mi.)	0.40 (g/mi.)			
Bhardwaj; O.; Abraham, M. A Comparative Study of Performance and Emission Characteristics of a CRDe SUV Fueled With Biodiesel Blends and Diesel Fuel. SAE International 2008, 2008-28-0075, 520-529.		B10 Jatropha and B10 Karanja	MD	Chassis Dyno.		Diesel Oxidation Catalyst and EGR	0.45 (gm/km)	0.9 (gm/km)	0.13 (gm/km)	0.48 (gm/km)	
Bhardwaj; O.; Abraham, M. A Comparative Study of Performance and Emission Characteristics of a CRDe SUV Fueled With Biodiesel Blends and Diesel Fuel. SAE International 2008, 2008-28-0075, 520-529.		B20 Jatropha and B20 Karanja	MD	Chassis Dyno.		Diesel Oxidation Catalyst and EGR	0.46 (gm/km)	0.8 (gm/km)	0.12 (gm/km)	0.44 (gm/km)	
Bhardwaj; O.; Abraham, M. A Comparative Study of Performance and Emission Characteristics of a CRDe SUV Fueled With Biodiesel Blends and Diesel Fuel. SAE International 2008, 2008-28-0075, 520-529.		Diesel	MD	Chassis Dyno.		Diesel Oxidation Catalyst and EGR	0.18 (gm/km)	0.10 (gm/km)	0.17 (gm/km)	0.60 (gm/km)	

Reference	Model Year	Fuel	Engine	Test	Test Cycle	Emission Control System	Nox	PM	HC	CO	CO_2
Patterson, J.; Hassan, M. G.; Clarke, A.; Shama, K.; Hellgardt, K.; Chen, R. Experimental Study of DI Diesel Engine Performance Using Three Different Biodiesel Fuels. New Diesel Engines and Components and CI Engine Performance for Use with Alternative Fuels 2006, SP-2014 (2006-01-0234).		B5 Waste Oil	LD	Engine Dyno.	Vary Load and Speed		11 - 22 (g/kWh)				
Patterson, J.; Hassan, M. G.; Clarke, A.; Shama, K.; Hellgardt, K.; Chen, R. Experimental Study of DI Diesel Engine Performance Using Three Different Biodiesel Fuels. New Diesel Engines and Components and CI Engine Performance for Use with Alternative Fuels 2006, SP-2014 (2006-01-0234).		B100 Waste Oil	LD	Engine Dyno.	Vary Load and Speed		6 - 10 (g/kWh)				
Patterson, J.; Hassan, M. G.; Clarke, A.; Shama, K.; Hellgardt, K.; Chen, R. Experimental Study of DI Diesel Engine Performance Using Three Different Biodiesel Fuels. New Diesel Engines and Components and CI Engine Performance for Use with Alternative Fuels 2006, SP-2014 (2006-01-0234).		B5 Soy Bean Oil	LD	Engine Dyno.	Vary Load and Speed		8 - 22 (g/kWh)				
Patterson, J.; Hassan, M. G.; Clarke, A.; Shama, K.; Hellgardt, K.; Chen, R. Experimental Study of DI Diesel Engine Performance Using Three Different Biodiesel Fuels. New Diesel Engines and Components and CI Engine Performance for Use with Alternative Fuels 2006, SP-2014 (2006-01-0234).		B50 Soy Bean Oil	LD	Engine Dyno.	Vary Load and Speed		6 - 20 (g/kWh)				
Patterson, J.; Hassan, M. G.; Clarke, A.; Shama, K.; Hellgardt, K.; Chen, R. Experimental Study of DI Diesel Engine Performance Using Three Different Biodiesel Fuels. New Diesel Engines and Components and CI Engine Performance for Use with Alternative Fuels 2006, SP-2014 (2006-01-0234).		B100 Soy Bean Oil	LD	Engine Dyno.	Vary Load and Speed		4 - 11 (g/kWh)				
Patterson, J.; Hassan, M. G.; Clarke, A.; Shama, K.; Hellgardt, K.; Chen, R. Experimental Study of DI Diesel Engine Performance Using Three Different Biodiesel Fuels. New Diesel Engines and Components and CI Engine Performance for Use with Alternative Fuels 2006, SP-2014 (2006-01-0234).		B5 Rapeseed	LD	Engine Dyno.	Vary Load and Speed		9 - 23 (g/kWh)				

Reference	Model Year	Fuel	Engine	Test	Test Cycle	Emission Control System	Nox	PM	HC	CO	CO_2
Patterson, J.; Hassan, M. G.; Clarke, A.; Shama, K.; Hellgardt, K.; Chen, R. Experimental Study of DI Diesel Engine Performance Using Three Different Biodiesel Fuels. New Diesel Engines and Components and CI Engine Performance for Use with Alternative Fuels 2006, SP-2014 (2006-01-0234).		B50 Rapeseed	LD	Engine Dyno.	Vary Load and Speed		9 - 22 (g/kWh)				
Patterson, J.; Hassan, M. G.; Clarke, A.; Shama, K.; Hellgardt, K.; Chen, R. Experimental Study of DI Diesel Engine Performance Using Three Different Biodiesel Fuels. New Diesel Engines and Components and CI Engine Performance for Use with Alternative Fuels 2006, SP-2014 (2006-01-0234).		B100 Rapeseed	LD	Engine Dyno.	Vary Load and Speed		6 - 10 (g/kWh)				
Patterson, J.; Hassan, M. G.; Clarke, A.; Shama, K.; Hellgardt, K.; Chen, R. Experimental Study of DI Diesel Engine Performance Using Three Different Biodiesel Fuels. New Diesel Engines and Components and CI Engine Performance for Use with Alternative Fuels 2006, SP-2014 (2006-01-0234).		Diesel	LD	Engine Dyno.	Vary Load and Speed		8 - 12 (g/kWh)				
Kawano, D.; Ishii, H.; Goto, Y.; Noda, A. Optimization of Engine System for Application of Biodiesel Fuel. SAE International 2007, JSAE 20077256 (SAE 2007-01-2028), 1254-1260.		B100 Rapeseed Oil	LD		Steady State	EGR, NSR (Nox Sorage Reduction Catalyst), DPNR, OC	0.6 - 1.5 (g/kWh)		.025 - .03 (g/kWh)	.11 - .52 (g/kWh)	
Kawano, D.; Ishii, H.; Goto, Y.; Noda, A. Optimization of Engine System for Application of Biodiesel Fuel. SAE International 2007, JSAE 20077256 (SAE 2007-01-2028), 1254-1260.		Diesel	LD		Steady State	EGR, NSR (Nox Sorage Reduction Catalyst), DPNR, OC	0 - 1.0 (g/kWh)				
Krahl, J.; Munack, A.; Ruschel, Y.; Schroder, O.; Bunger, J. Comparison of Emissions and Mutagenicity from Biodiesel, Vegetable Oil, GTL and Diesel Fuel. SAE International 2007		B100 Rapeseed Oil	LD	Engine Dyno.	ESC		5.6 (g/kWh)	.03 (g/kWh)		0.26 (g/kWh)	
Krahl, J.; Munack, A.; Ruschel, Y.; Schroder, O.; Bunger, J. Comparison of Emissions and Mutagenicity from Biodiesel, Vegetable Oil, GTL and Diesel Fuel. SAE International 2007		Diesel	LD	Engine Dyno.	ESC		4.8 (g/kWh)	0.07 (g/kWh)		0.55 (g/kWh)	

Reference	Model Year	Fuel	Engine	Test	Test Cycle	Emission Control System	Nox	PM	HC	CO	CO_2
Reksowardojo, I. K.; Lubis, I. H.; Manggala, S. A.; Brodjonegoro, T. P.; Soerawidjaya, T. H.; Arismunandar, W. Performance and Exhaust Gas Emissions of Using Biodiesel Fuel from Physic Nut (Jatropha Curcas L.) Oil on a Direct Injection Diesel Engine (DI). SAE International 2007, JSAE 20077278 (SAE 2007-01-2025), 1232-1236.		B10 Jatropha	Test Engine		ESC		180 - 1400 (ppm)		390 - 950 (ppm)	500 - 2600 (ppm)	
Reksowardojo, I. K.; Lubis, I. H.; Manggala, S. A.; Brodjonegoro, T. P.; Soerawidjaya, T. H.; Arismunandar, W. Performance and Exhaust Gas Emissions of Using Biodiesel Fuel from Physic Nut (Jatropha Curcas L.) Oil on a Direct Injection Diesel Engine (DI). SAE International 2007, JSAE 20077278 (SAE 2007-01-2025), 1232-1236.		B20 Jatropha	Test Engine		ESC		200 - 1280 (ppm)		420 - 770 (ppm)	400 - 2300 (ppm)	
Reksowardojo, I. K.; Lubis, I. H.; Manggala, S. A.; Brodjonegoro, T. P.; Soerawidjaya, T. H.; Arismunandar, W. Performance and Exhaust Gas Emissions of Using Biodiesel Fuel from Physic Nut (Jatropha Curcas L.) Oil on a Direct Injection Diesel Engine (DI). SAE International 2007, JSAE 20077278 (SAE 2007-01-2025), 1232-1236.		B50 Jatropha	Test Engine		ESC		150 - 1280 (ppm)		520 - 850 (ppm)	430 - 1900 (ppm)	
Reksowardojo, I. K.; Lubis, I. H.; Manggala, S. A.; Brodjonegoro, T. P.; Soerawidjaya, T. H.; Arismunandar, W. Performance and Exhaust Gas Emissions of Using Biodiesel Fuel from Physic Nut (Jatropha Curcas L.) Oil on a Direct Injection Diesel Engine (DI). SAE International 2007, JSAE 20077278 (SAE 2007-01-2025), 1232-1236.		B100 Jatropha	Test Engine		ESC		180 - 1380 (ppm)		450 - 750 (ppm)	440 - 1800 (ppm)	
Reksowardojo, I. K.; Lubis, I. H.; Manggala, S. A.; Brodjonegoro, T. P.; Soerawidjaya, T. H.; Arismunandar, W. Performance and Exhaust Gas Emissions of Using Biodiesel Fuel from Physic Nut (Jatropha Curcas L.) Oil on a Direct Injection Diesel Engine (DI). SAE International 2007, JSAE 20077278 (SAE 2007-01-2025), 1232-1236.		Diesel	Test Engine		ESC		200 - 1250 (ppm)		620 - 1280 (ppm)	480 - 2600 (ppm)	
Sze, C.; Whinihan, J. K.; Olson, B. A.; Schenk, C. R.; Sobotowski, R. A. Impact of Test Cycle and Biodiesel Concentration on Emissions. SAE 2007 Transactions Journal of Fuels and Lubricants 2007, V116-4 (2007-01-4040).	2006	B20 Soy Bean Oil	HD	Engine Dyno.	FTP,UDDS (28k), UDDS (6k), HWY, HWY (172), NRTC,WHTC	EGR	2.5 - 6.1 (g/bhphr)	.035 - .063 (g/bhphr)	.03 - .17 (g/bhphr)	0.48 - 1.70 (g/bhphr)	590 - 690 (g/bhphr)

Reference	Model Year	Fuel	Engine	Test	Test Cycle	Emission Control System	Nox	PM	HC	CO	CO_2
Sze, C.; Whinihan, J. K.; Olson, B. A.; Schenk, C. R.; Sobotowski, R. A. Impact of Test Cycle and Biodiesel Concentration on Emissions. SAE 2007 Transactions Journal of Fuels and Lubricants 2007, V116-4 (2007-01-4040).	2006	B50 Soy Bean Oil	HD	Engine Dyno.	FTP,UDDS (28k), UDDS (6k), HWY, HWY (172), NRTC,WHTC	EGR	2.8 - 6.2 (g/bhphr)	.022 - .03 (g/bhphr)	.025 - .13 (g/bhphr)	.37 - 1.50 (g/bhphr)	585 - 680 (g/bhphr)
Sze, C.; Whinihan, J. K.; Olson, B. A.; Schenk, C. R.; Sobotowski, R. A. Impact of Test Cycle and Biodiesel Concentration on Emissions. SAE 2007 Transactions Journal of Fuels and Lubricants 2007, V116-4 (2007-01-4040).	2006	Diesel	HD	Engine Dyno.	FTP,UDDS (28k), UDDS (6k), HWY, HWY (172), NRTC,WHTC	EGR	2.3 - 6.0 (g/bhphr)	0.06 - 0.09 (g/bhphr)	0.04 - 0.19 (g/bhphr)	0.6 - 1.8 (g/bhphr)	545 - 690 (g/bhphr)
Baiju, B.; Das, L. M.; GajendraBabu, M. K. Experimental Investigations on a Rubber seed oil Methyl Ester Fueled Compression Ignition Engine. SAE International 2008, 2008-28-0073, 505-513.		B100 Rubber seed oil	Test Engine	Engine Dyno.	Constant Speed		500 - 2150 (ppm)			.03 - .48 (% vol.)	
Baiju, B.; Das, L. M.; GajendraBabu, M. K. Experimental Investigations on a Rubber seed oil Methyl Ester Fueled Compression Ignition Engine. SAE International 2008, 2008-28-0073, 505-513.		B20 Rubber seed oil	Test Engine	Engine Dyno.	Constant Speed		500 - 2550 (ppm)			.03 - .63 (% vol.)	
Baiju, B.; Das, L. M.; GajendraBabu, M. K. Experimental Investigations on a Rubber seed oil Methyl Ester Fueled Compression Ignition Engine. SAE International 2008, 2008-28-0073, 505-513.		B10 Rubber seed oil	Test Engine	Engine Dyno.	Constant Speed		500 - 2520 (ppm)			.03 - .73 (% vol.)	
Baiju, B.; Das, L. M.; GajendraBabu, M. K. Experimental Investigations on a Rubber seed oil Methyl Ester Fueled Compression Ignition Engine. SAE International 2008, 2008-28-0073, 505-513.		Diesel	Test Engine	Engine Dyno.	Constant Speed		475 - 2100 (ppm)			.03 - .83 (% vol.)	
Wu, Y. P. G.; Lin, Y. F.; Chang, C. T. Combustion characteristics of fatty acid methyl esters derived from recycled cooking oil. Fuel 2007, 86, 2810-2816.		B100 Waste cooking oil	LD		Constant Speed		5 - 160 (ppm)	80 - 460 (mg/m^3)	10 - 50 (ppm)	.025 - .24 (% vol.)	2.5 - 4.0 (% vol.)
Wu, Y. P. G.; Lin, Y. F.; Chang, C. T. Combustion characteristics of fatty acid methyl esters derived from recycled cooking oil. Fuel 2007, 86, 2810-2816.		Diesel	LD		Constant Speed		5 - 25 (ppm)	15 - 100 (mg/m^3)	10 - 20 (ppm)	.03 - .09 (% vol.)	2.6 - 3.0 (% vol.)
Raheman, H.; Ghadge, S. V. Performance of compression ignition engine with mahua (Madhuca indica) biodiesel. Fuel 2007, 86, 2568-2573.		B20 Mahua Oil	Test Engine	Engine Dyno.	Constant Loads		18 - 45 (ppm)			.11 - .23 (% vol.)	

Reference	Model Year	Fuel	Engine	Test	Test Cycle	Emission Control System	Nox	PM	HC	CO	CO_2
Raheman, H.; Ghadge, S. V. Performance of compression ignition engine with mahua (Madhuca indica) biodiesel. Fuel 2007, 86, 2568-2573.		B40 Mahua Oil	Test Engine	Engine Dyno.	Constant Loads		18 - 50 (ppm)			.07 - .22 (% vol.)	
Raheman, H.; Ghadge, S. V. Performance of compression ignition engine with mahua (Madhuca indica) biodiesel. Fuel 2007, 86, 2568-2573.		B60 Mahua Oil	Test Engine	Engine Dyno.	Constant Loads		18 - 47 (ppm)			.06 - .12 (% vol.)	
Raheman, H.; Ghadge, S. V. Performance of compression ignition engine with mahua (Madhuca indica) biodiesel. Fuel 2007, 86, 2568-2573.		B80 Mahua Oil	Test Engine	Engine Dyno.	Constant Loads		23 - 48 (ppm)			.05 - .08 (% vol.)	
Raheman, H.; Ghadge, S. V. Performance of compression ignition engine with mahua (Madhuca indica) biodiesel. Fuel 2007, 86, 2568-2573.		B100 Mahua Oil	Test Engine	Engine Dyno.	Constant Loads		19 - 47 (ppm)			.02 - .07 (% vol.)	
Raheman, H.; Ghadge, S. V. Performance of compression ignition engine with mahua (Madhuca indica) biodiesel. Fuel 2007, 86, 2568-2573.		Diesel	Test Engine	Engine Dyno.	Constant Loads		17 - 44 (ppm)			.12 - .20 (% vol.)	
Sahoo, P. K.; Das, L. M.; Babu, M. K. G.; Naik, S. N. Biodiesel development from high acid value polanga seed oil and performance evaluation in a CI engine. Fuel 2007, 86 (3), 448-454.		B20 Polanga Oil	LD	AC Generator /Load bank	Constant Loads		25 - 88 (ppm)		1.3 - 3.4 (ppm)		.4 - .6 (% vol.)
Sahoo, P. K.; Das, L. M.; Babu, M. K. G.; Naik, S. N. Biodiesel development from high acid value polanga seed oil and performance evaluation in a CI engine. Fuel 2007, 86 (3), 448-454.		B40 Polanga Oil	LD	AC Generator /Load bank	Constant Loads		28 - 78 (ppm)		1.2 - 2.8 (ppm)		.5 - .6 (% vol.)
Sahoo, P. K.; Das, L. M.; Babu, M. K. G.; Naik, S. N. Biodiesel development from high acid value polanga seed oil and performance evaluation in a CI engine. Fuel 2007, 86 (3), 448-454.		B60 Polanga Oil	LD	AC Generator /Load bank	Constant Loads		28 - 80 (ppm)		1.2 - 2.2 (ppm)		.5 - .6 (% vol.)
Sahoo, P. K.; Das, L. M.; Babu, M. K. G.; Naik, S. N. Biodiesel development from high acid value polanga seed oil and performance evaluation in a CI engine. Fuel 2007, 86 (3), 448-454.		B80 Polanga Oil	LD	AC Generator /Load bank	Constant Loads		25 - 78 (ppm)		0 - 2.6 (ppm)		.4 - .6 (% vol.)
Sahoo, P. K.; Das, L. M.; Babu, M. K. G.; Naik, S. N. Biodiesel development from high acid value polanga seed oil and performance evaluation in a CI engine. Fuel 2007, 86 (3), 448-454.		B100 Polanga Oil	LD	AC Generator /Load bank	Constant Loads		27 - 76 (ppm)		.4 - 1.2 (ppm)		.4 - .6 (% vol.)
Sahoo, P. K.; Das, L. M.; Babu, M. K. G.; Naik, S. N. Biodiesel development from high acid value polanga seed oil and performance evaluation in a CI engine. Fuel 2007, 86 (3), 448-454.		Diesel Polanga Oil	LD	AC Generator /Load bank	Constant Loads		28 - 75 (ppm)		1.3 - 3.0 (ppm)		.4 - .6 (% vol.)

Reference	Model Year	Fuel	Engine	Test	Test Cycle	Emission Control System	Nox	PM	HC	CO	CO_2
Lapuerta, M.; Armas, O.; Ballesteros, R.; Fernandez, J. Diesel emissions from biofuels derived from Spanish potential vegetable oils. Fuel 2005, 84 (6), 773-780.		B25 Cyrana Oil	LD	Hydraulic Brake	Transient cycle 70/220 amendment 2001/C 240 E/01	Turbo, intercooler	450 - 2250 (mg/kWh)	0.2 - 0.6 (g/kWh)	0.1 - .026 (g/kWh)		
Lapuerta, M.; Armas, O.; Ballesteros, R.; Fernandez, J. Diesel emissions from biofuels derived from Spanish potential vegetable oils. Fuel 2005, 84 (6), 773-780.		B100 Cyrana Oil	LD	Hydraulic Brake	Transient cycle 70/220 amendment 2001/C 240 E/01	Turbo, intercooler	700 - 2100 (mg/kWh)	0.22 - 0.25 (g/kWh)	0.08 - 0.16 (g/kWh)		
Lapuerta, M.; Armas, O.; Ballesteros, R.; Fernandez, J. Diesel emissions from biofuels derived from Spanish potential vegetable oils. Fuel 2005, 84 (6), 773-780.		B25 Sunflower Oil	LD	Hydraulic Brake	Transient cycle 70/220 amendment 2001/C 240 E/01	Turbo, intercooler	200 - 2050 (mg/kWh)	0.35 - 0.7 (g/kWh)	0.18 - 0.78 (g/kWh)		
Lapuerta, M.; Armas, O.; Ballesteros, R.; Fernandez, J. Diesel emissions from biofuels derived from Spanish potential vegetable oils. Fuel 2005, 84 (6), 773-780.		B100 Sunflower Oil	LD	Hydraulic Brake	Transient cycle 70/220 amendment 2001/C 240 E/01	Turbo, intercooler	500 - 2250 (mg/kWh)	0.22 - 0.42 (g/kWh)	0.15 - 0.12 (g/kWh)		
Lapuerta, M.; Armas, O.; Ballesteros, R.; Fernandez, J. Diesel emissions from biofuels derived from Spanish potential vegetable oils. Fuel 2005, 84 (6), 773-780.		Diesel	LD	Hydraulic Brake	Transient cycle 70/220 amendment 2001/C 240 E/01	Turbo, intercooler	550 - 2300 (mg/kWh)	0.37 - 1.13 (g/kWh)	0.2 - 0.76 (g/kWh)		
Keskin, A.; Guru, M.; Altiparmak, D. Biodiesel production from tall oil with synthesized Mn and Ni based additives: Effects of the additives on fuel consumption and emissions. Fuel 2007, 86 (7-8), 1139-1143.		B60 Tall Oil	Test Engine	Electrical Dyno.	Constant Speeds		190 - 420 (ppm)			350 - 1900 (ppm)	
Keskin, A.; Guru, M.; Altiparmak, D. Biodiesel production from tall oil with synthesized Mn and Ni based additives: Effects of the additives on fuel consumption and emissions. Fuel 2007, 86 (7-8), 1139-1143.		Diesel	Test Engine	Electrical Dyno.	Constant Speeds		230 - 380 (ppm)			600 - 2900 (ppm)	
Basavaraja, T.; Reddy, R. P.; Swamy, V. Effect of Injection Pressure on Emission Performance of Bio-diesel and its Blends. Automotive Research Association of India 2005, 467-473.		B10 Pongamia Oil	Test Engine	Engine Dyno.	Constant Speed		1130 - 1160 (ppm)		50 - 55 (ppm)	0.3 - 0.38 (%)	
Basavaraja, T.; Reddy, R. P.; Swamy, V. Effect of Injection Pressure on Emission Performance of Bio-diesel and its Blends. Automotive Research Association of India 2005, 467-473.		B20 Pongamia Oil	Test Engine	Engine Dyno.	Constant Speed		1030 - 1120 (ppm)		43 - 52 (ppm)	0.27 - 0.33 (%)	
Basavaraja, T.; Reddy, R. P.; Swamy, V. Effect of Injection Pressure on Emission Performance of Bio-diesel and its Blends. Automotive Research Association of India 2005, 467-473.		B40 Pongamia Oil	Test Engine	Engine Dyno.	Constant Speed		1050 - 1165 (ppm)		53 - 63 (ppm)	0.3 - 0.4 (%)	

Reference	Model Year	Fuel	Engine	Test	Test Cycle	Emission Control System	Nox	PM	HC	CO	CO_2
Basavaraja, T.; Reddy, R. P.; Swamy, V. Effect of Injection Pressure on Emission Performance of Bio-diesel and its Blends. Automotive Research Association of India 2005, 467-473.		B100 Pongamia Oil	Test Engine	Engine Dyno.	Constant Speed		1125 - 1185 (ppm)		52 - 60 (ppm)	0.36 - 0.42 (%)	
Basavaraja, T.; Reddy, R. P.; Swamy, V. Effect of Injection Pressure on Emission Performance of Bio-diesel and its Blends. Automotive Research Association of India 2005, 467-473.		Diesel	Test Engine	Engine Dyno.	Constant Speed		1040 - 1110 (ppm)		65 - 72 (ppm)	0.48 - 0.6 (%)	
Malhotra, R. K.; Jain, P.; Chopra, A.; Maheshwari, M. Effect of Bio-diesel Blends on Performance and Exhaust Emissions in Passenger Car. Automotive Research Association of India 2005, 479-482.		B20 Pongamia	Average	Chassis Dyno.	Indian Driving Cycle			.051 (g/km)		.143 (g/km)	
Malhotra, R. K.; Jain, P.; Chopra, A.; Maheshwari, M. Effect of Bio-diesel Blends on Performance and Exhaust Emissions in Passenger Car. Automotive Research Association of India 2005, 479-482.		B20 Jatropha	Average	Chassis Dyno.	Indian Driving Cycle			.053 (g/km)		.141 (g/km)	
Malhotra, R. K.; Jain, P.; Chopra, A.; Maheshwari, M. Effect of Bio-diesel Blends on Performance and Exhaust Emissions in Passenger Car. Automotive Research Association of India 2005, 479-482.		Diesel	Average	Chassis Dyno.	Indian Driving Cycle			.065 (g/km)		.178 (g/km)	
Suryawanshi, J. G.; Deshpande, N. V. Overview of EGR, Injection Timing and Pressure on Emissions and Performance of CI Engine with Pongaia Methyl Ester. SAE Technical Paper Series 2005.		B20 Pongamia	Test Engine	Engine Dyno.	Various loads	EGR	75 - 1500 (ppm)		26 - 43 (ppm)		
Suryawanshi, J. G.; Deshpande, N. V. Overview of EGR, Injection Timing and Pressure on Emissions and Performance of CI Engine with Pongaia Methyl Ester. SAE Technical Paper Series 2005.		B40 Pongamia	Test Engine	Engine Dyno.	Various loads	EGR	100 - 1600 (ppm)		22 - 43 (ppm)		
Suryawanshi, J. G.; Deshpande, N. V. Overview of EGR, Injection Timing and Pressure on Emissions and Performance of CI Engine with Pongaia Methyl Ester. SAE Technical Paper Series 2005.		B60 Pongamia	Test Engine	Engine Dyno.	Various loads	EGR	75 - 1500 (ppm)		20 - 43 (ppm)		
Suryawanshi, J. G.; Deshpande, N. V. Overview of EGR, Injection Timing and Pressure on Emissions and Performance of CI Engine with Pongaia Methyl Ester. SAE Technical Paper Series 2005.		B80 Pongamia	Test Engine	Engine Dyno.	Various loads	EGR	150 - 1450 (ppm)		16 - 43 (ppm)		

Reference	Model Year	Fuel	Engine	Test	Test Cycle	Emission Control System	Nox	PM	HC	CO	CO_2
Suryawanshi, J. G.; Deshpande, N. V. Overview of EGR, Injection Timing and Pressure on Emissions and Performance of CI Engine with Pongaia Methyl Ester. SAE Technical Paper Series 2005.		B100 Pongamia	Test Engine	Engine Dyno.	Various loads	EGR	100 - 1500 (ppm)		13 - 44 (ppm)		
Suryawanshi, J. G.; Deshpande, N. V. Overview of EGR, Injection Timing and Pressure on Emissions and Performance of CI Engine with Pongaia Methyl Ester. SAE Technical Paper Series 2005.		Diesel	Test Engine	Engine Dyno.	Various loads	EGR	200 - 1400 (ppm)		33 - 43 (ppm)		
Sinha, S.; Agarwai, A. K. Ricebran Oil Biodiesel's Performance, Emission and Endurance Test on a CIDI Transport Engine. SAE International 2008.		B20 Rice Bran	MD	Engine Dyno.	Constant speeds and loads (IS 14599:1999		3.1 - 4.3 (g/kWh)		0.24 - 0.4 (g/kWh)	2.8 - 5.1 (g/kWh)	10.7 - 11.9 (%)
Sinha, S.; Agarwai, A. K. Ricebran Oil Biodiesel's Performance, Emission and Endurance Test on a CIDI Transport Engine. SAE International 2008.		B50 Rice Bran	MD	Engine Dyno.	Constant speeds and loads (IS 14599:1999		3.4 - 4.7 (g/kWh)		0.2 - 0.31 (g/kWh)	2.0 - 3.0 (g/kWh)	10.2 - 11.5 (%)
Sinha, S.; Agarwai, A. K. Ricebran Oil Biodiesel's Performance, Emission and Endurance Test on a CIDI Transport Engine. SAE International 2008.		Diesel	MD	Engine Dyno.	Constant speeds and loads (IS 14599:1999		3.0- 4.1 (g/kWh)		0.33 - 0.52 (g/kWh)	3.7 - 5.3 (g/kWh)	11.5 - 12.7 (%)
Bielaczyc, P.; Szczotka, A. A Study of RME-Based Biodiesel Blend Influence on Performance, Reliability and Emissions from Modern Light-Duty Diesel Engines. SAE International 2008.		B5 Rapeseed	LD	Engine Dyno.	Elementary ECE (UDC) driving cycle	turbo	0.38 (g/km)	.010 (g/km)	0.07 (g/km)	0.78 (g/km)	145 (g/km)
Bielaczyc, P.; Szczotka, A. A Study of RME-Based Biodiesel Blend Influence on Performance, Reliability and Emissions from Modern Light-Duty Diesel Engines. SAE International 2008.		B20 Rapeseed	LD	Engine Dyno.	Elementary ECE (UDC) driving cycle	turbo	0.37 (g/km)	.0095 (g/km)	0.075 (g/km)	0.85 (g/km)	145 (g/km)
Bielaczyc, P.; Szczotka, A. A Study of RME-Based Biodiesel Blend Influence on Performance, Reliability and Emissions from Modern Light-Duty Diesel Engines. SAE International 2008.		B30 Rapeseed	LD	Engine Dyno.	Elementary ECE (UDC) driving cycle	turbo	0.37 (g/km)	.008 (g/km)	0.085 (g/km)	0.92 (g/km)	150 (g/km)
Bielaczyc, P.; Szczotka, A. A Study of RME-Based Biodiesel Blend Influence on Performance, Reliability and Emissions from Modern Light-Duty Diesel Engines. SAE International 2008.		Diesel	LD	Engine Dyno.	Elementary ECE (UDC) driving cycle	turbo	0.37 (g/km)	.010 (g/km)	0.080 (g/km)	0.90 (g/km)	140 (g/km)
Okamoto, T.; Nakasato, T.; Konno, M. Fuel Properties and Engine Performance of Dimethyl Ether-Blended Biodiesel Fuels. SAE International 2007, JSAE-20077080.		B100 Palm Oil	Single Cylinder farm engine		Constant Speed		325 - 1200 (ppm)				

Reference	Model Year	Fuel	Engine	Test	Test Cycle	Emission Control System	Nox	PM	HC	CO	CO_2
Okamoto, T.; Nakasato, T.; Konno, M. Fuel Properties and Engine Performance of Dimethyl Ether-Blended Biodiesel Fuels. SAE International 2007, JSAE-20077080.		B50 Palm Oil	Single Cylinder farm engine		Constant Speed		325 - 1125 (ppm)				
Okamoto, T.; Nakasato, T.; Konno, M. Fuel Properties and Engine Performance of Dimethyl Ether-Blended Biodiesel Fuels. SAE International 2007, JSAE-20077080.		B25 Palm Oil	Single Cylinder farm engine		Constant Speed		320 - 1180 (ppm)				
Okamoto, T.; Nakasato, T.; Konno, M. Fuel Properties and Engine Performance of Dimethyl Ether-Blended Biodiesel Fuels. SAE International 2007, JSAE-20077080.		Diesel	Single Cylinder farm engine		Constant Speed		400 - 1100 (ppm)				
Myo, T.; Kinoshita, E.; Tsuru, H.; Hamasaki, K. Combustion Characteristics of a DI Diesel Engine with Palm Kernel Oil Biodiesel and Its Blend (B20). SAE International 2007, JSAE-20076568.		Palm Kernel Oil	Test Engine	Engine Dyno.	Varying Load		175 - 1125 (ppm)		17 - 39 (ppm)	200 - 415 (ppm)	
Myo, T.; Kinoshita, E.; Tsuru, H.; Hamasaki, K. Combustion Characteristics of a DI Diesel Engine with Palm Kernel Oil Biodiesel and Its Blend (B20). SAE International 2007, JSAE-20076568.		Palm Oil	Test Engine	Engine Dyno.	Varying Load		200 - 1100 (ppm)		20 - 45 (ppm)	200 - 400 (ppm)	
Myo, T.; Kinoshita, E.; Tsuru, H.; Hamasaki, K. Combustion Characteristics of a DI Diesel Engine with Palm Kernel Oil Biodiesel and Its Blend (B20). SAE International 2007, JSAE-20076568.		Cottonseed Oil	Test Engine	Engine Dyno.	Varying Load		175 - 1075 (ppm)		18 - 40 (ppm)	200 - 410 (ppm)	
Myo, T.; Kinoshita, E.; Tsuru, H.; Hamasaki, K. Combustion Characteristics of a DI Diesel Engine with Palm Kernel Oil Biodiesel and Its Blend (B20). SAE International 2007, JSAE-20076568.		Diesel	Test Engine	Engine Dyno.	Varying Load		175 - 1200 (pm)		32 - 73 (ppm)	225 - 565 (ppm)	
Sundarapandian; Devaradjane Theoretical and Experimental Investigation of the Performance of Vegetable Oil Operated CI Engine. SAE International 2007, JSAE-20076567.		B100 Jatropha	Test Engine	Engine Dyno.	Constant Speed with varying injection timing		680 - 890 (ppm)		72 - 84 (ppm)	0.28 - 0.30 (%)	
Sundarapandian; Devaradjane Theoretical and Experimental Investigation of the Performance of Vegetable Oil Operated CI Engine. SAE International 2007, JSAE-20076567.		B100 Mahua Oil	Test Engine	Engine Dyno.	Constant Speed with varying injection timing		650 - 880 (ppm)		76 - 86 (ppm)	0.27 - .031 (%)	

Reference	Model Year	Fuel	Engine	Test	Test Cycle	Emission Control System	Nox	PM	HC	CO	CO_2
Sundarapandian; Devaradjane Theoretical and Experimental Investigation of the Performance of Vegetable Oil Operated CI Engine. SAE International 2007, JSAE-20076567.		B100 Neem Oil	Test Engine	Engine Dyno.	Constant Speed with varying injection timing		660 - 875 (ppm)		78 - 86 (ppm)	0.28 - 0.31 (%)	
Sundarapandian; Devaradjane Theoretical and Experimental Investigation of the Performance of Vegetable Oil Operated CI Engine. SAE International 2007, JSAE-20076567.		Diesel	Test Engine	Engine Dyno.	Constant Speed with varying injection timing		700 - 910 (ppm)		90 - 110 (ppm)	0.34 - 0.37 (%)	
Suryawanshi, J. G.; Deshpande, N. V. The Effects of Combination of EGR, Injection Retard and Injection Pressure on Emissions and Performance of Diesel Engine Fuelled With Jatropha Oil Methyl Ester. ASME International Mechanical Engineering Congress and Exposition 2006, IMECE2006-13021 , 1-12.		B20 Jatropha	Test Engine	Engine Dyno.	Constant Speed	EGR	100 - 1350 (ppm)		25 - 42 (ppm)		
Suryawanshi, J. G.; Deshpande, N. V. The Effects of Combination of EGR, Injection Retard and Injection Pressure on Emissions and Performance of Diesel Engine Fuelled With Jatropha Oil Methyl Ester. ASME International Mechanical Engineering Congress and Exposition 2006, IMECE2006-13021 , 1-12.		B40 Jatropha	Test Engine	Engine Dyno.	Constant Speed	EGR	100 - 1350 (ppm)		20 - 45 (ppm)		
Suryawanshi, J. G.; Deshpande, N. V. The Effects of Combination of EGR, Injection Retard and Injection Pressure on Emissions and Performance of Diesel Engine Fuelled With Jatropha Oil Methyl Ester. ASME International Mechanical Engineering Congress and Exposition 2006, IMECE2006-13021 , 1-12.		B80 Jatropha	Test Engine	Engine Dyno.	Constant Speed	EGR	150 - 1350 (ppm)		17 - 27 (ppm)		
Suryawanshi, J. G.; Deshpande, N. V. The Effects of Combination of EGR, Injection Retard and Injection Pressure on Emissions and Performance of Diesel Engine Fuelled With Jatropha Oil Methyl Ester. ASME International Mechanical Engineering Congress and Exposition 2006, IMECE2006-13021 , 1-12.		B100 Jatropha	Test Engine	Engine Dyno.	Constant Speed	EGR	175 - 1350 (ppm)		17 - 28 (ppm)		

Reference	Model Year	Fuel	Engine	Test	Test Cycle	Emission Control System	Nox	PM	HC	CO	CO_2
Suryawanshi, J. G.; Deshpande, N. V. The Effects of Combination of EGR, Injection Retard and Injection Pressure on Emissions and Performance of Diesel Engine Fuelled With Jatropha Oil Methyl Ester. ASME International Mechanical Engineering Congress and Exposition 2006, IMECE2006-13021 , 1-12.		Diesel	Test Engine	Engine Dyno.	Constant Speed	EGR	225 - 1500 (ppm)		33 - 44 (ppm)		
Li, H.; Andrews, G. E.; Balsevich-Prieto, J. L. Study of Emission and Combustion Characteristics of RME B100 Biodiesel from a Heavy Duty DI Diesel Engine. SAE International 2007.	1999	B100 Rapeseed	HD		Steady State	Turbo, Oxidation catalyst	392 - 566 (ppm)	0.022 - 0.05 (g/kWh)	33 - 106 (ppm)	12 - 75 (ppm)	3.98 - 5.94 (ppm)
Li, H.; Andrews, G. E.; Balsevich-Prieto, J. L. Study of Emission and Combustion Characteristics of RME B100 Biodiesel from a Heavy Duty DI Diesel Engine. SAE International 2007.	1999	Diesel	HD		Steady State	Turbo, Oxidation catalyst	385 - 547 (ppm)	0.032 - 0.06 (g/kWh)	44 - 218 (ppm)	12 - 160 (ppm)	3.50 - 5.91 (ppm)
Li, H.; Andrews, G. E.; Balsevich-Prieto, J. L. Study of Emission and Combustion Characteristics of RME B100 Biodiesel from a Heavy Duty DI Diesel Engine. SAE International 2007.	1999	B100 Rapeseed	HD		Steady State	Turbo	388 - 560 (ppm)	0.027 - 0.07 (g/kWh)	180 - 181 (ppm)	116 - 167 (ppm)	3.99 - 5.84 (ppm)
Li, H.; Andrews, G. E.; Balsevich-Prieto, J. L. Study of Emission and Combustion Characteristics of RME B100 Biodiesel from a Heavy Duty DI Diesel Engine. SAE International 2007.	1999	Diesel	HD		Steady State	Turbo	380 - 539 (ppm)	0.043 - 0.08 (g/kWh)	254 - 320 (ppm)	133 - 220 (ppm)	3.60 - 5.83 (ppm)
Nagaraju, V.; Henein, N.; Quader, A.; Wu, M.; Bryzik, W. Effect of Biodiesel (B-20) on Performance and Emissions in a Single Cylinder HSDI Diesel Engine. SAE International 2008.		B20 Soy Bean Oil	Test Engine		Steady State	Turbo, EGR (50%)	50 (ppm)		190 - 220 (ppm)	1480 - 2250 (ppm)	
Nagaraju, V.; Henein, N.; Quader, A.; Wu, M.; Bryzik, W. Effect of Biodiesel (B-20) on Performance and Emissions in a Single Cylinder HSDI Diesel Engine. SAE International 2008.		Diesel	Test Engine		Steady State	Turbo, EGR (50%)	50 (ppm)		220 - 320 (ppm)	1475 - 2500 (ppm)	
Nagaraju, V.; Henein, N.; Quader, A.; Wu, M.; Bryzik, W. Effect of Biodiesel (B-20) on Performance and Emissions in a Single Cylinder HSDI Diesel Engine. SAE International 2008.		B20 Soy Bean Oil	Test Engine		Steady State	Turbo, EGR (25%)	440 - 450 (ppm)		105 - 150 (ppm)	300 - 700 (ppm)	
Nagaraju, V.; Henein, N.; Quader, A.; Wu, M.; Bryzik, W. Effect of Biodiesel (B-20) on Performance and Emissions in a Single Cylinder HSDI Diesel Engine. SAE International 2008.		Diesel	Test Engine		Steady State	Turbo, EGR (25%)	440 - 500 (ppm)		110 - 180 (ppm)	275 - 800 (ppm)	

Reference	Model Year	Fuel	Engine	Test	Test Cycle	Emission Control System	Nox	PM	HC	CO	CO_2
Verhaeven, E.; Pelkmans, L.; Govaerts, L.; Lamers, R.; Theunissen, F. Results of demonstration and evaluation projects of biodiesel from rapeseed and used frying oil on light and heavy duty vehicles. SAE International 2005.		B100 Used Vegetable Oil	LD	On Road	Traffic conditions	Oxidation Catalyst	27 - 31 (g/km)		1.4 - 2.0 (g/km)	7.8 - 8.7 (g/km)	
Fernando Contadini, J.; Moore, R. M.; Sperling, D.; Sundaresan, M. Life-Cycle Emissions of Alternative Fuels for Transportation: Dealing with Uncertanties. SAE International 2000, 2000-01-0597.		B100 Jatropha	Test Engine	Engine Dyno.	Constant Speed		550 - 825 (ppm)		185 - 295 (ppm)	0.30 -0.50 (% vol)	
Fernando Contadini, J.; Moore, R. M.; Sperling, D.; Sundaresan, M. Life-Cycle Emissions of Alternative Fuels for Transportation: Dealing with Uncertanties. SAE International 2000, 2000-01-0597.		B75 Jatropha	Test Engine	Engine Dyno.	Constant Speed		550 - 815 (ppm)		210 - 380 (ppm)	0.40 - 0.50 (% vol.)	
Fernando Contadini, J.; Moore, R. M.; Sperling, D.; Sundaresan, M. Life-Cycle Emissions of Alternative Fuels for Transportation: Dealing with Uncertanties. SAE International 2000, 2000-01-0597.		B50 Jatropha	Test Engine	Engine Dyno.	Constant Speed		545 - 800 (ppm)		230 - 425 (ppm)	0.40 - 0.50 (% vol.)	
Fernando Contadini, J.; Moore, R. M.; Sperling, D.; Sundaresan, M. Life-Cycle Emissions of Alternative Fuels for Transportation: Dealing with Uncertanties. SAE International 2000, 2000-01-0597.		Diesel	Test Engine	Engine Dyno.	Constant Speed		550 - 785 (ppm)		235 - 460 (ppm)	0.30 - 0.60 (% vol.)	
Marques, A.; Monteiro, E.; Moreira, N. A.; Malheir, S. NOx Emissions Reductions in a Biodiesel Engine by Means of EGR Technology. SAE International 2007.		B15	Test Engine	Engine Dyno.	Varying BMEP	EGR	305 - 325 (ppm)			560 (ppm)	
Marques, A.; Monteiro, E.; Moreira, N. A.; Malheir, S. NOx Emissions Reductions in a Biodiesel Engine by Means of EGR Technology. SAE International 2007.		Diesel	Test Engine	Engine Dyno.	Varying BMEP	EGR	285 - 305 (ppm)			580 (ppm)	
Marques, A.; Monteiro, E.; Moreira, N. A.; Malheir, S. NOx Emissions Reductions in a Biodiesel Engine by Means of EGR Technology. SAE International 2007.		B15	Test Engine	Engine Dyno.	Varying EGR %	EGR	85 - 330 (ppm)			385 - 450 (ppm)	
Marques, A.; Monteiro, E.; Moreira, N. A.; Malheir, S. NOx Emissions Reductions in a Biodiesel Engine by Means of EGR Technology. SAE International 2007.		Diesel	Test Engine	Engine Dyno.	Varying EGR %	EGR	310 - 350 (ppm)			395 - 500 (ppm)	

Reference	Model Year	Fuel	Engine	Test	Test Cycle	Emission Control System	Nox	PM	HC	CO	CO_2
Sinha, S.; Agarwal, A. K. Performance Evaluation of a Biodiesel (Rice Bran Oil Methyl Ester) Fuelled Transport Diesel Engine. SAE Technical Paper Series 2005.		B50 Rice Bran Oil	LD	Engine Dyno.	Constant speeds and loads		4.7 - 5.3 (g/kWh)		0.4 - 1.0 (g/kWh)	3.0 - 5.0 (g/kWh)	
Sinha, S.; Agarwal, A. K. Performance Evaluation of a Biodiesel (Rice Bran Oil Methyl Ester) Fuelled Transport Diesel Engine. SAE Technical Paper Series 2005.		B30 Rice Bran Oil	LD	Engine Dyno.	Constant speeds and loads		4.2 - 5.1 (g/kWh)		0.5 - 0.8 (g/kWh)	2.8 - 6.1 (g/kWh)	
Sinha, S.; Agarwal, A. K. Performance Evaluation of a Biodiesel (Rice Bran Oil Methyl Ester) Fuelled Transport Diesel Engine. SAE Technical Paper Series 2005.		B10 Rice Bran Oil	LD	Engine Dyno.	Constant speeds and loads		4.5 - 6.6 (g/kWh)		1.3 - 4.6 (g/kWh)	4.0 - 8.0 (g/kWh)	
Sinha, S.; Agarwal, A. K. Performance Evaluation of a Biodiesel (Rice Bran Oil Methyl Ester) Fuelled Transport Diesel Engine. SAE Technical Paper Series 2005.		Diesel	LD	Engine Dyno.	Constant speeds and loads		3.0 - 4.2 (g/kWh)		0.5 - 1.4 (g/kWh)	5.0 - 9.5 (g/kWh)	
Sharp, C. A.; Ryan, T. W.; Knothe, G. Heavy-Duty Diesel Engine Emissions Tests using Special Biodiesel Fuels. SAE International 2005.	2003	B100 Soy bean oil	HD		CFR title 40 part 86 subpart N	turbo, EGR	2.54 - 2.56 (g/hp-hr)	0.024 - 0.026 (g/hp-hr)	0.02 - 0.06 (g/hp-hr)	0.40 (g/hp-hr)	
Sharp, C. A.; Ryan, T. W.; Knothe, G. Heavy-Duty Diesel Engine Emissions Tests using Special Biodiesel Fuels. SAE International 2005.	2003	Diesel	HD		CFR title 40 part 86 subpart N	turbo, EGR	2.20 - 2.26 (g/hp-hr)	0.102 - 0.1.4 (g/hp-hr)	0.05 - 0.07 (g/hp-hr)	0.51 - 0.53 (g/hp-hr)	
Kumar, C.; Gajendra Babu, M. K.; Das, L. M. Experimental Investigations on a Karanja Oil Methyl Ester Fueled DI Diesel Engine. SAE International 2006, 2006-01-0238.		B100 Karanja	Test Engine	Electric Generator	Constant Speed, varying load		22 - 54 (g/kWh)		0.18 - 0.38 (g/kWh)	1.0 - 7.0 (g/kWh)	
Kumar, C.; Gajendra Babu, M. K.; Das, L. M. Experimental Investigations on a Karanja Oil Methyl Ester Fueled DI Diesel Engine. SAE International 2006, 2006-01-0238.		B60 Karanja	Test Engine	Electric Generator	Constant Speed, varying load		24 - 45 (g/kWh)		0.16 - 0.64 (g/kWh)	2.0 - 11.0 (g/kWh)	
Kumar, C.; Gajendra Babu, M. K.; Das, L. M. Experimental Investigations on a Karanja Oil Methyl Ester Fueled DI Diesel Engine. SAE International 2006, 2006-01-0238.		B20 Karanja	Test Engine	Electric Generator	Constant Speed, varying load		20 - 42 (g/kWh)		0.11 - 0.55 (g/kWh)	2.5 - 17.0 (g/kWh)	
Kumar, C.; Gajendra Babu, M. K.; Das, L. M. Experimental Investigations on a Karanja Oil Methyl Ester Fueled DI Diesel Engine. SAE International 2006, 2006-01-0238.		Diesel	Test Engine	Electric Generator	Constant Speed, varying load		19 - 52 (g/kWh)		0.15 - 0.54 (g/kWh)	3.0 - 28 (g/kWh)	

Reference	Model Year	Fuel	Engine	Test	Test Cycle	Emission Control System	Nox	PM	HC	CO	CO_2
Hasegawa, M.; Sakurai, Y.; Kobayashi, Y.; Oyama, N.; Sekimoto, M.; Watanabe, H. Effects of Fuel Properties (Content of FAME or GTL) on Diesel Emissions under Various Driving Modes. SAE International 2007, 2007-01-4041.		B100 Rape seed Oil	HD	Chassis Dyno.	JC08, JE05	EGR, DOC, DPD	1.65 - 1.70 (g/km)	0.002 (g/km)	0.02 - 0.03 (g/km)		
Hasegawa, M.; Sakurai, Y.; Kobayashi, Y.; Oyama, N.; Sekimoto, M.; Watanabe, H. Effects of Fuel Properties (Content of FAME or GTL) on Diesel Emissions under Various Driving Modes. SAE International 2007, 2007-01-4041.		B100 Palm Oil	HD	Chassis Dyno.	JC08	EGR, DOC, DPD	1.55 - 1.60 (g/km)	0.002 (g/km)	0.01 - 0.02 (g/km)		
Hasegawa, M.; Sakurai, Y.; Kobayashi, Y.; Oyama, N.; Sekimoto, M.; Watanabe, H. Effects of Fuel Properties (Content of FAME or GTL) on Diesel Emissions under Various Driving Modes. SAE International 2007, 2007-01-4041.		B100 Soy Bean Oil	HD	Chassis Dyno.	JC08	EGR, DOC, DPD	1.70 - 1.75 (g/km)	0.002 (g/km)	0.02 - 0.03 (g/km)		
Hasegawa, M.; Sakurai, Y.; Kobayashi, Y.; Oyama, N.; Sekimoto, M.; Watanabe, H. Effects of Fuel Properties (Content of FAME or GTL) on Diesel Emissions under Various Driving Modes. SAE International 2007, 2007-01-4041.		Diesel	HD	Chassis Dyno.	JC08	EGR, DOC, DPD	1.40 - 1.65 (g/km)	0.002 (g/km)	0.03 - 0.05 (g/km)		
Martin, M. L. J.; Prithviraj, D.; Velappan, K. C. Performance and Emission Characteristics of a CI Engine Fueled with Esterified Cottonseed Oil. SAE International 2005, 2005-26-355.		B100 Cottonseed Oil	Test Engine		Constant Speed				12 - 76 (ppm)	0.07 - 0.28 (%)	
Martin, M. L. J.; Prithviraj, D.; Velappan, K. C. Performance and Emission Characteristics of a CI Engine Fueled with Esterified Cottonseed Oil. SAE International 2005, 2005-26-355.		Diesel	Test Engine		Constant Speed				5 - 48 (ppm)	0.05 - 0.18 (%)	
Kinoshita, E.; Myo, T.; Hamasaki, K.; Nishi, S. Combustion Characteristics of Diesel Engine with Coconut Oil Ethyl Ester. SAE International 2007, JSAE 20077065.		B100 Coconut oil	Test Engine	Engine Dyno.	Constant Loads		190 - 1100 (ppm)		17 - 40 (ppm)	200 - 415 (ppm)	
Kinoshita, E.; Myo, T.; Hamasaki, K.; Nishi, S. Combustion Characteristics of Diesel Engine with Coconut Oil Ethyl Ester. SAE International 2007, JSAE 20077065.		B100 Palm oil	Test Engine	Engine Dyno.	Constant Loads		200 - 1150 (ppm)		20 - 45 (ppm)	210 - 400 (ppm)	
Kinoshita, E.; Myo, T.; Hamasaki, K.; Nishi, S. Combustion Characteristics of Diesel Engine with Coconut Oil Ethyl Ester. SAE International 2007, JSAE		B100 Rapeseed oil	Test Engine	Engine Dyno.	Constant Loads		200 - 1225 (ppm)		23 - 56 (ppm)	225 - 660 (ppm)	

Reference	Model Year	Fuel	Engine	Test	Test Cycle	Emission Control System	Nox	PM	HC	CO	CO_2
20077065.											
Kinoshita, E.; Myo, T.; Hamasaki, K.; Nishi, S. Combustion Characteristics of Diesel Engine with Coconut Oil Ethyl Ester. SAE International 2007, JSAE 20077065.		Diesel	Test Engine	Engine Dyno.	Constant Loads		190 - 1200 (ppm)		32 - 73 (ppm)	220 - 560 (ppm)	
Cho, H. M.; Maji, S.; Pathak, B. D. Waste Cooking Oil as Fuel in Diesel Engines. SAE International 2008, 2008-28-0013.		B100 Waste cooking oil	LD	Electrical Generator	Constant Loads		100 - 2500 (ppm)		22 - 40 (ppm)		
Cho, H. M.; Maji, S.; Pathak, B. D. Waste Cooking Oil as Fuel in Diesel Engines. SAE International 2008, 2008-28-0013.		Diesel	LD	Electrical Generator	Constant Loads		100 - 2000 (ppm)		45 - 65 (ppm)		
Reksowardojo, I. K.; Brodjonegoro, T. P.; Arismunandar, W.; Sopheak, R.; Ogawa, H. The Combustion and Exhaust Gas Emission of a Direct Injection Compression Ignition Engine Using Physic Nut Oil (Jatropha Curcas L.oil). SAE International 2007, 2007-01-3622.		B100 Jatropha	Test Engine	Engine Dyno.	Full Load		100 - 950 (ppm)		580 - 1400 (ppm)	1100 - 8200 (ppm)	
Reksowardojo, I. K.; Brodjonegoro, T. P.; Arismunandar, W.; Sopheak, R.; Ogawa, H. The Combustion and Exhaust Gas Emission of a Direct Injection Compression Ignition Engine Using Physic Nut Oil (Jatropha Curcas L.oil). SAE International 2007, 2007-01-3622.		B10 Jatropha	Test Engine	Engine Dyno.	Full Load		200 - 1350 (ppm)		300 - 700 (ppm)	500 - 3800 (ppm)	
Reksowardojo, I. K.; Brodjonegoro, T. P.; Arismunandar, W.; Sopheak, R.; Ogawa, H. The Combustion and Exhaust Gas Emission of a Direct Injection Compression Ignition Engine Using Physic Nut Oil (Jatropha Curcas L.oil). SAE International 2007, 2007-01-3622.		Diesel	Test Engine	Engine Dyno.	Full Load		200 - 1450 (ppm)		250 - 575 (ppm)	500 - 3200 (ppm)	
Sinha, S.; Agarwal, A. K.; Garg, S. Biodiesel development from rice bran oil: Transesterification process optimization and fuel characterization. Energy Conversion and Management 2008, 49 (5), 1248-1257.		B100 Rice Bran Oil	LD	Engine Dyno.	Constant Loads		6.82 (g/kWh)		0.26 (g/kWh)	1.7 (g/kWh)	
Sinha, S.; Agarwal, A. K.; Garg, S. Biodiesel development from rice bran oil: Transesterification process optimization and fuel characterization. Energy Conversion and Management		B50 Rice Bran Oil	LD	Engine Dyno.	Constant Loads		6.80 (g/kWh)		0.3 (g/kWh)	2.0 (g/kWh)	

Reference	Model Year	Fuel	Engine	Test	Test Cycle	Emission Control System	Nox	PM	HC	CO	CO_2
2008, 49 (5), 1248-1257.											
Sinha, S.; Agarwal, A. K.; Garg, S. Biodiesel development from rice bran oil: Transesterification process optimization and fuel characterization. Energy Conversion and Management 2008, 49 (5), 1248-1257.		B20 Rice Bran Oil	LD	Engine Dyno.	Constant Loads		6.60 (g/kWh)		0.49 (g/kWh)	2.3 (g/kWh)	
Sinha, S.; Agarwal, A. K.; Garg, S. Biodiesel development from rice bran oil: Transesterification process optimization and fuel characterization. Energy Conversion and Management 2008, 49 (5), 1248-1257.		Diesel	LD	Engine Dyno.	Constant Loads		6.15 (g/kWh)		0.65 (g/kWh)	2.9 (g/kWh)	
Biodiesel Handling and Use Guide;DOE/G0-102006-2358; Sep, 06.		B100 Lard					3% increase from diesel				
Biodiesel Handling and Use Guide;DOE/G0-102006-2358; Sep, 06.		B100 tallow					1.8 - 2%				
Biodiesel Handling and Use Guide;DOE/G0-102006-2358; Sep, 06.		B100 Yellow Grease					2.5 - 5.5%				
Biodiesel Handling and Use Guide;DOE/G0-102006-2358; Sep, 06.		B100 Canola					12%				
Biodiesel Handling and Use Guide;DOE/G0-102006-2358; Sep, 06.		B100 Soy bean oil					15%				
Lebedevas, S.; Vaicekauskas, A.; Lebedeva, G.; Makareviciene, V.; Janulis, P.; Kazancev, K. Use of waste fats of animal and vegetable origin for the production of biodiesel fuel: Quality, motor properties, and emissions of harmful components. Energy & Fuels 20[5], 2274-2280. 2006.		B100 Rapeseed oil		hydraulic brake	Steady state		13 - 14 (g/kWh)				3.2 - 9.0 (%)
Lebedevas, S.; Vaicekauskas, A.; Lebedeva, G.; Makareviciene, V.; Janulis, P.; Kazancev, K. Use of waste fats of animal and vegetable origin for the production of biodiesel fuel: Quality, motor properties, and emissions of harmful components. Energy & Fuels 20[5], 2274-2280. 2006.		60% Rapeseed oil, 32% Palm Oil, 8% Linseed Oil		hydraulic brake	Steady state		13 - 13.5 (g/kWh)				3.5 - 9.0 (%)
Lebedevas, S.; Vaicekauskas, A.; Lebedeva, G.; Makareviciene, V.; Janulis, P.; Kazancev, K. Use of waste fats of animal and vegetable origin for the production of biodiesel fuel: Quality, motor properties, and emissions of		Diesel		hydraulic brake	Steady state		12 (g/kWh)				3.5 - 9. (%)

Reference	Model Year	Fuel	Engine	Test	Test Cycle	Emission Control System	Nox	PM	HC	CO	CO_2
harmful components. Energy & Fuels 20[5], 2274-2280. 2006.											
Rantanen, L.; Linnaila, R.; Aakko, P.; Harju, T. NExBTL - Biodiesel Fuel of the Second Generation. SAE International 2005, 2005-01-3771.	1999 - 2004	B5 NExBTL	LD		Steady State	Oxidation Catalyst	2 - -4 % change	-3 - -5 % change	0 - -6 % change	-4 - -7 % change from Diesel	-1 - 1 % change
Rantanen, L.; Linnaila, R.; Aakko, P.; Harju, T. NExBTL - Biodiesel Fuel of the Second Generation. SAE International 2005, 2005-01-3771.	1999 - 2004	B20 NExBTL	LD		Steady State	Oxidation Catalyst	-1 - -3 % change	-1 - -3 % change	-20 - -30 % change	-24 - -40 % change	-2 - -3 % change
Rantanen, L.; Linnaila, R.; Aakko, P.; Harju, T. NExBTL - Biodiesel Fuel of the Second Generation. SAE International 2005, 2005-01-3771.	1999 - 2004	B85 NExBTL	LD		Steady State	Oxidation Catalyst	1 - 7 % change	-18 - -30 % change	-44 - -56 % change	-50 - -52 % change	-3 - -4 % change
Agarwal, A. K. Biofuels (alcohols and biodiesel) applications as fuels for internal combustion engines. Progress in Energy and Combustion Science 33[3], 233-271. 2007.		B100 Sunflower Oil			Steady State		200 - 2100 (ppm)		150 - 350 (ppm)	0.025 - 0.065 (%)	
Agarwal, A. K. Biofuels (alcohols and biodiesel) applications as fuels for internal combustion engines. Progress in Energy and Combustion Science 33[3], 233-271. 2007.		Diesel			Steady State		200 - 1700 (ppm)		365 - 690 (ppm)	0.03 - 0.058 (%)	
Kuronen, M.; Mikkonen, S.; Aakko, P.; Murtonen, T. Hydrotreated Vegetable Oil as Fuel for Heavy Duty Diesel Engines. SAE International 2007, 2007-01-4031.	2007	B100 Hydrotreated Vegetable oil	HD	On Road	Braunschweig	SCR	-8 % change	-30 % change		-6 % change	
Kuronen, M.; Mikkonen, S.; Aakko, P.; Murtonen, T. Hydrotreated Vegetable Oil as Fuel for Heavy Duty Diesel Engines. SAE International 2007, 2007-01-4031.	2007	B100 Hydrotreated Vegetable oil	HD	On Road	Braunschweig	EGR	-10 % change	-46 % change		-50 % change	
Graboski, M. S.; McCormick, R. L.; Alleman, T. L.; Herring, A. M. The Effect of Biodiesel Composition on Engine Emissions from a DDC Series 60 Diesel Engine, Final Report: Report 2 in a series of 6. NREL 2003.	1991	B20 Soy bean Oil	HD		40 CFR Part 86 Subpart N		4.627 - 5.119 (g/bhp-h)	0.221 (g/bhp-h)	0.031 - 0.113 (g/bhp-h)	2.747 - 4.854 (g/bhp-h)	564 - 567 (g/bhp-h)
Graboski, M. S.; McCormick, R. L.; Alleman, T. L.; Herring, A. M. The Effect of Biodiesel Composition on Engine Emissions from a DDC Series 60 Diesel Engine, Final Report: Report 2 in a series of 6. NREL 2003.	1991	B20 Tallow	HD		40 CFR Part 86 Subpart N		4.510 (g/bhp-h)	0.066 - 0.236 (g/bhp-h)	0.069 (g/bhp-h)	4.986 (g/bhp-h)	586 (g/bhp-h)

Reference	Model Year	Fuel	Engine	Test	Test Cycle	Emission Control System	Nox	PM	HC	CO	CO_2
Graboski, M. S.; McCormick, R. L.; Alleman, T. L.; Herring, A. M. The Effect of Biodiesel Composition on Engine Emissions from a DDC Series 60 Diesel Engine, Final Report: Report 2 in a series of 6. NREL 2003.	1991	B100 Canola	HD		40 CFR Part 86 Subpart N		5.178 (g/bhp-h)	0.081 (g/bhp-h)	0.069 (g/bhp-h)	3.129 (g/bhp-h)	572 (g/bhp-h)
Graboski, M. S.; McCormick, R. L.; Alleman, T. L.; Herring, A. M. The Effect of Biodiesel Composition on Engine Emissions from a DDC Series 60 Diesel Engine, Final Report: Report 2 in a series of 6. NREL 2003.	1991	B100 Lard	HD		40 CFR Part 86 Subpart N		4.765 (g/bhp-h)	0.072 (g/bhp-h)	0.077 (g/bhp-h)	2.660 (g/bhp-h)	585 (g/bhp-h)
Graboski, M. S.; McCormick, R. L.; Alleman, T. L.; Herring, A. M. The Effect of Biodiesel Composition on Engine Emissions from a DDC Series 60 Diesel Engine, Final Report: Report 2 in a series of 6. NREL 2003.	1991	B100 tallow	HD		40 CFR Part 86 Subpart N		4.692 - 4.712 (g/bhp-h)	0.067 - 0.071 (g/bhp-h)	0.059 - 0.068 (g/bhp-h)	2.725 - 2.978 (g/bhp-h)	561 - 566 (g/bhp-h)
Graboski, M. S.; McCormick, R. L.; Alleman, T. L.; Herring, A. M. The Effect of Biodiesel Composition on Engine Emissions from a DDC Series 60 Diesel Engine, Final Report: Report 2 in a series of 6. NREL 2003.	1991	Diesel	HD		40 CFR Part 86 Subpart N		4.586 (g/bhp-h)	0.263 (g/bhp-h)	0.105 (g/bhp-h)	5.521 (g/bhp-h)	568 (g/bhp-h)
Graboski, M. S.; McCormick, R. L.; Alleman, T. L.; Herring, A. M. The Effect of Biodiesel Composition on Engine Emissions from a DDC Series 60 Diesel Engine, Final Report: Report 2 in a series of 6. NREL 2003.		B20 Soy Bean Oil	various HD 2-Stroke	On Road	Regular driving conditions		4.25 - 12.11 (g/bhp-hr)	0.11 - 0.81 (g/bhp-hr)	0.12 - 1.43 (g/bhp-hr)	0.45 - 2.73 (g/bhp-hr)	
Graboski, M. S.; McCormick, R. L.; Alleman, T. L.; Herring, A. M. The Effect of Biodiesel Composition on Engine Emissions from a DDC Series 60 Diesel Engine, Final Report: Report 2 in a series of 6. NREL 2003.		B30 Soy Bean Oil	various HD 2-Stroke	On Road	Regular driving conditions		4.78 - 10.7 (g/bhp-hr)	0.173 - 0.258 (g/bhp-hr)	0.29 - 0.54 (g/bhp-hr)	1.03 - 1.69 (g/bhp-hr)	
Graboski, M. S.; McCormick, R. L.; Alleman, T. L.; Herring, A. M. The Effect of Biodiesel Composition on Engine Emissions from a DDC Series 60 Diesel Engine, Final Report: Report 2 in a series of 6. NREL 2003.		B40 Soy Bean Oil	various HD 2-Stroke	On Road	Regular driving conditions		4.86 - 4.89 (g/bhp-hr)	0.162 - 0.258 (g/bhp-hr)	0.38 - 0.43 (g/bhp-hr)	0.95 - 1.07 (g/bhp-hr)	
Graboski, M. S.; McCormick, R. L.; Alleman, T. L.; Herring, A. M. The Effect of Biodiesel Composition on Engine Emissions from a DDC Series 60 Diesel Engine, Final Report: Report 2 in a series of 6. NREL 2003.		B10 Soy Bean Oil	various HD 2-Stroke	On Road	Regular driving conditions		4.38 - 4.97 (g/bhp-hr)	0.186 - 0.286 (g/bhp-hr)	0.53 - 0.72 (g/bhp-hr)	1.43 - 2.33 (g/bhp-hr)	

Reference	Model Year	Fuel	Engine	Test	Test Cycle	Emission Control System	Nox	PM	HC	CO	CO_2
Graboski, M. S.; McCormick, R. L.; Alleman, T. L.; Herring, A. M. The Effect of Biodiesel Composition on Engine Emissions from a DDC Series 60 Diesel Engine, Final Report: Report 2 in a series of 6. NREL 2003.		B100 Soy Bean Oil	various HD 2-Stroke	On Road	Regular driving conditions		5.79 (g/bhp-hr)	0.152 (g/bhp-hr)	0.12 (g/bhp-hr)	0.87 (g/bhp-hr)	
Graboski, M. S.; McCormick, R. L.; Alleman, T. L.; Herring, A. M. The Effect of Biodiesel Composition on Engine Emissions from a DDC Series 60 Diesel Engine, Final Report: Report 2 in a series of 6. NREL 2003.		B10 Rapeseed Oil	various HD 2-Stroke	On Road	Regular driving conditions		5.81 (g/bhp-hr)	0.243 (g/bhp-hr)	0.376 (g/bhp-hr)	1.02 (g/bhp-hr)	
Graboski, M. S.; McCormick, R. L.; Alleman, T. L.; Herring, A. M. The Effect of Biodiesel Composition on Engine Emissions from a DDC Series 60 Diesel Engine, Final Report: Report 2 in a series of 6. NREL 2003.		B20 Rapeseed Oil	various HD 2-Stroke	On Road	Regular driving conditions		5.54 - 5.87 (g/bhp-hr)	0.238 - 0.257 (g/bhp-hr)	0.363 - 0.467 (g/bhp-hr)	1.04 - 1.20 (g/bhp-hr)	
Graboski, M. S.; McCormick, R. L.; Alleman, T. L.; Herring, A. M. The Effect of Biodiesel Composition on Engine Emissions from a DDC Series 60 Diesel Engine, Final Report: Report 2 in a series of 6. NREL 2003.		B40 Rapeseed Oil	various HD 2-Stroke	On Road	Regular driving conditions		5.82 (g/bhp-hr)	0.244 (g/bhp-hr)	0.346 (g/bhp-hr)	0.95 (g/bhp-hr)	
Graboski, M. S.; McCormick, R. L.; Alleman, T. L.; Herring, A. M. The Effect of Biodiesel Composition on Engine Emissions from a DDC Series 60 Diesel Engine, Final Report: Report 2 in a series of 6. NREL 2003.		B100 Rapeseed Oil	various HD 2-Stroke	On Road	Regular driving conditions		5.61 (g/bhp-hr)	0.164 (g/bhp-hr)	0.09 (g/bhp-hr)	0.81 (g/bhp-hr)	
Graboski, M. S.; McCormick, R. L.; Alleman, T. L.; Herring, A. M. The Effect of Biodiesel Composition on Engine Emissions from a DDC Series 60 Diesel Engine, Final Report: Report 2 in a series of 6. NREL 2003.		B20 Tallow	various HD 2-Stroke	On Road	Regular driving conditions		4.01 - 4.7 (g/bhp-hr)	0.22 - 0.254 (g/bhp-hr)	0.37 - 0.38 (g/bhp-hr)	1.49 - 1.8 (g/bhp-hr)	
Graboski, M. S.; McCormick, R. L.; Alleman, T. L.; Herring, A. M. The Effect of Biodiesel Composition on Engine Emissions from a DDC Series 60 Diesel Engine, Final Report: Report 2 in a series of 6. NREL 2003.		Diesel	various HD 2-Stroke	On Road	Regular driving conditions		4.4 - 11.72 (g/bhp-hr)	0.20 - 0.83 (g/bhp-hr)	0.29 - 2.01 (g/bhp-hr)	0.71 - 3.59 (g/bhp-hr)	
Morris, R. E.; Pollak, A. K.; Mansell, G. E.; Lindhjem, C.; Jia, Y.; Wilson, G. Impact of Biodiesel Fuels on Air Quality and Human Health;NREL/SR-540-33793; NREL: May, 03.	<1991	B20	various 2-Stroke	On Road	Regular driving conditions		3.2 % change	-1.8 % change	-20.9 % change	-13.9 % change	
Morris, R. E.; Pollak, A. K.; Mansell, G. E.; Lindhjem, C.; Jia, Y.; Wilson, G. Impact of Biodiesel Fuels on Air Quality and Human Health;NREL/SR-540-33793; NREL: May, 03.	1991	B20	various 2-Stroke	On Road	Regular driving conditions		3.9 % change	-17.8 % change	-17.5 % change	-12.0 % change	

Reference	Model Year	Fuel	Engine	Test	Test Cycle	Emission Control System	Nox	PM	HC	CO	CO_2
Morris, R. E.; Pollak, A. K.; Mansell, G. E.; Lindhjem, C.; Jia, Y.; Wilson, G. Impact of Biodiesel Fuels on Air Quality and Human Health;NREL/SR-540-33793; NREL: May, 03.	<1991	B20	various 4-Stroke	On Road	Regular driving conditions		2.9 % change	-15.7 % change	-12.2 % change	-13.6 % change	
Morris, R. E.; Pollak, A. K.; Mansell, G. E.; Lindhjem, C.; Jia, Y.; Wilson, G. Impact of Biodiesel Fuels on Air Quality and Human Health;NREL/SR-540-33793; NREL: May, 03.	1991 - 1993	B20	various 4-Stroke	On Road	Regular driving conditions		-0.9 % change	-15.7 % change	-2.8 % change	-12.0 % change	
Morris, R. E.; Pollak, A. K.; Mansell, G. E.; Lindhjem, C.; Jia, Y.; Wilson, G. Impact of Biodiesel Fuels on Air Quality and Human Health;NREL/SR-540-33793; NREL: May, 03.	1994+	B20	various 4-Stroke	On Road	Regular driving conditions		2.8 % change	-9.8 % change	-17.9 % change	-15.2 % change	
Morris, R. E.; Pollak, A. K.; Mansell, G. E.; Lindhjem, C.; Jia, Y.; Wilson, G. Impact of Biodiesel Fuels on Air Quality and Human Health;NREL/SR-540-33793; NREL: May, 03.	1991+	B100	various 2-Stroke	On Road	Regular driving conditions		19.6 % change	-33.0 % change	-72.7 % change	-42.4 % change	
Morris, R. E.; Pollak, A. K.; Mansell, G. E.; Lindhjem, C.; Jia, Y.; Wilson, G. Impact of Biodiesel Fuels on Air Quality and Human Health;NREL/SR-540-33793; NREL: May, 03.	1991 - 1993	B100	various 4-Stroke	On Road	Regular driving conditions		13.3 % change	-68.3 % change	-38.7 % change	-41.8 % change	
Morris, R. E.; Pollak, A. K.; Mansell, G. E.; Lindhjem, C.; Jia, Y.; Wilson, G. Impact of Biodiesel Fuels on Air Quality and Human Health;NREL/SR-540-33793; NREL: May, 03.	1994+	B100	various 4-Stroke	On Road	Regular driving conditions		9.9 % change	-36.6 % change	-76.3 % change	-41.5 % change	
McCormick, R. L. The Impact of Biodiesel on Pollutant Emissions and Public Health. Inhalation Toxicology 2006, 19 (1033-1039), 1033-1039.		B20	various	Chassis Dyno.			-7 - 7 % change				
McCormick, R. L. The Impact of Biodiesel on Pollutant Emissions and Public Health. Inhalation Toxicology 2006, 19 (1033-1039), 1033-1039.		B50	various	Chassis Dyno.			-8 - -3 % change				
McCormick, R. L. The Impact of Biodiesel on Pollutant Emissions and Public Health. Inhalation Toxicology 2006, 19 (1033-1039), 1033-1039.		B100	various	Chassis Dyno.			-12 - 12 % change				
Korres, D. M.; Karonis, D.; Lois, E.; Linck, M. B.; Gupta, A. K. Aviation fuel JP-5 and biodiesel on a diesel engine. Fuel 2008, 87, 70-78.		B20 Animal Fat	Test Engine	Electrical Generator	Constant Speed		8 % change	-13 % change			
Korres, D. M.; Karonis, D.; Lois, E.; Linck, M. B.; Gupta, A. K. Aviation fuel JP-5 and biodiesel on a diesel engine. Fuel 2008, 87, 70-78.		B60 Animal Fat	Test Engine	Electrical Generator	Constant Speed		13 % change	-22 % change			

Reference	Model Year	Fuel	Engine	Test	Test Cycle	Emission Control System	Nox	PM	HC	CO	CO_2
Korres, D. M.; Karonis, D.; Lois, E.; Linck, M. B.; Gupta, A. K. Aviation fuel JP-5 and biodiesel on a diesel engine. Fuel 2008, 87, 70-78.		B100 Animal Fat	Test Engine	Electrical Generator	Constant Speed		15 % change	-27 % change			
Williams, A.; McCormick, R. L.; Hayes, R. R.; Ireland, J.; Fang, H. L. Effect of Biodiesel Blends on Diesel Particulate Filter Performance. SAE: 2006.	2002	B20 Soy Bean Oil	HD	Engine Dyno.	Steady State	EGR, DPF	2.22 - 2.27 (g/bhp-hr)	0.0009 - 0.0012 (g/bhp-hr)	-0.001 - 0.001 (g/bhp-hr)	0.01 - 0.05 (g/bhp-hr)	
Williams, A.; McCormick, R. L.; Hayes, R. R.; Ireland, J.; Fang, H. L. Effect of Biodiesel Blends on Diesel Particulate Filter Performance. SAE: 2006.	2002	Diesel	HD	Engine Dyno.	Steady State	EGR, DPF	2.14 - 2.20 (g/bhp-hr)	.0010 - 0.0017 (g/bhp-hr)	0.001 - 0.004 (g/bhp-hr)	0.02 - 0.06 (g/bhp-hr)	
Kegl, B. Effects of biodiesel on emissions of a bus diesel engine. Bioresource Technology . 2007.		B100 Rapeseed	HD	Engine Dyno.	Constant Speeds (ESC test)		-10 - -60 % change		-25 - -60 % change	-60 - 30 % change	
Szybist, J. P.; Kirby, S. R.; Boehman, A. L. NOx emissions of alternative diesel fuels: A comparative analysis of biodiesel and FT diesel. Energy & Fuels 2005, 19 (4), 1484-1492.		B20 Soy Bean Oil	Test Engine		Constant Speed		7 - 15 (g/kWh)				
Szybist, J. P.; Kirby, S. R.; Boehman, A. L. NOx emissions of alternative diesel fuels: A comparative analysis of biodiesel and FT diesel. Energy & Fuels 2005, 19 (4), 1484-1492.		B40 Soy Bean Oil	Test Engine		Constant Speed		8 - 17 (g/kWh)				
Szybist, J. P.; Kirby, S. R.; Boehman, A. L. NOx emissions of alternative diesel fuels: A comparative analysis of biodiesel and FT diesel. Energy & Fuels 2005, 19 (4), 1484-1492.		B100 Soy Bean Oil	Test Engine		Constant Speed		7 - 17 (g/kWh)				
Szybist, J. P.; Kirby, S. R.; Boehman, A. L. NOx emissions of alternative diesel fuels: A comparative analysis of biodiesel and FT diesel. Energy & Fuels 2005, 19 (4), 1484-1492.		Diesel	Test Engine		Constant Speed		8 - 17.5 (g/kWh)				
Srivastava, P. K.; Verma, M. Methyl ester of karanja oil as an alternative renewable source energy. Fuel 2008, 87 (8-9), 1673-1677.		B20 Karanja Oil	LD	Engine Dyno.	Constant Speed		175 - 600 (ppm)		40 - 105 (ppm)	0.10 - 0.20 (%)	
Srivastava, P. K.; Verma, M. Methyl ester of karanja oil as an alternative renewable source energy. Fuel 2008, 87 (8-9), 1673-1677.		B70 Karanja Oil	LD	Engine Dyno.	Constant Speed				48 - 135 (ppm)	0.13 - 0.20 (%)	
Srivastava, P. K.; Verma, M. Methyl ester of karanja oil as an alternative renewable source energy. Fuel 2008, 87 (8-9), 1673-1677.		B100 Karanja Oil	LD	Engine Dyno.	Constant Speed		190 - 680 (ppm)		32 - 90 (ppm)	0.075 - 0.15 (%)	
Srivastava, P. K.; Verma, M. Methyl ester of karanja oil as an alternative renewable source energy. Fuel 2008, 87 (8-9), 1673-1677.		Diesel	LD	Engine Dyno.	Constant Speed		125 - 590 (ppm)		25 - 80 (ppm)	0.07 - 0.11 (%)	

Reference	Model Year	Fuel	Engine	Test	Test Cycle	Emission Control System	Nox	PM	HC	CO	CO$_2$
Kocak, M. S.; Ileri, E.; Utlu, Z. Experimental study of emission parameters of biodiesel fuels obtained from canola, hazelnut, and waste cooking oils. Energy & Fuels 2007, 21, 3622-3626.		B100 Waste Cooking Oil	LD	hydraulic Dyno.	Full Load at various speeds	Turbo	410 - 465 (ppm)			75 - 675 (ppm)	7 - 10.2 (%)
Kocak, M. S.; Ileri, E.; Utlu, Z. Experimental study of emission parameters of biodiesel fuels obtained from canola, hazelnut, and waste cooking oils. Energy & Fuels 2007, 21, 3622-3626.		B100 Canola	LD	hydraulic Dyno.	Full Load at various speeds	Turbo	415 - 470 (ppm)			75 - 720 (ppm)	6.2 - 10.0 (%)
Kocak, M. S.; Ileri, E.; Utlu, Z. Experimental study of emission parameters of biodiesel fuels obtained from canola, hazelnut, and waste cooking oils. Energy & Fuels 2007, 21, 3622-3626.		B100 Hazelnut Oil	LD	hydraulic Dyno.	Full Load at various speeds	Turbo	410 - 460 (ppm)			75 - 675 (ppm)	7.2 - 10.0 (%)
Kocak, M. S.; Ileri, E.; Utlu, Z. Experimental study of emission parameters of biodiesel fuels obtained from canola, hazelnut, and waste cooking oils. Energy & Fuels 2007, 21, 3622-3626.		Diesel	LD	hydraulic Dyno.	Full Load at various speeds	Turbo	410 - 485 (ppm)			100 - 875 (ppm)	8.0 - 10.7 (%)
Kaufman, J. Renewable Diesel. 2007.		B20 Conoco Phillips (Soy)					-7.70%	-9%	-50%	-36%	

Appendix VI. Life-Cycle Studies of Biodistillate Fuels

Appendix VI-1. Overview of Biodistillate Life-Cycle Assessment (LCA) Literature

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Study No.	Ref. No.	Reference	Year	Outline/Objective	Results
1 ✠	(307)	Sheehan, J., Camobreco, V., Duffield, J., Graboski, M., Shapouri, H.; A Life Cycle Inventory of Biodiesel and Petroleum Diesel for Use in an Urban Bus. NREL/SR-580-24089.	1998	Commonly cited early LCA of B100 and B20 for national averages scenarios compared to petroleum fuel. Sensitivity analysis included.	A side by side comparison of biodiesel to petroleum diesel shows that biodiesel has the benefit of both energy and CO_2 emissions. The sensitivity analysis in this study showed robust results for energy and CO_2.
2	(314)	Delucchi, M.; Overview of the Lifecycle Emissions Model (LEM). UCD-ITS-RR-03-17	2002	A summary and overview of updates and changes to previous Life-cycle Emissions Model (LEM) from UC Davis. No numbers to report	LEM uses larger conversion rates for N_2O from N_2 fertilization and other cultivation issues than other models like GREET. This results in biodiesel having a negative impact.
3	(335)	Cardone, M., Mazzoncini, M., Menini, S., Rocco, V., Senatore, A., Seggiani, M., Vitolo, S.; *Brassica carinata* as an alternative oil crop for the production of biodiesel in Italy: agronomic evaluation for the production by transesterification and characterization. Biomass and Bioenergy 25,. (6) 623-623	2003	Investigated use of *B. Carinata* for biodiesel production in comparison to the more common *B. napus* in middle-west Italy. Focused on crop growth.	*B. Carinata* oil is more suitable for biodiesel production than *B. napus* and grows better in adverse conditions. Not a Full-fuel LCA with no emissions to report. Focuses mostly on crop production.
4	(331)	Gartner, S., Reinhardt, G., Braschkat, J.; Life Cycle Assessment of Biodiesel: Update and New Aspects. IFEU Final Report 530-025	2003	Overall comparison of RME w/ diesel fuel and including recent increase in availability of co-products for use.	Comparison shows RME saves CO_2 equivalent emissions compared to diesel. Rape-honey is not a significant co-product.
5 ✠	(324)	Venturi, P., Venturi, G.; Analysis of energy comparison for crops in European agricultural systems. Biomass and Bioenergy 25, (3), 235-255	2003	Investigated 3 feedstocks with ranges of crop yield and co-product allocation.	Bioenergy production is limited by land. Rapeseed is the only crop that gives favorable results in the ranges studied.
6	(336)	Baitz, M., Binder, M., Degen, W., Deimling, S., Krinke, S., Rudloff, M.; Executive summary: Comparative Life-Cycle Assessment for SunDiesel (Choren Process) and Conventional Diesel Fuel. Volkswagen and Daimler Chrysler	2004	Summary of Results of three scenario LCA on SunDiesel produced via the Choren Process (gasification)	Concludes SunDiesel has a great potential to reduce GWP compared w/ conventional diesel. For three different scenarios of H_2 production and utilization: self sufficient/ future and partial self-sufficient.
7 ✠	(317)	Bernesson. S., Nilsson, D., Hansson, P.A.; A Limited LCA Comparing Large- and Small-scale production of rape methyl ester (RME) under Swedish conditions. Biomass and Bioenergy 26, 549-559	2004	A limited LCA to assess the environmental impacts of small-, medium- and large-scale production systems with investigation into four different methods of co-product allocation.	There are negligible changes to environmental impacts between small- medium- and large-scale plants. However, economics are not included in this study. Results were largely dependent on type of allocation method for by-products.
8	(330)	Carraretto, C., Macor, A., Mirandola, A., Stoppato, A., Tonon, S.; Biodiesel as alternative fuel: Experimental Analysis and Energetic Evaluations. Energy 29, 2195-2211	2004	Use of biodiesel in boilers and diesel engines when compared with diesel oil. Provides test results and LCA.	Global CO_2 emissions are reduced, net energy requirement is positive, and there is an appreciable reduction in pollutants for biodiesel, which justifies its promotion.
9 ✠	(296)	Janulis, P.; Reduction of Energy consumption in Biodiesel Fuel Life Cycle. Renewable Energy 29, (6) 861-871	2004	Life-cycle energy balance to determine benefit of RME or REE for different methods of production and processing at different levels of agricultural productivity and different methods of co-product allocation.	EU value of EROI = 1.9 must be met, which can only be done by producing REE using energy-efficient high-productivity transesterification methods and obtaining at least 3 t/ ha productivity. Currently Lithuania averages 1.8 t/ha rapeseed.

Study No.	Ref. No.	Reference	Year	Outline/Objective	Results
10	(337)	Dai, D., Hu, Z., Pu, G., Li, H., Wang, C.; Energy Efficiency and potentials of cassava fuel ethanol in Guangzi region of China. Energy and Conversion Management 47, 1686-1699	2006	Comparative analysis of ethanol produced from cassava in China. Compares to biodiesel results of 1998 NREL study.	The fuel produced is less efficient than biodiesel (compared to results of 1998 NREL study)
11	(327)	Gartner, S.O., Helms, H., Reinhardt, G., Rettenmaier, N.; An Assessment of Energy and Greenhouse Gases of NExBTL. IFEU Final Report 530-025	2006	Energy and GHG of production of NExBTL (through hydro-treating) compared to conventional diesel for different conditions at an existing plant in Porvoo, Finland.	NExBTL has an advantage over conventional diesel in terms of energy and GHG for options and scenarios studied. Results mainly depend on feedstocks and alternative uses of land. LHV of NExBTL =44MJ/kg
12	(328)	Hill, J., Nelson, E., Tilman, D., Polasky, S., Tiffany, D.; Environmental, economic, and energetic costs and benefits of biodiesel and ethanol biofuels. PNAS vol. 103, no. 30	2006	LCA determination of biodiesel from soybean and corn ethanol in the US.	Biodiesel provides energy and GWP advantages over both diesel and ethanol.
13	(318)	Niederl, A., Narodoslawsky, M.; Ecological Evaluation of Processes Based on By-Products or Waste from Agriculture: Life Cycle Assessment of Biodiesel from Tallow and Used Vegetable Oil. Chapter 18 in Feedstocks for the Future, American Chemical Society	2006	Biodiesel from genuine waste material (used vegetable oil). Three different scenarios based on the origin of the UVO.	Biodiesel from tallow and UVO have GWP benefit. Also have lower environmental impacts (EUP,ACP, POCP, ABD) than biodiesel that is not produced from waste (RME for example).
14	(325)	Cocco, D.; Comparative study on energy sustainability of biofuel production chains. Proceedings of the Institution of Mechanical Engineers, Part A: J. Power and Energy. Vol. 221. 637-645	2007	Comparative analysis of three most promising bio-energy: power from lignocellulose; biodiesel from oil crops; and, bioethanol from sugar crops.	Study included bioethanol and electricity. Only press cake and glycerin were considered as by-products. Straw can also be used for feedstock in thermoelectric plants. Biodiesel energy investment can be increased if cultivation residues (straw) can be considered a by-product used for power generation. Allocation to co-products increases output/input energy ratios.
15	(338)	Cunningham, J.; Analysis of lifecycle of biodiesel from farmer's field to pump reveals a startling reduction in overall carbon emissions compared to regular fuel.. Professional Engineering Article. June 13, 2007	2007	Short article describing LCA research by Northeast Biofuels.	Biodiesel LCA results completed show a 94% reduction in CO_2 equivalent emissions.
16 ✠	(301)	Edwards, R., Larive, J-F., Mahieru, V., Rouveirolles, P.; WTW Analysis of future automotive fuels and power trains in the European context: WTT Report (Version 2c 2007). EUCAR, CONCAWE JRC, Version c, 2007	2007	Large study on many pathways to alternative fuels. Parts of study include WTT, TTW and WTW. Biodiesel study includes comparison of RME, REE and SME. Also incl. syn-diesel and DME from NG, Coal and Wood.	Biodiesel study: Using grazing or forest land for planting in short or medium term would be counter-productive. Advanced biofuels have potential of substituting fossil fuels, but with potentially higher energy and economical costs. Biofuel GHG savings are dependent on manufacturing process. 2nd generation biofuel production such as BTL have substantially higher GHG savings than traditional biofuels, but with high energy costs. DME has the best GHG savings and lowest energy costs compared to other GTL or BTL fuels.

Appendix VI-1 (cont.)

Study No.	Ref. No.	Reference	Year	Outline/Objective	Results
17	(306)	EPA; Greenhouse Gas Impacts of Expanded Renewable and Alternative Fuels Use. EPA420-F-07-035	2007	Brief brochure on the importance of full fuel LCA. Comparison between different alternative fuel types.	A brief discussion of comparison between a variety of fuels. The best choice: Cellulosic ethanol reduces CO_2 emissions by 91%.
18	(339)	Fleming. J.S., Stanciulescu, V., Reilly-Roe, P.; Policy considerations derived from transportation fuel life cycle assessment. SAE 2007-01-1606	2007	23 fuel-vehicle pathways were considered to test viability of each and make policy recommendations; 4 are for biodiesel specifically.	Next generation pathways have high GHG emissions reduction potential.
19	(319)	Guinee, J.B., Heijungs, R.; Calculating the Influence of Alternative Allocation Scenarios in Fossil Fuel Chains. Int. J. LCA 12, (3) 173-180	2007	A quick scan LCA to elaborate on different allocation scenarios (economic, physical and ecoinvent default) for multi-output processes for average Dutch passenger car.	A scan of other LCA models shows that different allocation methods of co-products generate large differences in LCA results.
20	(323)	Hansson, P-A., Baky, A., Ahlgren, S., Bernesson, S., Nordberg, A., Noren, O., Pettersson, O.; Self-sufficiency of motor fuels on organic farms--Evaluation of systems based on fuels produced in industrial scale plants. Agricultural Systems 94, (2007) 704-714	2007	LCA of RME, ethanol and biogas produced from processing raw material from an organic farm in industrial scale plants for use on the farm to make it self sufficient.	RME showed best energy efficiency and favorable GWP. The technology for conversion is well known, and no engine modifications were necessary. However, the cost is higher than fossil diesel.
21	(333)	Harding, K.G., Dennis, J.S., von Blottnitz, H., Harrison, S.T.L.; A life-cycle comparison between inorganic and biological catalysis for the production of biodiesel. Journal of Cleaner Production 16, (2007) 1368-1378	2007	5 cases of 1000kg biodiesel production from different catalyst types (NaOH or biological enzyme Candida antarctica), use of ethanol or methanol, and efficiency of alcohol recovery.	LCA results in lower GHG benefit for alkali catalyzed process w/ low alcohol recovery. Ethanol instead of methanol gives mixed results.
22	(174)	Kalnes, T., Marker, T., Shonnard, D.; Green Diesel: A Second Generation Biofuel. Int. J Chemical Reactor Engineering 5. A48	2007	LCA of Ecofining (hydro-treating) soy oil. Two scenarios for different H_2 production.	Green diesel compares favorably to biodiesel and fossil energy. Fossil energy consumption is reduced by 84-90% when H_2 is produced from byproducts.
23	(175)	Kaufman, J.; Renewable Diesel. Presentation, SAE Govt/ Industry Meeting May 15, 2007	2007	Presentation of results of LCA study of renewable diesel from soybean oil compared to Biodiesel and Petroleum diesel	LCA results are presented on a relative basis. Renewable Diesel is a good way to incorporate fats and oils into diesel fuels.
24	(320)	Kreider, J.F., Curtiss, P.S.; Comprehensive Evaluation of Impacts from Potential, Future Automotive Replacement Fuels. Proceedings of ES2007; ES2007-36264	2007	Study investigating potential future fuels and their sources to determine the most sustainable direction for US transportation fuels.	Biodiesel yields are smallest per acre of any land based fuel; water demands are high. Soybean based biodiesel has a low potential to reduce oil imports.
25	(172)	Kuronen, M., Mikkonen, S.; Hydro treated Vegetable Oil as Fuel for Heavy Duty Diesel Engines. SAE 2007-01-4031	2007	Summary of emissions testing on NExBTL 2nd generation biodiesel fuel.	Results of an LCA discussed showed that NExBTL reduces emissions by 40-60% compared to fossil diesel.
26	(322)	Prueksakorn, K., Gheewala, S.H.; Full Chain Energy Analysis of Biodiesel from Jatropha curcas L. in Thailand. Environmental Science Technology, 42, 3388-3393	2007	Investigated the energy consumption for 20-year investment of Jatropha Methyl Ester production in Thailand.	Study includes a wide range of sensitivity to efficiencies and yields. Overall, results show a net energy benefit for using jatropha as a feedstock for biodiesel, and will support policy decisions.

Appendix VI-1 (cont.)

Study No.	Ref. No.	Reference	Year	Outline/Objective	Results
27	(340)	Reinhardt, G., Rettenmaier, N., Gartner, S., Pastowski, A.; Rain Forest for Biodiesel? Ecological effects of using palm oil as a source of energy. WWF Germany	2007	Non-RE and GHG of palm oil cultivation, including various LUC. Comparison to conventional diesel and biodiesel for use in vehicles or power stations.	Energy balance is positive for palm oil compared to other biofuels. However, only cultivation of fallow land has a positive effect on GHG.
28	(332)	Ahlgren, S., Baky, A., Bernesson, S., Nordber, A., Noren, O., Hansson, P.A.; Future fuel supply systems for organic production based on Fischer-Tropsch diesel and dimethyl ether from on-farm grown biomass. Biosystems Engineering 99, 145-155	2008	Conducted 4-scenarios of either Fischer-Tropsch diesel (FTD) or Dimethyl ether (DME) from two different organically grown feedstocks.	FTD is more likely alternative, although it requires more land to be set aside, it produces more useful co-products. It produces 12% more GWP than DME but has lower cost. Compared to diesel, all scenarios showed reduced environmental impact. NOTE: "functional unit" not defined well. Requirement for 1000 ha of land, same as in Hansson, 2007.
29	(311)	Crutzen, P.J., Mosier, A.R., Smith, K.A., Winiwarter, W.; N_2O release from agro-biofuel production negates global warming reduction by replacing fossil fuels. Atmospheric Chemistry and Physics, 8. 389-395	2008	IPCC estimate of N_2O conversion from N is too low, resulting in LCA models underestimating global impacts	N_2O emissions estimates from current modeling techniques need to be reexamined, may underestimate N_2O emissions, which have 246 times the impact of CO_2.
30	(341)	Halleux, H., Lassaux, S., Renzoni, R., Germain, A.; Comparative Life Cycle Assessment of Two Biofuels: Ethanol from Sugar Beet and Rapeseed Methyl Ester. International Journal of Life Cycle Assessments, (3) 184-190	2008	Comparison of biofuels to fossil diesel with a base-case scenario and different sensitivity analyses for allocation method and N_2O emission. WTT and WTW.	Allocation by mass is the most favorable method of considering by-products due to the high quantity produced.
31	(342)	Dale, N., Howes, P., Miller, R., Watson, P.; Advice on the Economic and Environmental Impacts of Government Support for Biodiesel Production from Tallow. DOT ED05914001	2008	Examined the effects of tallow use--including GHG effects. 2 policy scenarios: biodiesel from tallow is 1) ineligible for support, or 2) eligible for support under EU's RTFO.	Use of tallow would increase CO_2 emissions due to renderers using low sulphur fuel oil as a replacement to tallow. Not a good solution. Tallow is compared relative to other markets like palm oil. Not compared to conventional diesel.
32	(315)	Delucchi, M.; Lifecycle Analyses of Biofuels--Draft Report.UCD-ITS-RR-06-08	2008	Draft report of LEM model results and improvements, with only draft numbers.	LEM model predicts that soy diesel has higher GHG emissions than conventional diesel due to large N_2O emissions from soy fields and large emissions of carbon due to land use change (cultivation).
33	(313)	Delucchi, M.; Important Issues in Lifecycle Analysis of CO_2-Equivalent Greenhouse Gas Emissions from Biofuels. Presentation at Workshop on Measuring and Modeling the Lifecycle GHG Impacts of Transportation Fuels at U.C. Berkeley. July 1, 2008.	2008	Presentation on LEM model to discuss how improvements to Nitrogen cycle and climate impacts have been included.	LUC, cultivation is largest source of emissions upstream of biofuels. Soy diesel has higher LCA GHG emissions than conventional diesel.

Study No.	Ref. No.	Reference	Year	Outline/Objective	Results
34	(343)	Mbarawa, M.; Performance, emissions and economic assessment of clove stem oil—diesel blended fuels as alternative fuels for diesel engines. Renewable Energy 33, 871-882.	2008	A societal life-cycle cost (LCC) study was performed in addition to vehicle testing to determine the benefits of 25% and 50% straight CSO in diesel.	LCC analysis showed that CSO-diesel blended fuels would not be competitive with pure diesel because of the high price of CSO. However, there are some environmental benefits for the blend.
35	(329)	Panichelli, L., Gnansounou, E.; Life Cycle Assessment of Soybean-Based Biodiesel in Argentina for Export. Submitted to Int. J LCA	2008	Abstract from report submitted to Int. J. LCA for biodiesel from soy in Argentina w/ regional specificities.	Significant emissions from preparation of land. Can be avoided if deforestation is avoided.
36	(326)	Prieur, A., Bouvart, F., Gabrielle, B., Lehuger, S.; Well to Wheels Analysis of Biofuels vs. Conventional Fossil Fuels: a Proposal for Greenhouse gases and Energy Savings Accounting in the French Context. SAE 2008-01-0673	2008	Comparison of biofuels to fossil diesel with a base-case scenario and different sensitivity analyses for allocation method and N_2O emission. WTT and WTW	Allocation by mass is the most favorable method of allocation because of high quantity of co products.
37	(30)	Russi, Daniela; An Integrated Assessment of a Large-Scale Biodiesel Production in Italy: Killing Several Birds with One Stone?. Energy Policy 36, (2008) p 1169-118	2008	An integrated assessment for large-scale biodiesel production for Italy to meet EU Directive goals of 3.2MT biodiesel in 2010	1/3 of Italian agricultural land would be needed to meet the EU Directive resulting in considerable increase in food imports and large environmental impacts with decreased Italian energy revenue due to de-taxation of biodiesel.
38 ✠	(297)	S&T2 Consultants; Cheminfo Services Inc., Dr, Heather MacLean; Fugacity Technology Consulting.; Sensitivity Analysis of Biodiesel LCA Models to Determine Assumptions With the Greatest Influence on Outputs. ChemInfo Final Report	2008	Comparison of biodiesel pathways in GREET 1.8 and GHGenius 3.12 in 2007. Comparison limited to data easily extracted from GREET. Second comparison of results from different feedstocks in GHGenius	GREET and GHGenius have several different assumptions, especially in N_2O release. Sensitivity analysis of GHGenius looked at different oil extraction methods, different process fuels. The N_2O sensitivity analysis produces the widest range of differences.
39	(174)	Kalnes, T., Marker, T., Shonnard, D., Koers, K.; Green diesel production by hydrorefining renewable feedstocks. Biofuels-Q4. www.biofuels-tech.com	2008	Description of UOP EcoFining process for Green Diesel (GD) production and compares ER and GWP of GD to bio-, petroleum and syn-diesel.	LCA of green diesel produced from renewable feedstocks indicates relatively high energy efficiency and low GHG emissions.

✠ Designates a study identified as “critical”

🟩	Included in Both Energy and GWP charts (Figures XXX- and XXX)
🟨	Included in GWP chart only (Figure XXX)
🟦	Included in Energy chart only (Figure XXX)
🟥	Relative GWP results only (Figure XXX)
⬜	Not included in any charts

Appendix VI-2. Biodistillate Life-Cycle Assessment (LCA) Results

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Study No. Ref. No	Feedstock and Production Method	Location And LCA tool used	Critical Assumptions	Scenarios And Method of Co-Product Allocation.	Land Use Change	Reference Fuel	GWP*/ Change in GWP relative to conv. Diesel	EROI**	Other considerations***
1 ✠ (307)	Soybean: Trans-esterification	USA; Not mentioned	▪ Weighted averages for 14 soy-oil producing states. ▪Energy efficiencies of biodiesel vehicles are identical to conv. Diesel vehicles. ▪ Carbon neutral principle. ▪ Nat'l avg. transport distance 571 mi.	1 with investigation of fossil energy and primary energy using Mass Allocation	Direct: cultivation of land	Petroleum Diesel: GWP: 235.9 EROI: 0.833 Primary and Fossil Energy.	WTW (not incl. tailpipe emissions gm CO_2 only) B20: 198.9 B100:50.9	Biodiesel: 0.806 (Primary Energy) 3.215 (Fossil Energy)	Wastewater production (L/MJ) Diesel : 0.175 B20: 0.147 B100: 0.0369
2 (314)	Soybean oil: Trans-esterification WTT and WTW	USA; LEM	LEM specific assumptions.	None; Uses combination of expansion and displacement.	Direct LUC in cultivation. Heavy consideration of N rates.	None	None	None	None
3 (335)	Rapeseed (*Brassica* carinata): Crop Production only	Southern Italy; Not mentioned	▪ 100 km distances ▪ data inputs from literature ▪ no co-product allocation	None, no-allocation: comparison of different cropping methods and productivity.	None discussed	None discussed	None discussed	Energy requirement to product crop only.	None
4 (331)	Rapeseed: Trans-esterification WTW	Germany; IFEU	▪ Agriculture assumptions calculated under average German conditions. ▪ Base case processing	One with expanded allocation. Co-product assessment incl. rapeseed honey and meal fermentation to produce biogas.	No land use change--reference used is set-aside land w/ fertilizers.	Diesel	2.2 kg CO_2 eq / Liter RME saved compared to diesel (that emitted in 6L of diesel)	Saves energy required to produce 8L of Diesel.	Considers ACP, OZD, POCP relative impact to diesel. Advantage for diesel for ACP, Nutrient inputs, and OZD. Small POCP benefit for RME.
5 ✠ (324)	Sunflower, Rapeseed, Soybean: Trans-esterification WTT	EU- Italy; Not-mentioned	▪ Ranges of crop yields are EU average	Range of values for 3 feedstocks; with or without co-product allocation and a range of harvest yields. Allocation method likely by energy.	Direct land use by crop yield and fertilizer inputs. Must fall within sustainable agriculture.	Comparison of results and to ethanol produced from ligno-cellulose and traditional feedstocks.	N/A	With: Without Allocation Sunflower: 0.4-1.2: 0.3-0.9; Rapeseed: 1.0-1.5: 0.7-1.0; Soybean: 0.7-1.6: 0.2-0.6;	None
6 (336)	Wood (farmed): Choren Process--gasification for FTD	Germany—(plant in Freiburg); compliance with DIN EN ISO 14040	▪ Based on data for 43MW Choren process plant in Freiburg (under construction when published)	Three: scenarios for H_2 production; allocation method not discussed. For self sufficient/ future and partial self-sufficient better than conventional diesel:	Not discussed	Conventional Diesel: No value given; other impacts are relative.		Efficiency of Process 64%, 45%, 55%	GWP 91% , 87% and 61 % less compared to conv. Diesel EUP: 29%, 13%, 3% ACP: 42% 27% 5%

Appendix VI-2 (cont.)

Study No. Ref. No	Feedstock and Production Method	Location And LCA tool used	Critical Assumptions	Scenarios And Method of Co-Product Allocation.	Land Use Change	Reference Fuel	GWP*/ Change in GWP relative to conv. Diesel	EROI**	Other considerations***
7 ✠ (317)	Rapeseed (*brassica napus*): Trans-esterification WTT	Sweden; Not mentioned	▪40 ha, 1000 ha, and 50,000 ha for small, medium and large production, respectively. Large scale has high extraction efficiencies, longer transport distances. Small scale-low extraction efficiencies, but no or short transport distances. ▪ Annual yield: 2670 kg/ ha w/ moisture content of 15% at harvest. 8% moisture after drying with 45% oil ▪ Swedish electricity: 48% hydro, 44% nuclear, 4% fossil fuels, 3% biofuels LHV of biodiesel = 38.5MJ/kg	Twelve: 4 types of co-product allocation: (energy, economic, none, expansion) for small, medium or large scale production facility.	Direct land use change from agriculture	Comparison of allocation method and facility size. Comparison made between large-scale facility w/ physical allocation to literature values for MK1 diesel oil. GWP: 217 g CO2/ MJ engine (vs. 127) ;	For sm, med, lg-, resp.: Physical allocation: 40.3,39.5,40.2 Economic allocation: 51.1, 49.1, 45.8 No allocation: 87.6, 79.5, 61.9, Expanded: 34.5, 32.1, 30.9	For sm, med, lg-respectively: Physical: 3.4, 3.6, 3.5 Economic:2.8, 3.1, 3.2 None: 1.8, 2.0, 2.5 Expanded: -2.74; -2.92; -6.81 Lg, Physical= 4.8 times higher than diesel.	ACP=0.019-0.519 EU= 0.0385-0.0862 POCP= -5.67-7.15 (Relative to Diesel, AP and EP increased by 79% and 81%. POCP reduced by 66%.) Results of sensitivity analysis, which varied production factors by plus or minus 20% not reflected in reported values.
8 (330)	Soybean: Trans-esterification (WTT)	Italy; Based on Emergy analysis by Odum HT	▪ Soybean harvest: 2445 kg/ ha ▪ fuel 116.5 kg/ ha ▪fertilizer consumption is 80, 43, and 51kg/ha for nitrogen, phosphates, and potassium, respectively conversion ▪ Analysis includes combustion of fuel--65% of emissions in combustion process.	Two: co-product allocation by mass vs. none.	Direct agricultural impact.	Commercial Diesel Oil D2. GWP= 22.2 (12-75% reduction)	(Including combustion) w. allocation 5.7 w/o allocation: 19.5	2.09	1 MJ biofuel = 1.398 MJ primary energy, 35% of which is derived from fossil fuels. Additional Emergy analysis shows biofuels requires a larger amount of resources for final product than diesel
9 ✠ (296)	Rapeseed : Trans-esterification WTT	Lithuania; Independent using ISO 14040-14049	▪Ag inputs incl. fuel and fertilizer use. ▪Data are specific to Lithuania ▪Two different ag methods: 1) mineral fertilizers and drying of seed, 2) biofertilizers and seed preservation.	Forty: methanol vs. ethanol as process fuel; harvest yield; different ag methods; ; productivity high with hot pressing or low with cold pressing.		Fossil Diesel 0.885 (presented for comparison)	N/A	RME: 1.04-2.82 REE 1.20-3.22 Only showing the high and low for 20 scenarios.	None
10 (337)	Cassava: Ethanol production*	Guangxi region of China; Not mentioned	No pathway for biodiesel: ethanol production compared to results of 1998 NREL study for biodiesel.	One; allocation method not discussed	Not discussed	Biodiesel: Compares cassava ethanol relative to biodiesel.	N/A	3.2 (from NREL)	None

Study No. Ref. No	Feedstock and Production Method	Location And LCA tool used	Critical Assumptions	Scenarios And Method of Co-Product Allocation.	Land Use Change	Reference Fuel	GWP*/ Change in GWP relative to conv. Diesel	EROI**	Other considerations***
11 **(327)**	Rapeseed and Palm oil: NExBTL process--hydro treating WTT	Finland—NExBTL plant in Poorvoo.) IFEU	▪Data from Poorvoo plant operation ▪Electricity split Finland and NG from Russia, rapeseed from EU and overseas, and palm oil imported from Malaysian. ▪ European electricity split (UCTE) and NG. Palm oil from various countries in international market. Same scenarios as Poorvoo for rapeseed. All feedstock is transported to central Europe.	Six: investigates different feedstocks and feedstock origins. Allocation method is rape meal substitution of soy meal from N. America (expansion).	Looks at both natural and set-aside land for crop growth in both Europe and overseas in the Reference cases	Rapeseed vs. conv. Diesel: GWP: saves 1.2-2.5 t CO_2 eq/ t of NExBTL (33-69%) EROI: 30-33GJ primary energy saved per t NExBTL. (primary ≠ fossil) (61-68%) Malaysian Palm oil in reference to different land uses.	Rapeseed EU-set-aside: 30.0 EU Natural : 44.7 Overseas (OS) Natural:56.4 Reference Cases Palm Oil Nat. forest: 53.4 Food Oil: 33.2 Coconut:62.0 Reduction: t CO2 eq per t NExBTL Rapeseed: 1.2-2.5 Malaysian Palm Oil: 1.4	Rapeseed EU-set-aside: **2.8** EU Natural : **2.7** OS Natural: **2.2** Reference cases for other uses of land. Palm Oil Nat. forest: **8.3** Food Oil: **2.6** Coconut: **1.3**	(Non-RE only) NExBTL from rapeseed: 30-33 GJ primary energy per t of NExBTL; from palm oil: 44 GJ primary energy per t on NExBTL Values reported per t NExBTL. Converted using energy value per ton of fuel.
12 ✠ **(328)**	Soybean: Trans-esterification WTT	US; Not mentioned	▪ Boundaries include energy to grow seed; produce farm machinery and buildings; and, sustaining farmers' households.	Different allocation methods: no credit, by mass, by economics, and by energy. Also looks at two types of energy ratios.	Considers direct land use change/ release of GHG from fertilizers from land already in production.	Diesel: GWP: 82.3 (41% reduction) Energy gain 2.9%	GWP= 49	No credit: 1.16 Mass: 1.83 Economic: 1.81 Energy: 3.38 NEB (incl. energy in co-prod)= 1.93 ER (energy in biodiesel alone= 3.67	None
13 **(318)**	Tallow and Used Vegetable Oil (UVO): Trans-esterification WTT	Austria; EcoIndicator 99 database	Results discussed for Scenario I for UVO only.	Three: origin of UVO with mass and economic allocation methods.	None considered	Fossil Diesel: GWP: 90 (80% reduct.) EUP=0.225 ACP=0.23 ABD=0.054 POCP=0.019	GWP= 18	None	EUP:.033; ACP:.21; ABD:.037; POCP:.012
14 **(325)**	Rape and sunflower seed : Trans-esterification WTT	Italy; Not mentioned	▪Yield of 1.8t/ ha and 2.2t/ ha of rapeseed and sunflower seed, respectively.	Four: co-product allocation by economics vs. none of two feedstocks.	Direct land use cultivation is considered for energy effects-- no emissions calculations.	Comparative between types of biofuel energy.	None	1.3-1.4 – w/o co-products 2.1-1.9 - with co-products for rape and sunflower respectively	More energy GJ/ha NET) w/o co-products Rape= 10.31 Sunflower= 10.17 w/ co-products Rape= 24.96 Sunflower= 28.08

Appendix VI-2 (cont.)

Study No. Ref. No	Feedstock and Production Method	Location And LCA tool used	Critical Assumptions	Scenarios And Method of Co-Product Allocation.	Land Use Change	Reference Fuel	GWP*/ Change in GWP relative to conv. Diesel	EROI**	Other considerations***
15 **(338)**	Rapeseed: Trans-esterification (WTT)	Sweden; Not mentioned	Not mentioned	One; allocation method not discussed	Not mentioned	Conventional low-sulfur diesel.	94% reduction		None
16 ✠ **(301)**	Biodiesel: Trans-esterification of Rapeseed and Sunflower Gasification to DME or syn-diesel of wood-waste (WW), farmed wood (FW), or waste wood via black liquor (BL)*	EU; Program developed by LBST.	▪ Commercially available tech in 2010-2020 time horizon ▪ Energy on LHV basis ▪ Fertilizer and farming input data from FfE 1998, which has higher N_2 rates than EU25, but with higher yields. ▪ 85% efficiency for process estimated/ depends strongly on performance of FT catalyst. ▪ Wood conversion processes are made electricity neutral. ▪ Vehicles in WTW are 2010	Biodiesel: Six: three feedstock and two uses of glycerin with expanded allocation. FTD and DME: Six: Three feedstocks and process to DME or Syn-Diesel with energy allocation.	Direct LUC: crops grown on set-aside land otherwise left fallow with grass. GHG breakeven period for converting grassland to arable land ; Not included for DME	Conventional Diesel (and other types of alternative fuels) GWP = 88 gm CO_2 eq / MJ fuel (including combustion for comparison) EROI= 0.863	WTT Glycerin as (1)chemical: RME=46.5 /48.0 REE=43.3/ 45.2 SME=24.7 /26.6 as (2) animal feed RME= 51.8/ 53.7 REE =48.0/ 49.7 SME= 30.0 /31.6 Before/After comb. DME WW: 4.5 / 5.8 FW: 7.0 / 8.1 BL: 2.2 / 3.5 Syn-Diesel WW: 4.8/ 5.7 FW: 7.4/ 8.5 BL: 2.4 / 3.4	WTT (= WTW) Glycerin as chemical.; RME =2.17 REE=2.44 SME = 2.78 as animal feed RME= 1.96 REE = 2.22 SME= 2.44 DME (incl. E final fuel) WW:16.7 / -- FW: 16.7 / 356 BL: 33.3 / 269 SynDiesel WW: 14.3 / -- FW:16.3/ 385 BL: 25 /350	Economic estimation included. Brief paragraph of threat of increase EUP and ACP potential for biodiesel and lowering of watertable. No calculations.
17 **(306)**	Average mix of soybean and yellow grease: Trans-esterification WTT	USA; GREET	Average mix of soybean and yellow grease, same as analysis completed for the Renewable Fuel Standard. Uses GREET default assumptions for electricity mixes, etc.	None discussed	Indirect land use change not included in GREET. Cultivation included.	Diesel	67.7 % decrease in CO_2	None	None
18 **(339)**	Gasification to FTD of Canola, Tallow, Wood: Trans-esterification, SuperCetane hydrogenation WTW	Canada; GHGenius	None discussed	None discussed	None discussed	Conventional fuels and other alternative fuels to determine best option.	N/A	None discussed	None
19 **(319)**	None for biodiesel WTW	The Neth-erlands; Swiss EcoInvent V1.1 data	None discussed for biodiesel	Different allocation methods and allocation coefficients	None dicussed	None: comparison of allocation methods w/o assessment of results.	N/A	Does not assess total values	None

Study No. Ref. No	Feedstock and Production Method	Location And LCA tool used	Critical Assumptions	Scenarios And Method of Co-Product Allocation.	Land Use Change	Reference Fuel	GWP*/ Change in GWP relative to conv. Diesel	EROI**	Other considerations***
20 **(323)**	Rapeseed, : Trans-esterification WTW (zero emissions during combustion)	Sweden; Matlab/ Simulink, with ISO-14040	▪25km transport distance between farm and plant ▪ 1000 ha cultivated▪ Includes fuel use in farm equipment, emissions assumptions for farm equipment provided. WTW, zero emission during combustion = WTT	Two: co-product allocation by economics vs. none.	Direct land use only.	Conventional Diesel. Also, comparison of ethanol and biogas use. GWP: 79.5	21.8 (73% decrease vs. diesel, also, 28% less than ethanol and 38% less than biogas.	With/ Without Allocation 8.3 / 4.2	EUP: 25.46 kg O2 eq/ MJ fuel (79% increase) ACP: .827 (31% increase) 8.5% of 1000 ha or land used for fuel production. Economic: .047 Euro for RME
21 **(333)**	Rapeseed: Trans-esterification	Location not discussed; SimPro V6.	▪ Process plant and equipment construction not incl. ▪Alcohol to oil ratio from 3:1- 6:1▪ Variety of process-based differences/ assumptions. ▪ Biological catalyst data from lab experiments. ▪ Cases: 1: NaOH cat, MeOH, HR. 2: Bio-cat, MeOH, 3: NaOH, MeOH, LR 4) NaOH ,EtOH,HR. 5) bio-cat, EtOH .	Five: process fuel (methanol vs. ethanol); catalyst type (NaOH cat vs bio-cat) ; and alcohol recovery efficiency (high recovery HR vs low recovery LR). Mass allocation of glycerol	Direct LUC-- ag inputs.	None: comparison of catalysis methods and other process differences.	Case 1: 153 Case 2: 149 Case 3: 161 Case 4: 151 Case 5: 147 (Converted using 27.1GJ in 1000kg biodiesel)	None	(gm eq/ MJ fuel) EUP: 1.37-1.39 ACP 1.08-1.17 ABD: .494-.664 OZD: 2.0E-5-3.3E-5; HT: 4.95-6.79; H2O tox: .458-1.55
22 **(174)**	Soybean : Eni Ecofining WTT	Western Europe; ISO 14040 with data from SimaPro.	▪Inventory data from NREL study (Sheehan 1998) includes cultivation, harvesting, and extraction w/ intermediate transportation steps. ▪ Transp. to end user is omitted ▪ Scenario A: H_2 is typical refinery blend. Scenario B: H_2 by conversion of green-diesel byproducts propane and naphtha	Two: method of H_2 production. Allocation method by mass.	None mentioned: N_2O emissions are neglected.	Diesel and Biodiesel. GWP 85.6 EROI: 0.78	Biodiesel= 23.6 Grn Diesel A=14 Grn Diesel B=12.7 Improvement Biodiesel = 62.0; 72.4% Green diesel A= 71.6 ; 83.6% Green Diesel B= 72.9 ; 85.1%	Biodiesel= 3.0 Grn Diesel A=3.4 Grn Diesel B=5.0 From Palm Oil: Biodiesel= 4.0 Grn Diesel A=5.0 Grn Diesel B=7.7	None
23 **(175)**	Soy oil: Conoco Philips-hydro treating WTT	US; Not mentioned	Not discussed	Summary of hydrotreating/ renewable diesel technologies.	Not discussed	Petroleum Diesel	COP soy 56% UOP soy 74% NExBTL rape 69%	Not discussed	None
24 **(320)**	Soybean : Trans-esterification WTT	US (Colorado); Not mentioned	Not described in detail * Delucchi and Lippmann CO_2 emissions data ▪ Emissions include driving cycle ▪ consumption of CO_2 by photosynthesis not included	Range for One feedstock: based on percentage displacement of transportation needs. Allocation method not discussed.	Not mentioned	Petroleum Diesel: GWP: 26 gm/MJ fuel Petroleum Diesel: GWP: 26 gm/MJ fuel EROI=11.1 (uses NREL but subtracts NG extraction energy.	gm CO_2/ MJ fuel 21-26 Saves 0-5 gm CO_2/ MJ fuel	1.32 (compared to 11.1 for conventional diesel)	H_20 : 900 gal/ gal fuel or 6900 gal/ MMBTU fuel Land to displace 10, 25, 50% of transportation energy: 253M, 380M, 1.2 B acres

Study No. Ref. No	Feedstock and Production Method	Location And LCA tool used	Critical Assumptions	Scenarios And Method of Co-Product Allocation.	Land Use Change	Reference Fuel	GWP*/ Change in GWP relative to conv. Diesel	EROI**	Other considerations***
25 (172)	Vegetable Oil: NExBTL--hydrogenation	Europe/ Finland; Not mentioned	None discussed/ LCA briefly discussed in paper ▪ Hydrogen produced from natural gas	None discussed	Not discussed	Fossil diesel.	40-60% lower than fossil diesel	Not discussed	None
26 (322)	Jatropha: Trans-esterification WTT	Thailand; Not mentioned	▪ Based on 1 ha of jatropha farming for 20 years 2/ 1100-3300 trees/ ha. ▪Best case and worst case scenarios for diff. inputs. ▪ Biodiesel factory sited close to refinery; transportation in that phase in not incl. ▪Average biodiesel from jatropha yield is 2.7 ton/ha/year for best case ▪It takes 2-3 years for jatropha trees to reach full yield, no change in yield until 20 years.	Over 20: Co-product yields; energy efficiency, and harvest yields. Allocation by energy.	Direct land use impacts include preparation: plough, harrowing, and furrowing.	None	N/A	Range of 0.53-11.99 (Average of all cases 4.77)	Net energy gain= 4720 GJ/ ha
27 (340)	Palm oil: Trans-esterification WTT	Europe; IFEU	▪ Yield of both 3.5 and 4.0 tones palm oil/ ha per year. ▪ Investigates direct LUC of natural forest, fallow land and existing plantations of other crops like coconut and rubber.	Not discussed	Cultivation of different types of land.	Diesel; avoided emissions are estimated. (30% avoided)	PME, natural forest, 7.3 t CO_2 eq/ ha*a: equivalent to 3.2 t CO_2 eq/ ha *a avoided.	Not discussed	-10 GJ/ ha*a, savings from conv. Diesel: 150 GJ/ ha*a
28 (332)	Straw or short-rotation willow coppice (Salix): Gasification	Sweden, organic farming; Not mentioned	▪Tech. feasible w/in 10-15 yr ▪ cultivation on 1000 ha of land, 100 km transport distance, trucks use fuel studied. Feedstock transported to processing plant, fuel back to farm. ▪Capital goods production not included. ▪Organic farming w/ 7 year rotation, Nitrogen supplied by nitrogen fixing plants planted every two years. ▪Yield of Salix est. 6300kg/hayr.	Four: two feedstock; process to DME or FTD. Uses economic allocation.	Direct LUC: N fertilizers and land for each feedstock which result in N_2O emissions for cases when most land was used.	Conv. diesel: FTD for straw/ salix: GWP =94.0/84.9% decrease. ACP: 55.7%/ 51.2% decrease. EUP: 26.7/ 16.2% decrease.	gm CO_2 equivalents per functional unit for Straw/ Salix respectively: FTD= 9.3/ 23.8 DME= 8.2/ 26.0 Functional unit is the amount of fuel needed to cultivate 1000 ha of land.	from Straw/ Salix, respectively FTD = 8.9 / 9.6 DME = 10.1/ 10.0	EUP (in O_2 equiv. / functional unit) FTD =9099/ 8832 DME =7728/8965 ACP FTD = 554/ 610 DME = 409 / 578 for straw/ Salix respectively Economic FTD €30780 DME €32040
29 (311)	Maize, Rapeseed, Sugar cane: Harvesting	Not specific; Not mentioned	▪ Not a full LCA-- leaves out fossil fuel use and co-products ▪ Conversion factor of 3-5% of newly applied N-fertilizer to N_20, higher than IPCC factor of 1%.	None Harvesting only to look at Nitrogen cycle.	Nitrogen cycle specific	None	Relative warming potential of biodiesel from rapeseed is 1.0-1.7	Not discussed	None

Appendix VI-2 (cont.)

Study No. Ref. No	Feedstock and Production Method	Location And LCA tool used	Critical Assumptions	Scenarios And Method of Co-Product Allocation.	Land Use Change	Reference Fuel	GWP*/ Change in GWP relative to conv. Diesel	EROI**	Other considerations***
30 **(341)**	Rapeseed : Trans-esterification WTT	Belgium; Simapro 7.1 databases and Eco-Indicator 99	▪Function unit was transport over 100 km for mid-size, recent car. ▪Specific local data for Belgium ▪ CO_2 from the combustion of biofuels is not taken is assumed to be net neutral with the uptake process in the natural cycle, and is not taken into account. ▪ Biodiesel combustion results in a net increase in NOx emissions.	Two: co-product allocation by expansion vs. none.	Qualitative assessment- 5.5 vs 12.8 m² for 100 km transportation 'global impact' for RME vs. Bio-ethanol respectively	Fossil diesel (also compare to petrol and bio-ethanol) ACP and EUP combined shows 32% decrease for biodiesel.	Relative results only 76% decrease from diesel	Relative results only	Global impact: RME shows 59% improvement in comparison to fossil diesel, Improvement would be 18 without valorization of by -products.
31 **(342)**	Tallow: Trans-esterification WTT	EU; Not mentioned	▪ Alt. supply of biodiesel in Scen.1 is from palm oil. ▪ Alt. supply of oleo chemicals in scen. 2 is from rendering	Two: feedstock. Allocation method not discussed.	Deforestation for palm in far east is discussed, but not quantitative.	Displacement of tallow into biodiesel production relative to other types of biodiesel.	increased emissions to 974 kg CO_2 eq/ tone tallow displaced	N/A	None
32 **(315)**	Soybean: Trans-esterification WTT and WTW	USA; LEM	LEM specific assumptions. Reported values are converted using reported density of 0.887 gm/mL and HHV of 40.37 MJ/kg. WTW for HDV with 3mpg.	Draft numbers only. Combination of expansion and displacement	Direct cultivation. N_2O rates.	Diesel. (4157 gm/ mi)	125.341 (6361 gm/mi)	.949	Draft numbers only, but indicated 50% increase in CO_2 emissions.
33 **(313)**	Soybean: Trans-esterification WTT and WTW	US; LEM	▪ LEM specific Nitrogen cycle	No scenarios: Combo of expansion and displacement	Direct impacts; N_2O rates, carbon sequestration.	Diesel.	Preliminary results only, not to be cited.	N/A	None
34 **(343)**	Clove stem: Distillation into CSO, WTW	Tanzania; Not mentioned	▪Diesel Isuzu is 4cylinder, 4-stroke naturally aspirated DI ▪ CSO is used directly as a fuel.	Two: different blends of CSO with fuel. No allocation method discussed.	None discussed	Pure diesel, and blends of diesel w/ straight CSO (no processing to biodiesel)	50% blend results in 7% increase in total emissions; the 25% blend results in 1% decrease.	Not discussed	CSO is more expensive
35 **(329)**	Soybean: Trans-esterification WTT	Argentina; Ecoinvent	Argentinean regional specificities--not defined.	One using economic allocation	Cultivation of land use is included	None	WTT: 48.9	WTT:2.29	None

Study No. Ref. No	Feedstock and Production Method	Location And LCA tool used	Critical Assumptions	Scenarios And Method of Co-Product Allocation.	Land Use Change	Reference Fuel	GWP*/ Change in GWP relative to conv. Diesel	EROI**	Other considerations***
36 (326)	Rapeseed and Sunflower: Trans-esterification WTT and WTW	France; TEAM database	▪ Carbon neutral principle- no CO_2 released during combustion since same amt is absorbed by crop during growth. WTT=WTW ▪ No land use change ▪ WTW analysis w/ Belingo Vehicle on normalized European driving cycle (NEDC)	Two: Type of feedstock with expanded allocation.	Direct land use-- considers fertilizers and direct ag inputs. No indirect changes.	Diesel (with comparisons for EtOH and gasoline also) GWP (WTW) Rape: 80% Sunflower 78%	WTT Rape: 12 Sunflower: 18 Diesel: 7	For WTT: Rape ~ 3.3 Sunflower ~2.7 Diesel ~7.7 For WTW: Diesel = 1.13, Rape, Sunflower stay the same	None
37 (30)	% 80 Rapeseed , % 20 Sunflower: Trans-esterification WTT	Italy; Not mentioned	▪ Linear trend in oil demand to 2010 ▪Imported Biodiesel is from Hungary ▪Oil seeds cultivated in abandoned lands; will not replace food crops ▪Domestic oil seeds replace equal shares of fodder plants and cereals ▪Entire oil seed production is from ear-marked crops ▪All biodiesel production is exempt from taxes ▪ Oil seeds are cultivated with intensive agricultural methods	Two: origin of feedstock with expanded allocation.	Direct land requirement for growing crop is considered.	Fossil Diesel, 1.1% reduction in 2004 emissions levels.	Domestic: 35.8 Imported: 15.4 =1.1% reduction in 2004 levels	Uses 2.5 from Bernesson et al. 2004 for analysis	2% reduction in energy dependency 3.2 MT biodiesel req'd to displace 5.75% total energy demand in 2010. 3.7 M ha req'd, which is 26% of agricultural land is required. Economic: 4.8% loss of total energy taxes and 0.3% loss of total revenues.
38 ✠ (297)	Soybean and Canola: Trans-esterification WTT and WTW	Canada and USA; GREET and GHGenius	▪ Year 2007 ▪ Results on a HHV basis. ▪ GHGenius includes energy required to manufacture farm equipment; GREET does not. ▪ Different land-use calculation in each Sensitivity analysis of paper incl. of different oil extraction methods, co-product allocation. Does not use zero combustion emissions	One for GHGenius vs. GREET comparison. GHGenius test: Two feedstocks, with multiple sensitivity analysis ranges. ▪ GHGenius: combo of expansion and displacement; GREET allocation selection.	GREET: emissions calculated for N_2O from applied N. GHGenius also includes N_2O created when seed N is fixed. Detailed discussion on potential effects of indirect LUC.	Comparison of two different model results, and compare to fossil diesel. Diesel: After Combustion (88.7-89.7) Soy: 60-71% Canola: 75-78% EROI=4.2594	2002 US scenarios GREET = 33.7 GHGenius= 29.7 For GHGenius before (after combust.): Soy= 24.2 (26.0) (N_20 sensitivity 18-35) Canola= 17.7-19.3 (19.5-21.1) (N_20 Sensitivity 25-42) Yellow Grease - 4.4 (-2.7) Tallow= -6.6 (-4.9)	GHGenius CAN= 3.82 GHGenius US = 3.92 GREET US = 1.84 GHGenius Comparison Soy = 3.8119 Canola= 3.9594	None

Appendix VI-2 (cont.)

Study No. Ref. No	Feedstock and Production Method	Location And LCA tool used	Critical Assumptions	Scenarios And Method of Co-Product Allocation.	Land Use Change	Reference Fuel	GWP*/ Change in GWP relative to conv. Diesel	EROI**	Other considerations***
39 **(174)**	Rapeseed (RSO), Palm Oil (PO), Tallow: Ecofining for Green Diesel (GD)	Average European. SimaPro data w/ data for UOP processes.	▪ GHG contributions from N_2O, CO_2, and CH_4. ▪ Combustion emissions are not incl (GD comb: CO_2 only from renewable oils, no offsets; Biodiesel combustion incl. only MeOH-derived CO_2 of fossil origin). ▪Farming rapeseed and palm. Tallow considered waste from meat plants. Only emissions for transport	4 scenarios for biodiesel, 4 for GD—different feedstock and if biogas (BG) is used as a fuel. No allocation for palm oil. Expanded allocation for rapeseed meal. Energy and Economic for tallow.	N_2O emissions are included, but no sensitivity to them. LUC out of scope.	GD compared to biodiesel from transesterification and to low sulfur petroleum. ER= .787 GWP= 84	Biodiesel: RSO: 2.4 PO: 2.4 PO w. BG: 2.5 Tallow: 4.2 GD: RSO:2.4 PO:2.7 P.O w. BG: 2.9 Tallow: 9.1	Biodiesel: RSO: 46 PO: 54 PO w. BG: 31 Tallow: 20 GD: RSO: 41 PO: 48 P.O w. BG: 26 Tallow: 5	

🟩	Included in Both Energy and GWP charts (Figures XXX- and XXX)
🟨	Included in GWP chart only (Figure XXX)
🟦	Included in Energy chart only (Figure XXX)
⬜	Not included in any chart

*Global Warming Potential: GWP in gm CO_2 equivalent/ MJ fuel

** Energy Return on Investment: (EROI) WTT reported as Energy in Fuel (LHV) / Life-cycle energy inputs. WTW reported Life-cycle energy input for 100 km unless otherwise stated.

***Other Considerations:

Eutrophication: (EUP) in g PO_4^{3-} equivalents/ MJ fuel unless otherwise stated

Acidification: (ACP) in g SO_2 equivalent/ MJ fuel unless otherwise stated.

Abiotic Depletion: (ABD) in g antimony (Sb) equivalent/ MJ fuel.

Photochemical Ozone Creation Potential: (POCP) in mg ethylene (C_2H_4) equivalent/ MJ fuel

Ozone Layer Depletion: (OZD) in g CFC -11 equivalent/ MJ fuel.

Human Toxicity: (HT) in gm 1,4 DB equivalent/ MJ fuel.

Fresh Water Aquatoxicity (H2O tox) in g 1,4 DB equivalent/ MJ fuel.

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From: DiCicco, Dominic (D.M.)
Sent: Friday, April 20, 2007 8:56 AM
To: Fulton, Brien (B.L.)
Subject: RE: Press Releases

Attachments: FAME Statement June 20041.pdf

Brien,

Here is part of the answer, I am trying to find the other document, no luck yet...

FAME Statement June 20041.pdf

End of the document may contain the desired words and statements.

Dominic

From: Fulton, Brien (B.L.)
Sent: Friday, April 20, 2007 8:41 AM
To: DiCicco, Dominic (D.M.)
Subject: Press Releases

Dominic,
I need to get a list of those press releases other OEMs have done for Bio-diesel, particularly the catch phrases to give them the out.
Thanks

Brien Fulton
Diesel Powertrain Systems Technical Expert
💻 bfulton1@ford.com ☎ (313)-59-43365

"Vehicle Programs are like a roll of toilet paper, the closer you get to the end, the faster it goes!"

DELPHI BOSCH SIEMENS VDO Automotive
DENSO STANADYNE

Fatty Acid Methyl Ester Fuels
As a Replacement or Extender for Diesel Fuels

Diesel Fuel Injection Equipment Manufacturers
Common Position Statement

Please note that this statement supersedes all previous joint statements

Background:

Diesel fuel injection equipment (FIE) manufacturers fully support the development of alternative sources of fuel for compression ignition engines. In Europe and in the United States of America, as well as in other countries, fuel resources such as rapeseed methyl ester (RME) and soybean methyl ester (SOME), collectively known as fatty acid methyl esters (FAME), are being used as alternatives and extenders for mineral oil derived fuels. Furthermore, the EU Biofuels Directive 2003/30/EC requires member states to ensure that a minimum proportion of biofuels or other renewable fuels are placed on the market.

The FIE manufacturers are aware of issues particular to FAME fuels, and have been active in the generation of standards for these fuels. At the time of the last common position statement in 2000 there existed national standards for vegetable oil methyl esters (VOME) in Austria, Italy, Germany and France. The European FAME standard EN14214 was ratified in 2003 and supersedes these national standards.

EN14214 provides the minimum requirements for FAME quality whether used as pure FAME or as a blend component. FAME may be blended in quantities of up to 5% in European diesel fuel according to the EN590 specification. **In order to reduce the risk of premature failure of the fuel system, FAME must conform to EN 14214.**

To date, experience in Europe has been mainly associated with the methyl esters of rapeseed oil. Whether or not the service experience with these fuels will apply/extend to all FAMEs (like those derived from soybean, tallow and used frying oil) has yet to be determined. FAMEs tested to date appear to have good lubricity and cetane numbers, but have risks which are discussed below.

FIE Manufacturers Concerns:

FAMEs are derived from a wide range of base stocks, resulting in a similarly wide range of finished fuel characteristics.

Amongst the concerns of the FIE manufacturers are the following fuel characteristics:

- free methanol

- water
- free glycerine
- mono, di- and triglycerides
- free fatty acids
- total solid impurity level
- alkali/alkaline earth metals
- oxidation stability

All FAMEs are less stable than mineral oil derived fuels. FAMEs are readily “bio-degradable” in the event of accidental spillage or leakage, which is claimed to be a marketing advantage. On the other hand, the reduced thermal oxidative stability is of major concern to the FIE manufacturers, as the products of fuel ageing can be potentially harmful to the fuel system.

Tests have shown that fuel deterioration can take place in the fuel supply chain and in the vehicle fuel system. Fuel ageing is accelerated in the presence of heat, oxygen, water, metal ions and other impurities. The products of oxidative ageing have been shown to be corrosive (e.g. organic acids like formic and acetic acids and acids of higher molecular weight). Polymerisation products are also formed and can drop out.

A detailed list of potential problems for FIE systems from FAME is presented in the attachment to this document.

Blends with FAME :

A particular concern is the oxidation stability of FAME blends with sulphur-free diesel fuel (S <10 ppm), which is already available in some parts of Europe and will become more widely used step by step. The oxidation stability of blends as low as B5 can greatly reduce when using sulphur-free diesel or 15 ppm sulphur diesel such as that planned for introduction in U.S.A. in June 2006.

The FIE manufacturers request their customers to support their efforts to obtain good oxidation stability for 5% FAME blends in Europe or for any other blends worldwide.

DELPHI BOSCH SIEMENS VDO Automotive
DENSO STANADYNE

Diesel Fuel Injection Equipment Manufacturers

Common Position Statement on Fatty Acid Methyl Ester (FAME) Fuels as a Replacement or Extender for Diesel Fuels

June 2004

The FIE manufacturers position:

FIE manufacturers encourage the development of renewable compression ignition fuels.

Experience to date with Rapeseed Methyl Ester fuels in Europe suggests that RME conforming to the European standard EN14214 at the point of sale used in mixtures of up to 5% by volume with mineral diesel fuel complying with the EN590 diesel fuel standard should not give end-users any serious problems. **The currently agreed position of all FIE manufacturers undersigned is to limit release of injection equipment for admixtures up to a maximum of 5% FAME (meeting the EN14214 standard) with unadulterated diesel fuel (meeting the EN590 standard). The final product B5 must also comply with EN 590.**

The required quality of the FAME fuel is defined in European standard EN14214, which covers relevant impurities and tramp chemicals from the processing. Suppliers of FAME fuels must be able to demonstrate compliance to this standard at the filling station. There are several risks associated with possible supply chains.

For the FIE manufacturers a key property of any FAME fuel is the resistance to oxidation. Aged or poor quality FAME contains organic acids like formic and acetic acids and acids of higher molecular weight as well as polymerisation products which attack many components, drastically reducing the service life of the FIE. A list of issues which have been witnessed in service is detailed in the attachment to this document.

The ASTM specification for FAME fuel (D6751) does not to date contain a requirement for oxidation stability. The ASTM diesel fuel specification (D975) makes no provision for the inclusion of FAME, although there are currently proposals to define a specification for blends up to B20. The FIE manufacturers are concerned both with the missing oxidation stability in the specification and the lack of sufficient safeguards against blend quantity.

The FIE manufacturers can accept no legal liability for failure attributable to operating their products with fuels for which the products were not designed, and no warranties or representations are made as to the possible effects of running these products with such fuels.

Non-compliance of the fuel to standards agreed by the FIE manufacturers, whether being evident by appearance of the known degradation products of these fuels, or their known effects within the fuel injection equipment, (see attached list of known issues) will render the FIE Manufacturers' guarantee null & void.

Attachment

Fuel Injection Equipment – Potential Problems with FAME
(non-exhaustive list)

Fuel Characteristic	**Effect**	**Failure Mode**
Fatty acid methyl esters (general)	Softening, swelling or hardening and cracking of some elastomers including nitrile rubbers (physical effect depends upon elastomer composition) Displacement of deposits from diesel operation	Fuel leakage Filter plugging
Free methanol in FAME	Corrosion of aluminium & zinc Low flash point	Corrosion of FIE
FAME process chemicals	Entry of potassium & sodium and water hardness (alkaline earth metals) Entry of free fatty acids hastens the corrosion of non ferrous metals, e.g. zinc Salt formation with organic acids (soaps) Sedimentation	Filter plugging Corrosion of FIE Filter plugging Sticking moving parts
Free water	Reversion (Hydrolysis) of FAME to fatty acid and methanol Corrosion Sustainment of bacterial growth Increase of electrical conductivity of the fuel	Corrosion of FIE Filter plugging
Free glycerine	Corrosion of non-ferrous metals Soaking of cellulose filters Sediment on moving parts and lacquering	Filter plugging Injector coking
Mono-, di- and tri-glyceride	Similar to glycerine	Injector coking
Higher modulus of elasticity	Increase of injection pressure	Potential for reduced service life
High viscosity at low temperature	Generation of excessive heat locally in rotary type distributor pumps Higher stressing of components	Fuel delivery problems Pump seizures Early life failures Poor nozzle spray atomization
Solid impurities / particles	Potential lubricity problems	Reduced service life Nozzle seat wear Blocked nozzles
Ageing products		
Corrosive acids (formic & acetic)	Corrosion of all metal parts May form simple cell	Corrosion of FIE
Higher molecular organic acids	Similar to fatty acid	
Polymerisation products	Deposits, precipitation especially from fuel mixes	Filter plugging Lacquer formation by soluble polymers in hot areas

DELPHI BOSCH SIEMENS VDO Automotive

DENSO STANADYNE

The views contained in this Common Position Statement are those of the Joint FIE Manufacturers, which comprises the following companies :-

Signed on behalf of
DELPHI DIESEL SYSTEMS……………… D.Schoeppe 28.6.2004
Dr Detlev Schoeppe, Director of Engineering

Signed on behalf of
ROBERT BOSCH GmbH DIESEL SYSTEMS……………… 09.07.04
Dr.-Ing. Ulrich Dohle, President

Signed on behalf of
SIEMENS VDO DIESEL SYSTEMS……………… J. Warga 10.8.04
Mr Johann Warga, CEO

Signed on behalf of
STANADYNE CORPORATION……………… 26 Aug 04
Mr William W Kelly, Sr. Vice President & General Manager

Signed on behalf of
DENSO CORPORATION……………… M. Miyaki 04.8.04
Mr Masahiko Miyaki, Managing Officer, Fuel Injection Product Division

From: Sharma, Manoj (M.)
Sent: Thursday, June 21, 2007 9:10 AM
To: Fulton, Brien (B.L.); Constantine, Ted (T.E.)
Subject: Re:

Attachments: 2006-01-3279.pdf

I came across a paper in SAE database on effect of Biodeisel on fuel system components. Since they evaluated bosch pumps, I thought I should share it with you incase it helps.

"......Bosch VE (in-line) rotary pumps were evaluated for wear after testing for 500 hours on the base fuel, B5 and B20 test fuels. Additionally, a test procedure was developed to accelerate wear on common rail pumps over 500 hours. This procedure was used to evaluate Bosch pumps from tests conducted on the base fuel, B5, and B20 fuels. B5 blends, even with highly oxidized biodiesel, appeared compatible with the materials and components tested. B20 blends from non-oxidized biodiesel also appeared to be compatible with these materials and components. Test results for B20 prepared from highly oxidized biodiesel suggest the potential for significant problems with oxidized fuels, highlighting the need to prevent biodiesel oxidation…."

2006-01-3279.pdf

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Impact of Biodiesel Blends on Fuel System Component Durability

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National Renewable Energy Laboratory

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Powertrain & Fluid Systems
Conference & Exhibition
Toronto, Canada
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Impact of Biodiesel Blends on Fuel System Component Durability

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ABSTRACT

An ultra-low sulfur diesel (ULSD) fuel was blended with three different biodiesel samples at 5 and 20 volume percent. The biodiesel fuels were derived from rapeseed and soybean oils, and in addition, a highly oxidized biodiesel was prepared from the soy biodiesel by oxidation under controlled conditions. A set of five elastomers commonly used in automotive fuel systems were examined before and after immersion in the six test blends and base fuel at 60°C for 1000 hours. The elastomers were evaluated for hardness, tensile strength, volume change and compression. Injector wear tests were also conducted on the base petrodiesel fuel and the biodiesel blends using a 500-hour test method developed for this study. Bosch VE (in-line) rotary pumps were evaluated for wear after testing for 500 hours on the base fuel, B5 and B20 test fuels. Additionally, a test procedure was developed to accelerate wear on common rail pumps over 500 hours. This procedure was used to evaluate Bosch pumps from tests conducted on the base fuel, B5, and B20 fuels. B5 blends, even with highly oxidized biodiesel, appeared compatible with the materials and components tested. B20 blends from non-oxidized biodiesel also appeared to be compatible with these materials and components. Test results for B20 prepared from highly oxidized biodiesel suggest the potential for significant problems with oxidized fuels, highlighting the need to prevent biodiesel oxidation. However, due to a lack of real-world field oxidized biodiesel samples for comparison, verifying the severity of the oxidization level of the biodiesel used in this study is not possible. There is some potential that the highly oxidized biodiesel sample used in the study represents an extreme condition that consumers may not encounter in the field; therefore, additional work is needed.

INTRODUCTION

Biodiesel is defined as the mono alkyl esters of long chain fatty acids derived from vegetable oils, waste cooking oil, or animal fats. Biodiesel contains almost no sulfur and no aromatics. This material is increasingly being applied as either a replacement for, or a blending component with petroleum diesel. There is great potential for significant variation in product quality and products generically described as biodiesel. Research has shown that there are fuel quality, handling, storage, and vehicle operability requirements, which need to be addressed when biodiesel is used automotive diesel vehicles [1, 2]. This has led to numerous initiatives by fuel producers, original equipment manufacturers (OEMs), and their industry associations to publicize these issues. Also, standard-setting organizations have developed initiatives that include a number of parameters in regional biodiesel specifications.

In the United States, these initiatives have led to the development of a specification for biodiesel, ASTM D6751-03a. This standard is intended to address the quality of pure biodiesel (termed B100) when used as a blend stock of 20% and lower. No separate ASTM quality specifications currently exist for biodiesel when blended with fossil-derived fuels. The ASTM D6751 standard specifies biodiesel as long chain fatty acid esters from vegetable or animal fats containing only one alcohol molecule on one ester linkage. This effectively excludes raw or unrefined vegetable oils which contain three ester linkages. Within the United States, soybean oil is the leading predominant biodiesel feedstock.

Within the European Union, rapeseed oil is the most widely available biodiesel feedstock. The European Committee for Standardisation developed a uniform standard, EN14214. Modifications have been made to the European diesel specification (EN590), which allows for the use of up to 5% of an EN14214-compliant biodiesel as long as the finished blend meets the cold flow properties specified for the geographic area where the fuel is to be used. It is worth noting that EN 14214 generally excludes pure soybean methyl esters as fuel due to the high natural iodine value of this product. This requirement is intended to help insure the oxidation stability of the product, but seems misguided given that iodine value has been shown to be unrelated to oxidation stability [3].

Efforts to produce low and ultra-low sulfur fuels by hydrotreating have resulted in the removal of polar sulfur, nitrogen, and oxygen compounds; and have potentially reduced the lubricity of resulting diesel fuel. Several investigations have reported that biodiesel can significantly improve the lubricity of low sulfur diesel fuel at relatively low concentrations [4, 5]. However, it has also been reported that the formation of corrosive materials (such as organic acids, water, and methanol), polymers, gums, thermal and oxidative instability, and water separation may give rise to vehicle operability problems [2]. The current state of knowledge regarding biodiesel stability has been recently reviewed [6].

Potential vehicle operability problems for use of biodiesel blends have been identified as the following:

- Corrosion of fuel injection equipment components
- Elastomeric seal failures
- Low-pressure fuel system blockage
- Fuel injector spray hole blockage and excessive fuel injector wear
- Increased dilution and polymerization of engine oil
- Pump seizures due to high fuel viscosity at low temperatures
- Excessive injection pressure and pump wear.

While the various biodiesel quality standards are intended to prevent these problems, there are little data available to support the specific limits in the quality standards. As a consequence, OEMs and industry associations have been cautious in their acceptance of biodiesel and biodiesel blends. This study is designed to provide additional information on several of the issues that may occur for biodiesel blends, specifically the impact on fuel system elastomers, and wear of injectors and two different types of fuel pump. In specification soy and rapeseed biodiesels were employed, as well as a highly oxidized sample of soy biodiesel. These were blended with a ULSD fuel at 5% and 20%.

EXPERIMENTAL

FUELS AND FUEL PROPERTIES

Base fuel

A quantity of 2-D grade ULSD known as BP15 was used throughout the study as the base fuel and for blending. This fuel was produced in a commercial refinery unit, but cracked stocks were excluded from the feed. Future ULSD production will likely employ more advanced processing to allow the inclusion of cracked stocks. The roll out of ULSD in the United States is slated for September 15, 2006, and commercial fuel may be different from the fuel used in this study. Analysis of the base fuel was conducted to ensure the quality of the fuel according to the standard method, ASTM D975 and results are listed in Appendix 1. All fuels were stored in 200-liter, mild steel drums that were stoppered and inverted to prevent ingress of water.

Soy-based biodiesel

The soybean oil derived biodiesel was obtained from Peter Cremer, NA and labeled NEXSOL BD-0100. The shipment consisted of two lots of slightly differing product quality. To avoid doubt about the contribution of the different physical properties of the two lots, the batches were blended together to form a single sample.

Half of this combined sample of soy biodiesel was treated shortly after receipt with a commercially available antioxidant additive, tert-butyl hydroquinone (TBHQ) at 200 ppm. The objective of this was to inhibit oxidation of the fuel for the life of the study. Laboratory analysis on this now stabilized soy biodiesel was conducted according to the ASTM D6751 standard. In addition, tests for iodine value, peroxide value, and oxidative stability were performed. This fuel is now referred to as stabilized soy biodiesel, and characterization results are reported in Appendix 2. This stabilized material was used to prepare all B5 and B20 blends requiring soybean oil methyl ester (SME).

Oxidized soy biodiesel

One 200-liter drum of soy-based biodiesel was taken from the remaining (unstabilized) lot and prepared so as to achieve an acid number of at least 3.5 mg/KOH/g. The sample was heated to an average temperature of 57°C using an electric belt heater around the outside of the drum and sparged with BTCA 178 grade air (British Technical Council for the Motor and Petroleum Industries Fuels Committee) from a gas cylinder at a flow rate of approximately 4 liters/min. This sparging technique was considered to provide adequate mixing, without causing the sample to foam and to prevent a temperature gradient between the top to the bottom of the drum. Bottled air was used to ensure that the dew point was not compromised and that hydrocarbons were not introduced into the sample from site air compressors. The temperature of the sample was monitored throughout the oxidation treatment using an electronic digital thermometer. Acid number was measured daily using method ASTM D664 until it exceeded the required 3.5 mg/KOH/g. In fact, an initial acid number of 4.013 mg/KOH/g was achieved after 29 days, at which point heating and sparging was stopped. Acid number, however, decreased during the following days (3.818 mg/KOH/g), stabilizing at around 3.605 mg/KOH/g. The stabilized value is taken as the final value for this report. It is thought that erroneous results might have been caused by high levels of dissolved carbon dioxide, introduced through agitation and sparging.

This sample was labeled as ‘Batch 1’ and used to prepare all subsequent B5 blends, which required oxidized soy-based biodiesel.

To fulfill the testing requirements of the project, a second 200 liter sample of oxidized soy biodiesel was prepared. An acid number of 5.1mg/KOH/g was achieved in much less time than the previous batch. This was accomplished due to the use of a large diffuser, providing small air bubbles with relatively large surface area, thus making better gas to liquid contact. This sample was labeled as ‘Batch 2’ and used to prepare all B20 test blends which required oxidized soy-based biodiesel.

Laboratory analysis of the oxidized soy biodiesel batches was conducted to the ASTM D6751 standard. Tests for iodine value, peroxide value, and oxidative stability were also carried out. Characterization results for both batches of oxidized soy and results are also shown in Appendix 2.

Rapeseed biodiesel

A quantity of European, additive-free rapeseed methyl ester meeting the EN14214 specification was obtained for this study. It was considered prudent to stabilize the rapeseed biodiesel for the duration of the study, and so the fuel was treated with 200 ppm of TBHQ in the same manner as the soy biodiesel.

The rapeseed biodiesel was tested to the ASTM D6751 standard. Tests for iodine value, peroxide value, and oxidative stability were also conducted, as shown in Appendix 2. This stabilized rapeseed biodiesel was used to prepare all B5 and B20 test blends requiring the addition of rapeseed oil methyl ester (RME).

Biodiesel blends

A total of seven fuel blends containing 5%v/v (B5) and 20%v/v (B20) biodiesel in BP15 base fuel were prepared for the study:

- B5 RME – Sample ID 2031510
- B5 SME – Sample ID 2031511
- B5 Oxidized SME (Batch 1) – Sample ID 2031512
- B20 RME – Sample ID 2031513
- B20 SME – Sample – ID 2031514
- B20 Oxidized SME (Batch 2) – Sample ID 2031942
- B20 Oxidized SME (Batch 1) – Sample ID 2050822.

Each blend was assigned a unique sample number which identified the sample throughout its test life. The untreated ultra-low sulfur base fuel (BP15) was assigned sample number 2031163. Product quality analysis was conducted on each test fuel as directed by the ASTM D975 standard, with results reported in Appendix 3.

It has been noted that Batch 2 oxidized soy biodiesel (acid number of 5.1mg/KOH/g) was more extensively oxidized than Batch 1 (acid number 3.605 mg/KOH/g). One additional test fuel was subsequently blended to determine the behavior and pump wear effects of a B20 blend prepared from a less highly oxidized soy biodiesel. This B20 blend was prepared from Batch 1 oxidized soy biodiesel, the balance being the BP15 ULSD. Limited product quality analysis was conducted on this additional biodiesel fuel blend.

ELASTOMER TESTING

Five candidate elastomer types typically used in automotive fuel systems were selected for this study and are described in Table 1. The selection was based on the recommendations of a leading specialist supplier of automotive elastomers. ‘O’ ring test samples were specially molded for the study to ensure consistency of material dimensions and production batch.

Table 1. Fuel system elastomers tested in this study.

Elastomer Code	Description
NO674-70	Sulfur-cured acrylonitrile butadiene nitrile rubber Medium acrylonitrile content of 30-35%.
NB104-75	Peroxide- cured acrylonitrile butadiene nitrile rubber. Higher acrylonitrile content.
KB162-80	Hydrogenated nitrile polymer.
VB153-75	Fluorocarbon polymer, 67% fluorine content.
V1164-75	Fluorocarbon polymer, 66% fluorine content.

The physical properties of the test specimens prior to and after ageing in each of the test fuels were measured. Samples were immersed in candidate fuels at 60°C for 1000 hours. Control samples were conditioned in air at 23°C plus or minus 2°C for the same period. Test measurements were taken as required by the standard test methods listed in Table 2. The standard test methods prescribe procedures and defined conditions for measuring changes to physical properties such as volume swell, hardness, dimensional changes, and compression and tensile properties.

Table 2. Test methods applied to elastomer samples.

Test Method	Method Title
ASTM D1414	Standard Test Methods for Rubber O-Rings
ASTM D471	Standard Test Method for Rubber Property—Effect of Liquids
ASTM D395	Standard Test Methods for Rubber Property-Compressions Set

INJECTOR WEAR TEST

Injector wear testing was conducted on the base fuel and three B20 blends. The main operational conditions of the test procedure were as follows:

- The rig was operated at a constant speed of 1440 rpm ± 25 rpm for a period of 500 hours ± 10 hours.
- Fuel is used in 40 liter lots and at the completion of 100 hours ± 10 hours the fuel is drained and exchanged for fresh fuel.
- The injector block was heated to 150°C ± 10 °C to simulate normal operating conditions of the injectors.
- The bulk fuel temperature was controlled to 40°C ± 5 °C. It was permissible for the bulk fuel temperature to be outside these limits for the first 3 hours after start up and following a fuel change.
- Lucas injector nozzles, part number RDNOSD6754, were selected for the study. They feature an indirect injection design with corresponding nozzles. The injectors were checked for spray pattern, leaks, and opening pressure at the start of each test. The opening pressures were set to 130 ±5 bar absolute.

The test rig consisted of an in-line diesel injection pump running at a constant speed of 1440 rpm. The fuel control rack was mechanically locked to ensure a consistent injection of fuel across all tests. The injection pump cam and followers were lubricated by a separate source and so were independent of the test fuel for lubrication. This ensured consistency of testing across all candidate fuels.

A set of four injector nozzles was tested on each fuel. Test injector nozzle needles were dimensionally profiled. By determining the mean and standard deviation for a large number of measurements on new injector components, it was possible to produce information relating to the new or manufacturers' acceptable 'out of roundness'. For the injectors used in this project, there were 4 sets of 4 injectors and each injector needle was assessed for 'out of roundness' at 5 different axial locations. This provided a set of 80 measurements, on new components, as the base line 'acceptable' level of 'out of roundness.'

It was then possible to compare the post-test 'out of roundness' measurements (for each fuel tested) with this pre-test distribution to assess whether the fuel was acceptable or not; i.e., were the post-test results inside or outside the acceptable distribution at the 95% confidence level.

ROTARY PUMP TEST

The rotary pump test method was developed from the CEC F-32-X-99 test method for diesel pump lubricity, but employs a 500-hour test duration rather than 1000 hours. This test was performed on the base fuel and six biodiesel blends. For each test, a totally new Bosch VE pump, model number 0460 494 168, was used. Care was taken to ensure that the purchased pumps were not rebuilt, reconditioned, or overhauled. It is normal practice in this instance not to conduct a pre-test rating of the test components. Experience has shown that this is not necessary as the quality control of the new components and assembly by the manufacturer are very good.

The test cycle is outlined in Table 3. The test cycle was originally developed by the pump manufacturer, Robert Bosch GmbH, and was designed to accelerate the wear of the pump components in the following manner:

- The fuel control lever is locked in the maximum fuel position so as to increase the load on the pumping element components as well as increasing the duration of injection.
- Fuel is used in 40 liter lots and at the completion of 100 hours ± 10 hours the fuel is drained and exchanged for fresh fuel.
- The stop/start cycle repeatedly removes the hydrodynamic lubrication film between the moving components and so accelerates wear. This also provides a more realistic test cycle as fuel pumps in normal use would undergo many thousand starts, from a static condition, during their lifetime.
- The test cycle includes an over-speed section to exercise the components of the mechanical governor mechanism. The controlled fuel temperature and pressure have been chosen to simulate real-life operating conditions. At start of test and after every fuel exchange the fuel temperature must reach its set value of 60 ± 5 °C after a maximum of 3 hours running time.

At the end of each test, the test pump was carefully dismantled for visual rating. This rating was conducted by raters who had attended training sessions by Bosch and also participated in comparative rating exercises with other companies undertaking this type of test work. This ensures some consistency of rating across all companies involved.

Table 3. Pump operating cycle for rotary pump wear tests.

Phase	Acc. Running Time [s]	Pump Speed [% of rated speed]
1	0	0
2	5	110%
3	7	110%
4	9	100%
5	118	100%
6	120	80%
7	170	80%
8	175	0
9	180	0

COMMON RAIL PUMP TEST

The common rail test rig consisted of a common rail fuel pump (the test pump) operating at a speed representative of the more arduous conditions. The common rail fuel pump selected for the study was a Bosch common rail pump, part number 0445 010 010. The test cycle was based on the pump rig test cycle used by Bosch but limited to a 500-hour test duration. The key test conditions are as follows:

- The running speed chosen was approximately 2000 rpm which represented 4000 rpm engine crankshaft speed if we assume a 2:1 pump to engine speed ratio. Note that for common rail systems this ratio can vary widely and will not always be 2:1. The actual speed range was between 1950 and 2000 rpm.
- The pump was operated through a test cycle consisting of 3 minutes running at this test speed and 5 seconds stationary. The stationary portion of the test cycle was designed to accelerate the wear and better represent the stop/start nature of real life conditions.
- The pump was arranged to operate at a target pressure of 1350 bar, which is typical of many vehicle applications. Throughout the test, the operating pressure was arranged to be between 1200 bar and 1400 bar gauge.
- The test fuel was supplied to the pump at a flow rate and feed pressure matching the specifications of the vehicle system. This was arranged to be between 2.0 and 3.0 bar gauge.
- The fuel inlet temperature was controlled at 40°C ± 5°C. Fuel heating and cooling units were employed to meet this condition.
- The high-pressure outlet of the pump was connected to a fuel rail and electronic injector, as it would have been in the vehicle application. The injector was supplied with electrical signals in order to operate it at a fixed frequency and fixed open/close time periods (mark/space ratio). The injector was supplied with electrical pulses of 5 ms duration.

Common rail wear tests were conducted on the base fuel and B5 and B20 biodiesel test blends. One additional common rail test was also conducted to further investigate the behavior of a B20 oxidized soy biodiesel prepared from Batch 1.

At the end of a test, each test pump was dismantled and the critical components visually rated. The pump rating examines surface abrasion, fretting, and corrosion as well as polishing and wear.

RESULTS AND DISCUSSION

ELASTOMER TESTING

Most elastomer materials will undergo a physical or chemical change when in contact with fuel. The degree of change depends upon the tendency of the material to absorb a fuel or on compounds being dissolved or extracted by the fuel. This can lead to a number of changes in the physical characteristic of the material including swelling, shrinkage, embrittlement and changes in tensile properties. Natarajan et al. have studied the corrosivity, elastomer compatibility, toxicity, and biodegradability of several oxygenated diesel fuels [8]; and have shown a wide range of effects for different oxygenate chemistry.

The limit of a permissible physical change varies with the application and some degree of change can usually be tolerated. For example, a material that swells in a fuel or suffers a decrease in hardness may well continue to be fit for purpose for a long time as a static seal. However, in dynamic applications, swelling may result in increased friction and wear, and so a lower degree of volume change can be tolerated. For example, significant volume shrinkage can result in 'O' ring leakage whether the mechanical application is static or dynamic. However, a compound—which swells or is subject to elongation or changes to hardness or tensile strength—may remain serviceable as a static seal despite unfavorable conditions. Many material combinations do not fall neatly into a single category and some engineering interpretation is necessary.

Results for volume swell, hardness, dimensional changes, compression set, and tensile properties are shown in Appendices 4 through 8.

Volume Swell

The test data shows that the fluorocarbon 'O' ring materials, VB153-75 and V1164-75 exhibit the best overall chemical resistance in the fuel combinations tested, in terms of volume change. The maximum measured volume change of 6.8 % is acceptable for both dynamic and static applications.

Both the B5 and B20 blends of oxidized soy biodiesels have significant effect on the N0674-70, NB104-75 and KB162-80 test samples. In the B20 oxidized SME blend, all three materials present measurements which exceed

30% volume swell. Values of between 15.1% and 20.8% volume swell were measured in contact with the B5 oxidized SME blends. These elastomers might be subject to deterioration of mechanical properties in oxidized fuels especially in terms of extrusion resistance.

Test sample KB162-80 demonstrates poor swell resistance (24.3% volume swell) in contact with the B20 soy biodiesel blend, which might be considered unacceptable for dynamic uses. With the exceptions noted here, volume change for these materials in other fuels examined is within acceptable limits.

Hardness Properties

Hardness measurements conducted before and after fluid immersion show the nitrile rubber samples to exhibit most overall reduction in hardness in all test fluids. The sulfur-cured NBR material (NO674-70) exhibited most hardness change in the B5 and B20 oxidized soy biodiesel, giving 9 and 14 point reductions respectively when compared to the un-aged samples. The hydrogenated nitrile polymer (KB162-80) was most significantly affected by the B20 soy biodiesel blend with a reduction in hardness of 16 points. Test sample NB104-75 performed well in all fuels, exhibiting most hardness change, only 7 points, in the B20 oxidized blend.

The fluorocarbon materials (VB153-75 and V1164-75) exhibited the least decrease in hardness with maximum measurements of 5 points in all candidate fuels. These candidate test samples showed the best performance under the prescribed test conditions. However, it should be noted that all the materials tested are within what might be considered acceptable limits.

Dimensional Changes

All materials showed a positive change in overall dimension measurements with greatest dimensional changes occurring following immersion in the B20 and B5 oxidized soy blends. In general, shrinkage of a material is considered to be the more usual cause of seal failure.

Fluorocarbon materials, V1164-75 and VB153-75, demonstrated the best overall resistance to dimensional change (1.3% maximum change) in all fuels tested. Test sample NB104-75 was the most significantly affected across the range of fuels with between 6.6% and 9.9% dimensional change occurring in the B5 and B20 oxidized fuels. Similarly, test samples NO674-70 and KB162-80 showed greatest dimensional change (5.0% to 9.0%) in the oxidized fuels.

Compression Set Properties

This is generally reported as percentage change by elastomer manufacturers rather than percentage change in compression set relative to the original material deflection as required by ASTM D395. It is a measurement of how the elastomer recovers after a fixed time under specified conditions of temperature and ‘squeeze’ (compression). Zero percent indicates that no relaxation of the material has taken place, whereas 100% indicates total relaxation. A seal may subsequently contact mating surfaces but may not exert sufficient force against those surfaces. As with all the physical properties of elastomers, a good balance is generally required. For example, swelling of an elastomer may compensate for a poor compression set. A high compression set and dimensional shrinkage can lead to early seal failure except under conditions of high mechanical squeeze.

Overall, fluorocarbon test sample V1164-75 exhibited the best compression set characteristics for all material tested across the range of fuels (maximum 10 % change). Fluorocarbon material, VB153-75 did not perform well under this test (24.5-57.4 % change) even in base fuel. However, it should be noted that the test sample which was air conditioned at standard temperature and humidity also yielded relatively high compression set measurements (29.3 % change).

Sample NB104-75 exhibited acceptable overall compression set in all fuels, with values ranging from -9.3% to 8.5% change. However, 32.4 % change was measured in contact with the base fuel. Test samples NO674-70 and KB162-80 demonstrated acceptable overall performance in all test fuels giving values of between -3.1 to 19.7 % change.

Tensile Properties

The data demonstrate that the tensile properties of the two fluorocarbon materials (VB153-75 and V1164-75) were not significantly affected by any of the test blends. A maximum value of 19.6 % change in tensile strength was measured in contact with the B20 oxidized fuel. The nitrile ‘O’ ring seals (KB104-75) were most substantially affected overall with up -85.3% change in tensile strength and -79.7% elongation at break in contact with the two oxidized soy biodiesel blends. Test samples NO674-70 and KB162-80 gave acceptable results of around 50% or less for changes in tensile strength and elongation at break in all candidate fuels.

INJECTOR WEAR TEST

Injector wear tests were conducted on the base fuel and three B20 biodiesel blends. The injector wear test on the B20 oxidized soy biodiesel was terminated after only 12 hours of running following separation of the test fuel. Injectors from the tests on B20 oxidized soy biodiesel (sample 2031942) were examined following the brief running period. No evidence of gum formation was observed but significant needle sticking was noted.

Although the injector wear test is designed to examine the wear of internal injector components, not deposits on the exterior surfaces, each injector was examined for any obvious sign of material deposition. With the exception of one injector set, all injectors were found to be free from obvious deposits or ‘lacquering.’ For the B20 soy biodiesel (sample number 2031514), which had been stabilized with antioxidant, some deposition was evident on the outside of the injector nozzles. However, this material is not thought to be lacquer, which is defined as a hard, dry, and generally lustrous, oil insoluble deposit, as it was easily removed on washing.

The test injectors were checked for opening pressures, spray pattern, and leakage before and after each injector wear test. Some small increases in the ‘leak back’ measurements after testing are thought to be due to the seating of the needle in the nozzle during the test operation. There is no evidence that the fuel caused appreciable wear of the fuel inlet passage in the injector nozzles. In addition, post test fuel delivery measurements were similar across all test fuels and measurements were repeatable across the individual injectors.

The major parameter of concern when dealing with diesel fuel injector components is the quality of the surface finish of the high-pressure mating components. It is important to determine if these have deteriorated from the original surface finish when the components were manufactured. For cylindrical components, the surface finish may be evaluated by the ‘out of roundness’ measurement. The post-test ‘out of roundness’ mean and standard deviation measurements for each fuel test are compared with these pre-test acceptable values to identify any which potentially fall outside the acceptable range, and results are summarized in Table 4 (additional detail on the methodology and data analysis can be found in reference 7). All of the post-test measurements lie within the 95% confidence interval of the pre-test data. Therefore it may be concluded that the lubricity values of the fuels tested are adequate for the protection of the diesel injector components running under conditions similar to this test method.

Caution must be exercised in relation to fuel 2031942 (B20 oxidized soy biodiesel) as other fuel performance factors prevented this test being operated to completion. It must also be noted that no correlation work has been conducted to demonstrate how this injector test might relate to real-life operating conditions.

ROTARY PUMP TEST

The tests conducted are based on the Bosch VE four cylinder rotary diesel injection pump with mechanical governor. The test protocol had a duration of 500 hours and included a stop/start regime. A total of seven fuels were tested on Bosch VE rotary pumps. At the end of each test a wear rating assessment was conducted on each test. Pump components examined for wear or damage are shown in Figure 1.

The rating scale is based on a scale of 1 to 10. Ratings up to 3 indicate normal wear levels, which would be expected, and show no signs of damage, which would lead to premature failure of the pump. A rating of 3.5 is the absolute limit of the 'normal' wear and is generally taken as the pass/fail border line. Ratings between 4 and 6 are given when there is some evidence indicating a reduced service life of the pump. This may be large amounts of wear, scuffing, or fretting of the rated components. Ratings of 7 and above indicate major problems and likely catastrophic failure of the pump. Most pump tests conducted produce ratings below 6. Very poor lubricity fuels tend to cause seizure of the pump after only a few hours of running. However, tests which fail to reach their full duration would receive an automatic 'fail', whatever the condition of the components.

Table 4. Out-of-roundness results from injector wear tests.

	Pre test Distribution ALL	**Base Fuel**	**B20 RME**	**B20 SME**	**B20 SME Oxidized**
Maximum	0.92	0.55	0.59	0.73	0.80
Minimum	0.10	0.30	0.31	0.34	0.34
Average	0.48	0.40	0.44	0.48	0.54
σ	0.22	0.09	0.09	0.13	0.15
Mean + 2 σ	0.92	0.58	0.62	0.74	0.83
Mean – 2 σ	0.05	0.22	0.26	0.22	0.25

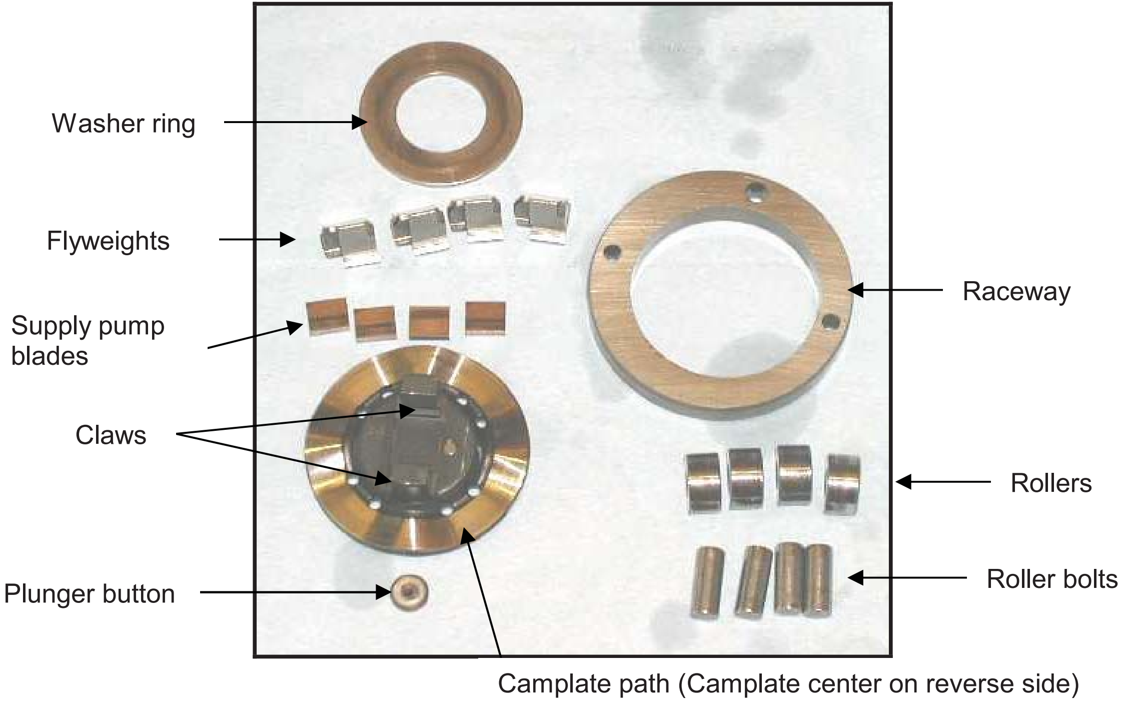

Figure 1. Bosch VE rotary pump components for wear rating.

The rotary pump test conducted on the B20 oxidized soy biodiesel blend failed to reach full duration, stopping after 66 hours. Examination of the data log showed that the computer control system had registered low pressure of the fuel supply system feeding the rotary pump. The cause was found to be blockage of the fuel filter. Closer inspection of the test fuel showed that it had separated into two distinct phases; the bottom phase being significantly more viscous and darker than the top phase. This was similar to our experience of the same fuel during the injector wear test and it would seem reasonable to conclude that the fuel had undergone decomposition during testing. It should be noted that the B5 oxidized soy biodiesel blend reached the full 500-hour test duration, and excessive wear was not evident on examination and rating of the corresponding fuel pump. Overall ratings are summarized in Table 5.

The ratings produced from the pump lubricity tests conducted indicate that all the fuels are within the range normally expected for commercial automotive diesel fuels. The amount of wear and consequently the ratings may have been slightly higher if the tests had continued to 1000 hours, but there is no evidence from the test components to suggest that the wear would have been outside the 'normal' range.

Table 5. Summary of wear rating assessments of Bosch VE rotary pumps.

Test Fuel/Blend	Overall Rating
Base fuel	2.5
B5 RME	2.5
B5 SME	2.5
B5 Oxidized SME (Batch 1)	3
B20 RME	3
B20 SME	3
B20 Oxidized SME (Batch 2)	Fail (2.5)

COMMON RAIL PUMP TEST

An in-house test method was developed to determine common rail pump wear using a 500-hour test procedure. Common rail wear tests were conducted on the base fuel, and B5 and B20 biodiesel test blends. At the end of the study, an additional common rail test was conducted to further investigate the behavior of a B20 oxidized soy biodiesel fuel prepared with Batch 2 of the oxidized soy biodiesel.

The pumps from these tests were dismantled and visually assessed for surface abrasion, fretting, and corrosion as well as polishing and wear steps. Pump components examined for wear or damage are shown in Figure 2. An overall rating was determined from the common rail pump wear tests, and these are summarized in Table 6.

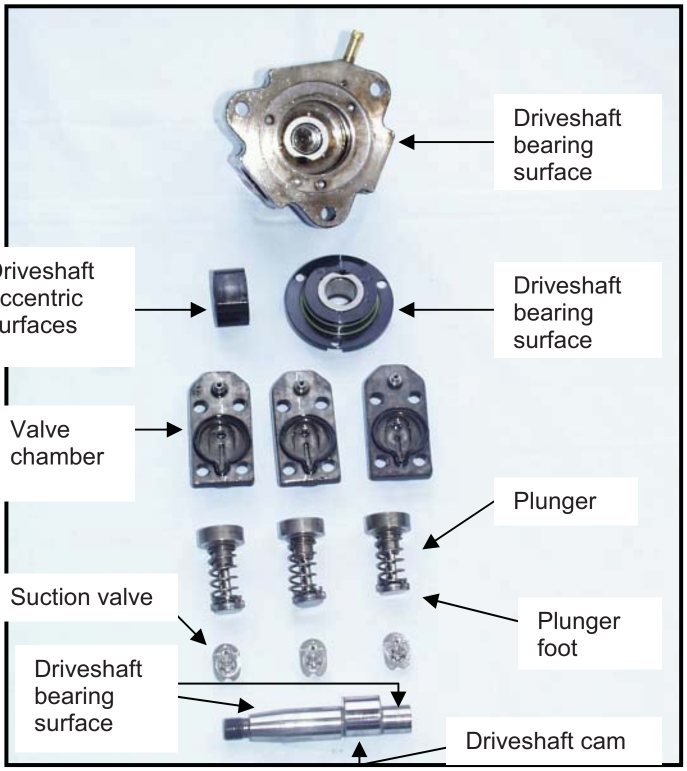

Figure 2. Dismantled Bosch common rail test pump showing components assessed for wear.

Table 6. Summary of wear rating assessments of Bosch Common Rail Test Pumps

Test Fuel/Blend	Overall Rating
Base fuel	2.0
B5 Rapeseed Methyl Ester	1.5
B5 Soy Biodiesel	1.5
B5 Oxidized Soy Biodiesel	2
B20 Rapeseed Methyl Ester	2
B20 Soy Biodiesel	2.5
B20 Oxidized SME (Batch 2)	1.5
B20 Oxidized SME (Batch 1)	1.5

All of the candidate test fuels completed the 500-hour test procedure. Overall, none of the fuel blends tested showed any adverse effects on the wear ratings of the common rail fuel pumps. With the exception of the B20 fuel blend (2031942) prepared from Batch 2 of the oxidized SME, there was no evidence of unusual deposits, gums, or lacquers on the pumps or any rated parts.

Examination of the fuel pump used to test the highly oxidized B20 fuel (2031942) revealed a thin lacquer coating on the shaft bearing surface. The lacquer was hard and dry with a lustrous appearance, oil insoluble and not removed on washing. In addition, there was evidence of seal swelling on dismantling the pump. Photographs of the lacquered component and the elastomer seal in the valve chamber which had become swollen are provided in Figures 3 and 4.

This test fuel consisted of 20% by volume of the highly oxidized soy biodiesel and had earlier resulted in failure of the Bosch VE rotary pump test and the injector test. Although the common rail test on this candidate fuel was completed without incident, a significant volume of a dark, viscous material was present in the bottom of the fuel tank when the fuel was changed after each scheduled 100 hours test run. Care had been taken to ensure that all test fuels were not subject to extremes of temperature in storage, and that representative and mixed samples were offered up for testing. Inspection of the test fuel revealed that two-phase separation had taken place: the bottom phase being significantly heavier and more viscous than the top phase. This was comparable to our experience of the same fuel during the injector wear test, and it would seem reasonable to conclude that the fuel had undergone decomposition during testing.

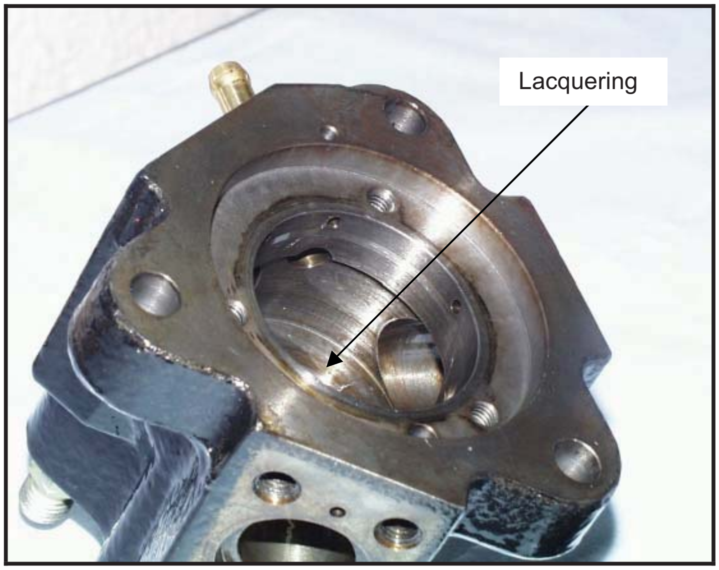

Figure 3. Lacquering on common rail test pump component.

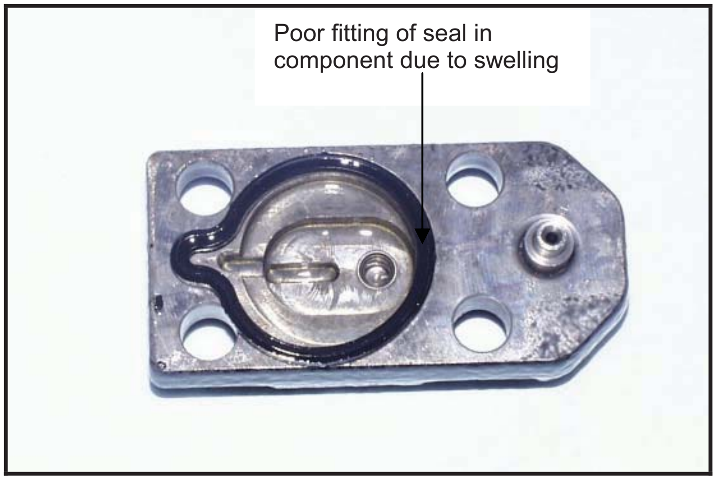

Figure 4. Common rail test pump component showing seal swell.

It is thought that filter blockage observed on the rotary pump rig did not occur on the common rail test rig due to the much higher feed pressures used: a 2.5 bar compared with 0.4 bar. In addition, the common rail test rig has a greater volume flow rate of fuel circulating via a by-pass system, and the outlet from the common rail test pump is higher (5 -10°C) than the VE pump. The fuel is also forced ('squeezed') through the filter which may prevent filter blockage.

The B20 fuel prepared from the less oxidized batch of soy biodiesel (sample number 2050822) completed the 500 hours of testing on the common rail test rig. Careful inspection of the fuel before testing provided no evidence of fuel separation, and heavier, more viscous fuel components were not evident in the fuel tank after completion of the test. However, there was clear evidence of seal swelling of the valve chamber seals on dismantling the pump. It has been established that fuel pump manufacturers typically employ 'O' ring seals prepared from hydrogenated nitrile polymers similar to test material KB162-80. From the results of the elastomer compatibility testing, this material exhibited significant volume swell (24.3%) and softening (16-point reduction in hardness) in the B20 oxidized SME fuel. Given these two physical changes, this might permit the extrusion of 'O' ring seals in certain applications such as in high pressure systems. However, it should be noted that the biodiesel used to produce both of the B20 test fuels discussed was oxidized and untypical of fuels meeting national specifications.

It is clear that the less oxidized B20 fuel (sample number 2050822) does not behave in the same way as the highly oxidized B20 fuel under the conditions of the test, i.e., significant phase separation does not take place. The test fuel was prepared immediately prior to testing and so was not subject to long periods of storage. Water and sediment content of 1% by volume was measured in the finished blend by the ASTM D2709 test method, well above the allowable limit in diesel fuel quality specifications. Acid value measured on Batch 1 oxidized SME at the end of the study showed that this parameter had not changed significantly on storage.

The available evidence indicates that phase separation did not occur in either of the B20 oxidized fuel blends on storage. Exposure to conditions occurring during the pump durability tests probably accelerated fuel separation in the more highly oxidized B20 test fuel. Phase separation did not occur during or after testing of the less oxidized B20 fuel. The B20 fuel prepared from less oxidized biodiesel contained lower amounts of water and sediment compared to the more highly oxidized B20 fuel. This indicates that the concentration of the oxidized component in the blend (the biodiesel) is not the main factor which determines fuel separation. The different behavior of the oxidized fuels is likely to be due to the extent of oxidation of the biodiesel component in the fuel.

CONCLUSION

- The highly oxidized B100 biodiesel and biodiesel blends prepared for this study have significantly different physical and chemical characteristics to non-oxidized biodiesel and biodiesel blends. The B20 test blend containing highly oxidized biodiesel may have been more highly oxidized than is likely to occur in the real world.
- Fuel filter blocking and fuel separation was observed during testing of the highly oxidized B20 test fuel in this study. Products of oxidation in the test fuel and decomposition reactions occurring under the conditions of test probably accelerated fuel separation in the fuel blend.
- Phase separation and filter blockage did not occur during testing of B5 and B20 blends prepared from biodiesel which had been less extensively oxidized and which contained lower water and sediment contents. The tests indicate the behavior of oxidized fuels under conditions of test are not dependant on the concentration of oxidized component and may be due to the extent of oxidation of the biodiesel component.
- B5 fuel prepared from oxidized biodiesel did not cause abnormal wear in either the injector or pump wear tests conducted in this study. Fuel filter blocking and fuel separation was not encountered during testing of this fuel.
- The results produced from injector wear tests indicate that the lubricity of the test fuels are adequate for the protection of diesel injector components running under similar conditions. The injector component wear test on the highly oxidized B20 blend failed to reach completion due to fuel filter blockage.
- The ratings produced from pump lubricity tests indicate that all test fuels are within the range normally expected for commercially available automotive diesel fuel running under the test conditions selected for this 500-hour test procedure. The rotary pump wear test on the highly oxidized B20 blend failed to reach completion due to fuel filter blockage.
- None of the candidate test fuel blends tested showed any adverse effects on the wear ratings of the common rail fuel pumps using a novel 500-hour test procedure. The test results indicate that the lubricity of the test fuels is adequate for the protection of common rail pumps running under similar conditions.
- Material compatibility testing of candidate elastomers has shown that fluorocarbon elastomers of medium to high fluorine content are most compatible with the test fuels under the specified conditions at concentrations of 20% or below. The results show that other candidate materials tested exhibited good resistance to changes in physical properties but exceeded the typically acceptable levels of degradation in one or more tests. These materials may be less compatible with biodiesel blends under certain applications.

ACKNOWLEDGMENTS

This study was supported by the Coordinating Research Council, Advanced Vehicle/Fuel/Lubricants Committee and by the U.S. Department of Energy, FreedomCAR and Vehicle Technologies Program. The authors are glad to acknowledge the help of many colleagues, most notably Mr. Ian Bradbury and Dr. Paul Richards for invaluable information on bed engine testing. In addition, the authors are grateful for the invaluable services and information supplied by Parker Hannifin Corporation, O Ring Division.

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CONTACT

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DEFINITIONS, ACRONYMS, ABBREVIATIONS

2-D: No. 2 diesel fuel

ASTM: American Society of Testing and Materials International

Bxx: Blend containing xx percent biodiesel, a 20% biodiesel blend is B20

HC: Hydrocarbons

NBR: Nitrile butadiene rubber

OEM: Original equipment manufacturer

RME: Rapeseed oil methyl ester

SME: Soybean oil methyl ester

TBHQ: tert-butyl hydroquinone

ULSD: Ultra-low sulfur diesel

APPENDIX 1: BASE DIESEL FUEL ANALYSIS

Property	ASTM Method or Equivalent	Limits	BP- 15 2031163
Flash Point	IP 34 (D93)	52°C min	57.5
Water & Sediment	D2709	0.050% vol.max	0.000
Kinematic Viscosity, 40°C	IP 71 (D445)	1.9-4.1mm^2/s ec.	2.499
Sulphur	D3120	0.05% mass max	16µg/g
Copper Strip Corrosion	IP 154 (D130)	No.3 max	1a
Cetane Number	D613	40 min	49.3
Cloud Point	D5772	Report to customer	-11°C
Ash	D482	0.01% mass max	0.0
Carbon Residue,100% sample	D524	0.35% mass max.	-
Distillation, temp., 90% vol recovered	IP 123 (D86)	282-338°C max	322
Calculated Cetane Index	D976	-	50.3
HFRR wsd 1.4	CEC F-06-A-96	460µm	584

APPENDIX 2: BIODIESEL ANALYSIS

Property	**Test Method**	**Limits**	**Rapeseed Biodiesel 2031040**	**Soy Biodiesel (Stabilized) 2031034**	**Batch 1 Soy Biodiesel (Oxidized) 2031382**	**Batch 2 Soy Biodiesel (Oxidized) 2031870**
Flash Point	IP 34 (D93)	130°C min	>130	>130	>120	113.5
Water & Sediment	D2709	0.050% vol.max	0.000	0.000	0.000	0.000
Kinematic Viscosity,40°C	IP 71 (D445)	1.9-6.0 mm^2/sec.	4.686	3.972	7.276	9.837
Sulphated Ash	D874	0.020% mass max.	0.003	>0.001	0.004	0.003
Sulphur	D3120	0.05% mass max	<1.0µg/g	<1.0µg/g	<0.2µg/g	N/A
Copper Strip Corrosion	IP 154 (D130)	No.3 max	1a	1a	1a	1a
Cetane Number	D613	47 min.	50.9	50.4	59.1	* Note 1
Cloud Point	D2500	Report	-6	0	3	6
Oxidation Stability	D2274	-	1.52mg/100 ml	1.15mg/100ml	8.28mg/100 ml	8.38mg/100ml
Iodine Value	D1510	-	115	131	106	94
Peroxide Value	Cd 8b-90	-	14.18 meq/kg	34.62 meq/kg	381.11 meq/kg	662.43 meq/kg
Carbon Residue,100% sample	D189	0.050% mass max.	0.23	0.019	6.24	9.4
Acid Number	D664	0.80mg KOH/g max.	0.492 *Note 2 0.490 *Note 3	0.036	3.605*Note 2 3.370 *Note 3	5.101*Note 2 4.55 *Note 3
Free Glycerine	D6584	0.020% mass max.	<0.01	<0.01	<0.01	<0.01
Total Glycerine	D6584	0.240% mass max.	0.21	<0.01	0.03	<0.01
Phosphorus	D4951	0.001% mass max.	<10mg/kg	<10mg/kg	<10mg/kg	N/A
Distillation, atmospheric equiv. temp., 90% recovered	D1160	360°C max	179	175	301	463 *See Note 4

Note 1: Unable to rate fuel. Result exceeds T22 secondary reference fuel, 74.8 cetane number
Note 2: Acid value measured immediately after oxidation
Note 3: Acid value measured after approximately six months storage
Note 4: 90% recovery not attained. Cracking temperature reported. Recovery at cracking temperature: 88.0% vol.

APPENDIX 3: BIODIESEL BLEND ANALYSIS

Property	ASTM Method	Limits (D975 limits for 2-D)	B5 RME Biodiesel	B5 Soy Biodiesel	B5 Soy Biodiesel (oxidized – Batch 1)	B20 RME Biodiesel	B20 Soy Biodiesel	B20 Soy Biodiesel (oxidized – Batch 2)	B20 Soy Biodiesel (oxidized – Batch 1)
Sample No.			2031510	2031511	2031512	2031513	2031514	2031942	2050822
Flash Point	IP 34 (D93)	52°C min	64	66	61	59	66	60.5	60.5
Water & Sediment	D2709	0.050% vol.max	0.000	0.000	0.000	0.000	0.000	0.007	1.0
Kinematic Viscosity,40°C	IP 71 (D445)	1.9-4.1mm^2/sec.	2.544	2.561	2.619	2.833	2.705	3.068	3.036
Sulphur	D3120	0.05% mass max	11µg/g	10µg/g	10µg/g	9µg/g	8µg/g	N/A	N/A
Copper Strip Corrosion	IP 154 (D130)	No.3 max	1a	1a	1a	1a	1a	1a	1a
Cetane Number	D613	40 min	48.2	48.6	52.7	49.2	49.2	60.8	N/A
Cloud Point	D2500	Report to customer	-15°C	-14°C	-10°C	-8°C	-9°C	-10°C	N/A
Ash	D482	0.01%mass max	0.007	0.006	0.002	0.004	0.009	0.00	N/A
Cetane Index	D976	40 min	50.2	49.5	51.2	50.1	51.4	47.5	N/A
Carbon Residue,100% sample	D524	0.35% mass max.	0.04	0.07	0.12	0.07	0.06	0.89	N/A
Distillation, equiv. temp.,90% vol recovered	IP 123 (D86)	282-338°C max	325.5	325.5	325.0	334.0	332.5	336.5	N/A
HFRR wsd 1.4	CEC F-06-A-96	460µm	188	355	234	178	399	167	272

APPENDIX 4: ELASTOMER VOLUME SWELL RESULTS

Material	Volume Swell (%)							
	Un-Aged	Fluid 1 B20 Soy Blend	Fluid 2 B20 RME Blend	Fluid 3 B5 Oxidized Soy Blend	Fluid 4 B20 Oxidized Soy Blend	Fluid 5 Base Fuel	Fluid 6 B5 RME Blend	Fluid 7 B5 Soy Blend
NO674-70	0.0	12.2	12.7	15.1	30.6	11.0	11.3	11.2
NB104-75	-0.1	16.1	15.6	20.8	33.7	12.1	13.8	15.1
KB162-80	0.9	24.3	14.3	20.8	30.9	12.5	15.5	13.8
VB153-75	0.3	6.8	6.2	4.3	2.7	1.1	2.4	3.4
V1164-75	-0.2	5.0	4.5	2.0	4.4	1.2	1.3	1.7

APPENDIX 5: ELASTOMER HARDNESS RESULTS

Material	Micro Hardness (IRDH)							
	Un-Aged	Fluid 1 B20 Soy Blend	Fluid 2 B20 RME Blend	Fluid 3 B5 Oxidized Soy Blend	Fluid 4 B20 Oxidized Soy Blend	Fluid 5 Base Fuel	Fluid 6 B5 RME Blend	Fluid 7 B5 Soy Blend
NO674-70	64	59	59	55	50	60	59	60
NB104-75	65	62	59	64	58	60	60	63
KB162-80	75	59	68	70	72	69	71	68
VB153-75	68	63	63	64	63	65	64	64
V1164-75	76	73	72	71	72	74	73	72

APPENDIX 6: ELASTOMER DIMENSIONAL CHANGE RESULTS

Material	Dimensional Change (%)							
	Un-Aged	Fluid 1 B20 Soy Blend	Fluid 2 B20 RME Blend	Fluid 3 B5 Oxidized Soy Blend	Fluid 4 B20 Oxidized Soy Blend	Fluid 5 Base Fuel	Fluid 6 B5 RME Blend	Fluid 7 B5 Soy Blend
NO674-70	0.2	4.0	3.9	5.0	9.0	3.7	3.6	3.5
NB104-75	-0.3	5.1	6.1	6.6	9.9	4.1	4.4	4.7
KB162-80	-0.4	4.5	4.2	5.6	8.6	3.8	4.6	3.6
VB153-75	-0.3	0.5	0.7	0.9	1.2	0.6	0.7	0.5
V1164-75	-0.4	0.5	0.4	0.9	1.3	0.8	0.6	0.9

APPENDIX 7: ELASTOMER COMPRESSION SET RESULTS

Material	Compression Set (% change)							
	Un-Aged	Fluid 1 B20 Soy Blend	Fluid 2 B20 RME Blend	Fluid 3 B5 Oxidized Soy Blend	Fluid 4 B20 Oxidized Soy Blend	Fluid 5 Base Fuel	Fluid 6 B5 RME Blend	Fluid 7 B5 Soy Blend
NO674-70	8.7	14.3	15.2	2.6	16.0	10.2	12.1	19.7
NB104-75	8.5	-2.6	-1.9	-2.2	-9.3	32.4	3.0	-0.4
KB162-80	9.4	3.4	12.2	4.5	-3.1	3.4	5.2	-3.8
VB153-75	29.3	44.7	32.2	57.4	24.5	31.4	40.6	31.7
V1164-75	13.9	9.5	10.0	8.1	9.0	4.7	10.0	9.3

APPENDIX 8: ELASTOMER TENSILE PROPERTIES

Material	Tensile Properties							
	Un-Aged		Fluid 1 B20 Soy Blend		Fluid 2 B20 RME Blend		Fluid 3 B5 Oxidized Soy Blend	
	Tensile Strength (MPa)	Elongation at Break (%)	Tensile Strength (MPa)	Elongation at Break (%)	Tensile Strength (MPa)	Elongation at Break (%)	Tensile Strength (MPa)	Elongation at Break (%)
NO674-70	17.2	605	14.0	380	14.4	405	13.3	385
NB104-75	15.6	395	3.1	120	4.6	170	2.3	80
KB162-80	21.8	255	14.8	160	12.8	160	16.7	175
VB153-75	10.2	340	9.9	300	9.8	290	8.9	280
V1164-75	11.2	270	11.2	270	11.5	280	11.8	290

Material	Tensile Properties							
	Fluid 4 B20 Oxidized Soy Blend		Fluid 5 Base Fuel		Fluid 6 B5 RME Blend		Fluid 7 B5 Soy Blend	
	Tensile Strength (MPa)	Elongation at Break (%)	Tensile Strength (MPa)	Elongation at Break (%)	Tensile Strength (MPa)	Elongation at Break (%)	Tensile Strength (MPa)	Elongation at Break (%)
NO674-70	9.7	300	15.2	400	11.3	265	12.0	280
NB104-75	3.7	135	10.6	275	10.7	270	2.6	100
KB162-80	14.8	175	19.3	200	15.6	165	11.9	145
VB153-75	8.2	265	11.1	310	9.4	280	10.0	300
V1164-75	11.1	270	11.6	265	10.5	250	11.5	275

From: DiCicco, Dominic (D.M.)
Sent: Friday, March 26, 2010 3:25 PM
To: Agarwal, Apoorv (A.); Anderson, James (J.E.); Wallington, Tim (T.J.); Ruona, William (W.C.); Fulton, Brien (B.L.)
Subject: US Cetane - Slides
Attachments: Cetane number increase request rationale_23_feb_2010.pptx

If you liked that one...you might like this one on Cetane...

Alliance plans to work jointly with EMA to attempt to request an increase in Cetane, if that was done what would be the minimum cetane number that you would want to see in the future..please specify Cetane Number and Index.

Best Regards,
Dominic

From: Agarwal, Apoorv (A.)
Sent: Friday, March 26, 2010 3:20 PM
To: DiCicco, Dominic (D.M.); Anderson, James (J.E.); Wallington, Tim (T.J.); Ruona, William (W.C.)
Subject: RE: US Octane Modeling - Slides

This is good stuff.

From: DiCicco, Dominic (D.M.)
Sent: Friday, March 26, 2010 1:25 PM
To: Agarwal, Apoorv (A.); Anderson, James (J.E.); Wallington, Tim (T.J.); Ruona, William (W.C.)
Subject: FW: US Octane Modeling - Slides

All,

Just received, thought you might have some interest. Will discuss during the meeting starting in 5minutes...let me know if you have any specific questions; otherwise, I can provide update on our next call.

Dominic

From: Ellen Shapiro [mailto:ESHAPIRO@autoalliance.org]
Sent: Friday, March 26, 2010 1:20 PM
To: ENV F&L Alliance Fuels Team; Marie Valentine
Subject: FW: US Octane Modeling - Slides

Octane slides for the Fuels Team meeting in 10 minutes. One version is the new PowerPoint, the other is the old. This will be webcast.

Ellen

From: william.studzinski@gm.com [mailto:william.studzinski@gm.com]
Sent: Friday, March 26, 2010 1:05 PM
To: Ellen Shapiro
Cc: Coleman Jones
Subject: US Octane Modeling - Slides

Ellen,

Slides for today's Fuels Team Meeting.   Will there be a MS Live Meeting?

Bill
Fuels Group Ldr.
GM Powertrain
Ph: 248-255-7785

Diesel Fuel Cetane Number Increase proposal for the North American Market

GM Powertrain Advance Engineering

P. Di Martino

Paul Battiston, Manuel Gonzalez,

Ibrahim Haskara

February 22nd , 2010

Contents:

- Conclusions
- Impact on combustion of the Cetane number
- North America Emission targets summary
- Summary of HD engine emission assessment
- Summary of passenger car emission assessment
- Summary of 2004 CRC survey on cold startability in European Euro 3 vehicles

Conclusions

Following documents provide the details to justify below statements:

- Cetane Number in the range of 53 (EN590) is one enabler for Diesel Engines to meet SULEV and T2B2 emission regulations and the new EPA CO_2 requirements.
- Biggest advantages in HD and passenger cars:
  - HC reduction
  - Fuel Efficiency increase
  - Impact on NOx, Soot and CO can be Managed trough calibration
- Other advantages are:
  - Cold startabilty
  - Calibration improvements in partial load
  - Reduction of Compression ratio.
- Highly recommended to update 2004 CRC study utilizing HD & LD USA specific applications and perform emission performance assessment.

Impact of Cetane Number on combustion quality

- The cetane number (CN) is a measure of how readily a fuel ignites in in a compression-ignition engine.
- A fuel with high CN will provide shorter ignition delay (lead time between injection and initial combustion) leading to a higher quality of the combustion hence higher system efficiency. Higher combustion temperature require a dedicated NO_x reduction calibration
- A fuel with low CN has larger ignition delay that can lead to incomplete combustion and misfire events hence higher production of Hydrocarbon (HC), Carbon monoxide (CO) and particulates. Lower combustion temperatures can facilitate NO_x emission management

North America Next generation emission requirements

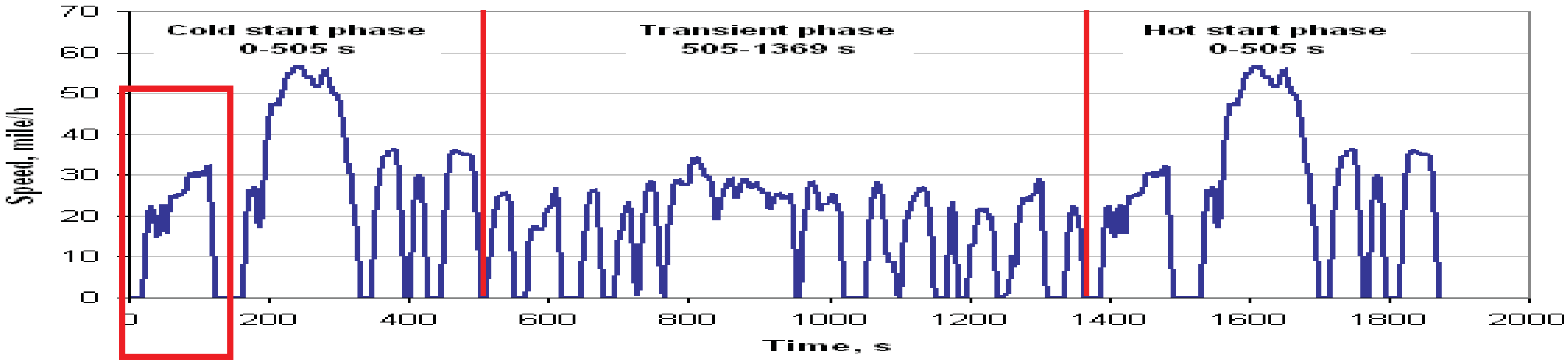
Table 1. LEVII criteria pollutant emission standards (PC/LDT1 and LDT2)

Vehicle emission category	Durability basis (miles)	NMOG (g/mi)	NO_x (g/mi)	CO (g/mi)	HCHO (g/mi)	PM (g/mi)
LEV	50,000	0.075	0.05	3.4	0.015	-
	120,000	0.090	0.07	4.2	0.018	0.01
ULEV	50,000	0.040	0.05	1.7	0.008	-
	120,000	0.055	0.07	2.1	0.011	0.01
SULEV	120,000	0.010	0.02	1.0	0.004	0.01
PZEV [a]	150,000	0.010	0.02	1.0	0.004	0.01

[a] *PZEV has same test emission levels as SULEV but also includes additional evaporative emissions control and a 150,000-mile warranty*

EPA standard: T2B8 corresponds to California LEV targets; T2B2 to SULEV.

- Total HC emission targets reduce 87% from LEV to SULEV requirements NOx 71%
- The cold start of the FTP cycle is the most critical part for HC generation



Properties of fuels assessed in Heavy Duty engine

Ultra Low Sulfur Diesel Fuel Specifications

	Cetane No. range	Aromatics, vol%	Density @ 15.6°C kg/m³	Distillation, °C					Viscosity @40°C cSt
				Initial Boiling Point	10% recovered	50% recovered	90% recovered	Final Boiling Point	
Low Cetane	39-41	18 min	830-865	171-204	204-238	243-282	293-332	321-366	2.0-3.2
Mid Cetane	44-46	27 max							
High Cetane	49-51	37 max							

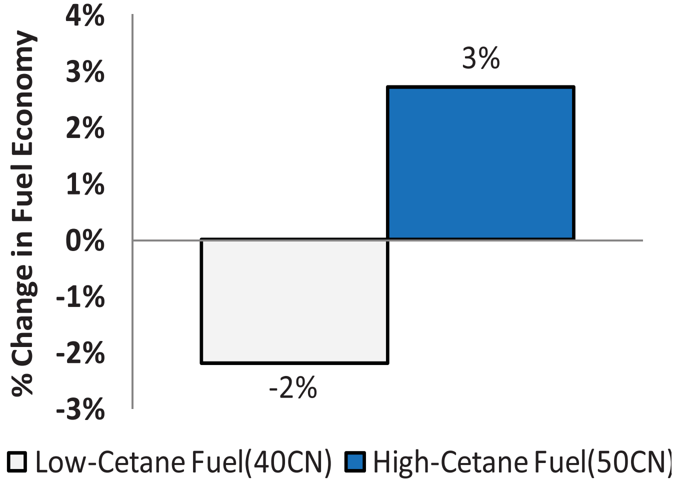
Tests performed without changing Engine calibration parameters

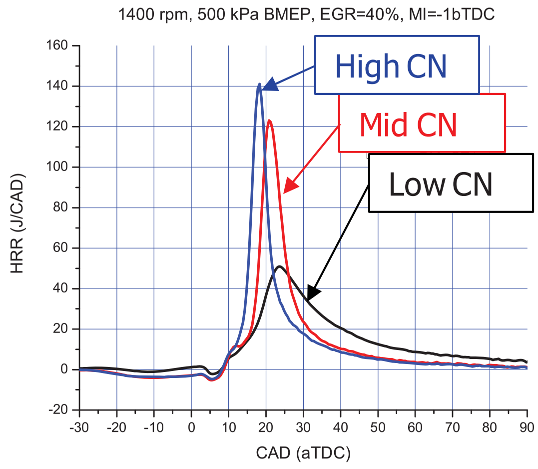
HD Engine: FTP72 Test Results for Varied Cetane Fuels

Test performed with same engine calibration, baseline CN 45

Impact on Fuel Economy

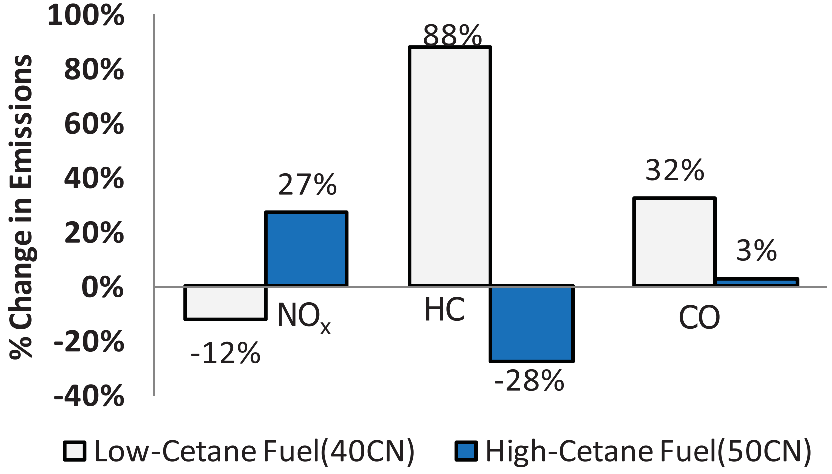
- **Increasing the CN allows 3% FE improvement potential**
- Increasing the CN has an impact on combustion delay that enables emission calibration improvements
- CN=40 deteriorates FE and engine overall performance





Impact on Emissions

- Emissions directly influenced by changes in combustion phasing from cetane variations
- Higher CN increases combustion temperatures and reduces mixing time
  - Lower HC & CO, higher NO_x *
  - Lower CN reduces combustion temperatures and increases mixing time
  - Higher HC and CO, lower NOx



*Calibaration optimization can neutralize NOx performance deterioration (see light duty example)

Properties of fuels assessed in passenger car engine

Property	**ASTM D975 - 09b Grade No. 2-D S15**	**Euro 4 Diesel Fuel with Maximum Sulfur**
Cetane number	45.5	51.0
H/C	1.7931	1.9108
Specific gravity	0.8471	0.8363
Viscosity cSt @ 40C	2.522	2.8
Sulphur content [ppm]	< 15	36
Net heating value [MJ/kg]	42.936	43.194

Tests performed adjusting the calibration to keep comparable NOx performance:

- Matching of fixed keypoint conditions (from baseline EU5 calibration)
  - Phasing main fuel injection calibration to match the crankangle for 50% mass of burned fuel (combustion phasing matching)
  - Setting EGR to achieve the NOx baseline engine-out targets (NOx emissions matching)

Brake Fuel Consumption Comparison:

Baseline 45.5 cetane number

Fix RPM/BMEP keypoints, Normal Mode of engine operation
Coolant @ 90C, EGR ON, Constant combustion phasing, Constant EU5 NOx target

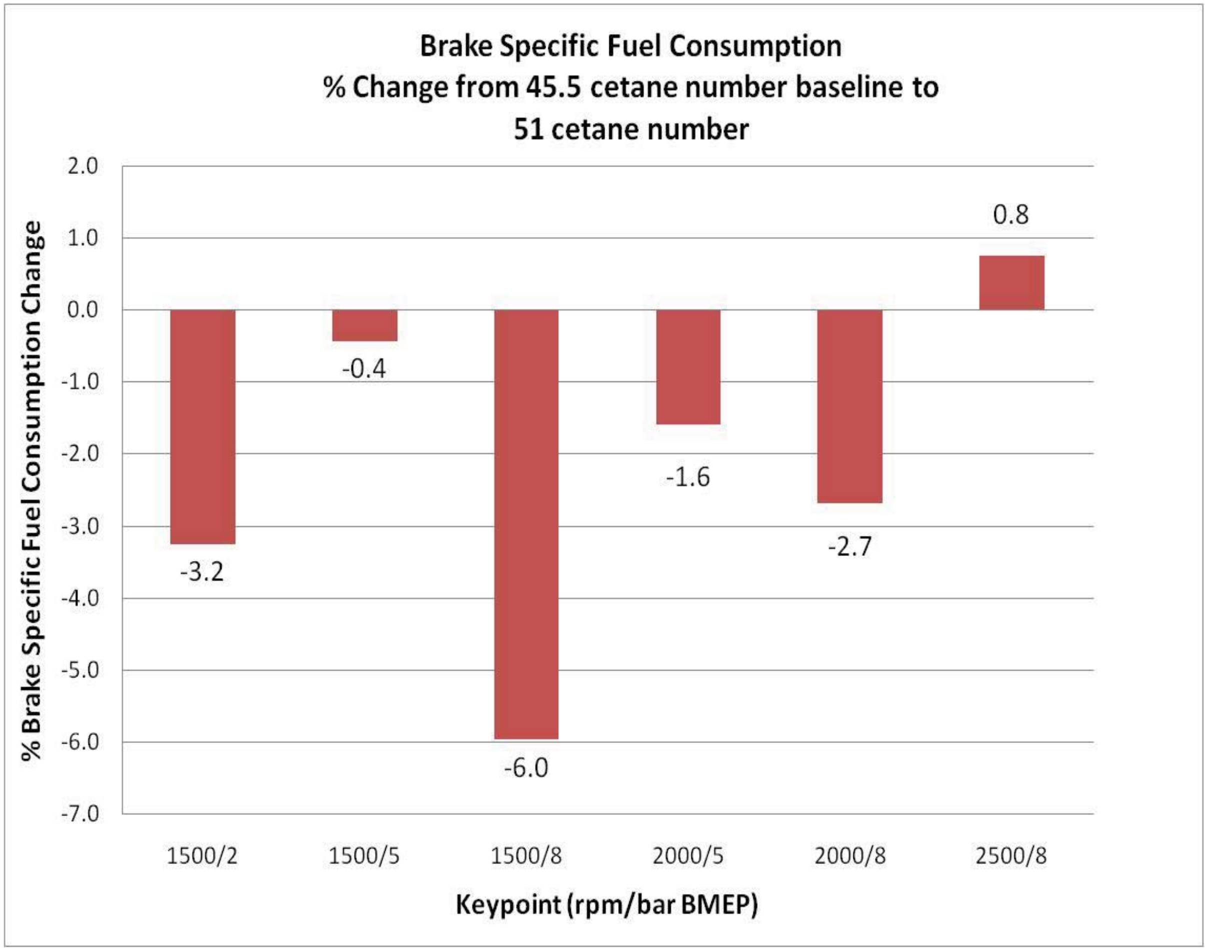
Impact on Fuel Economy*

- **Increasing the CN allows ~ 2.7% FE improvement potential (simulated FTP75 cycle based on key point measurements)**
- Increasing the CN has an impact on combustion delay that enables emission calibration improvements

Operating keypoints

RPM	BMEP (bar)	FTP Cycle Time based contribution (%)	FTP Cycle BSFC (%)
1500	2	65.9	2.2
1500	5	18.7	0.1
1500	8	4.1	0.3
2000	5	7.1	0.1
2000	8	2.3	0.1
2500	8	2.0	0.0

Overall FE improvement in the FTP cycle 2.7%



Brake Specific Fuel Consumption
% Change from 45.5 cetane number baseline to
51 cetane number

*** Net heating value of 45.5 cetane fuel is 0.6% lower per unit of mass, partially contributes to the overall BSFC difference**

Engine-out Hydrocarbons Emissions Comparison:

Baseline 45.5 cetane number

Fix RPM/BMEP keypoints, Normal Mode of engine operation
Coolant @ 90C, EGR ON, Constant combustion phasing, Constant EU5 NOx target

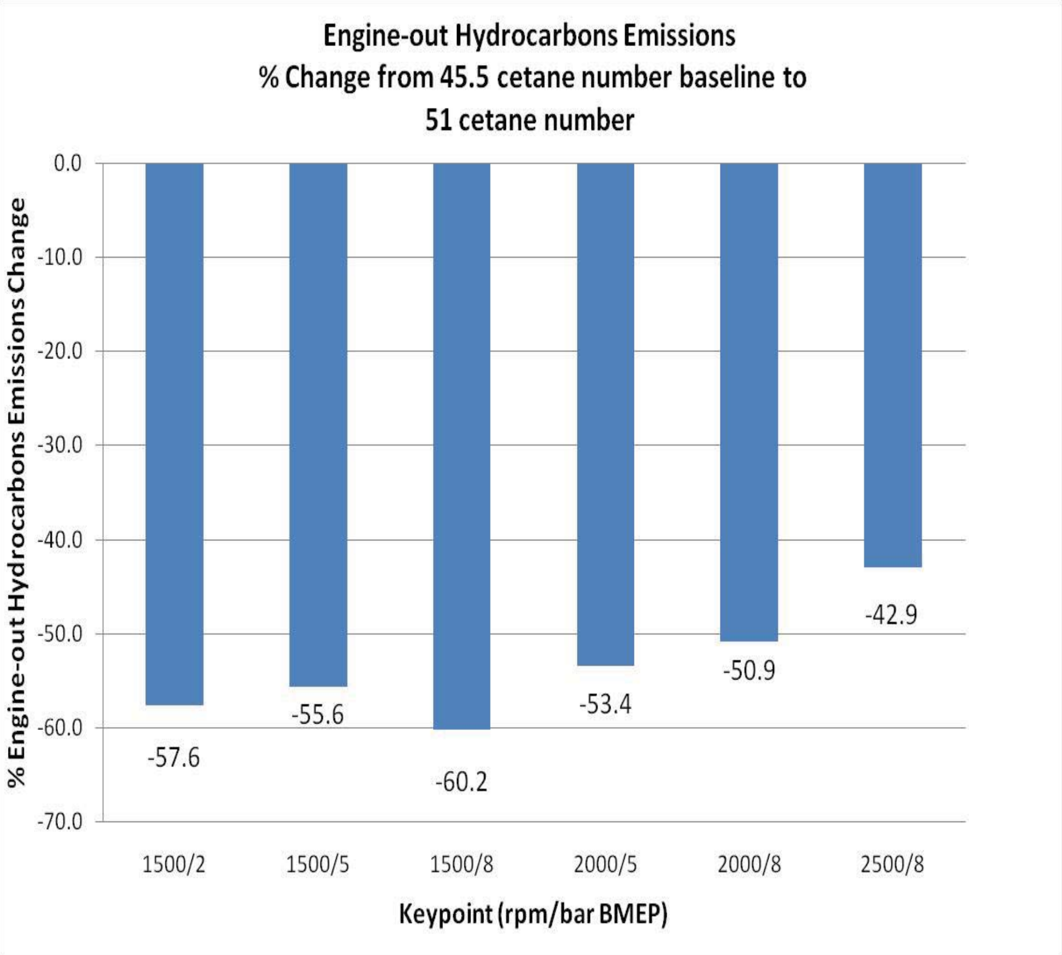
Impact on Emissions: HC

- **Higher CN enables**
  - **57% lower HC (simulated FTP75 cycle based on key point measurements)**
  - **NOx emission adjusted with "recalibration"**

Operating keypoints

RPM	BMEP (bar)	HC difference (%)	FTP Cycle Time based contribution (%)	FTP Cycle Time based contribution (%)
1500	2	57.6	65.9	37.96
1500	5	55.6	18.7	10.40
1500	8	60.2	4.1	2.47
2000	5	53.4	7.1	3.79
2000	8	50.9	2.3	1.17
2500	8	42.9	2	0.86

Overall HC reduction in the FTP cycle 56.64


Engine-out Hydrocarbons Emissions
% Change from 45.5 cetane number baseline to 51 cetane number

Engine-out NOx Emissions Comparison:

Baseline 45.5 cetane number

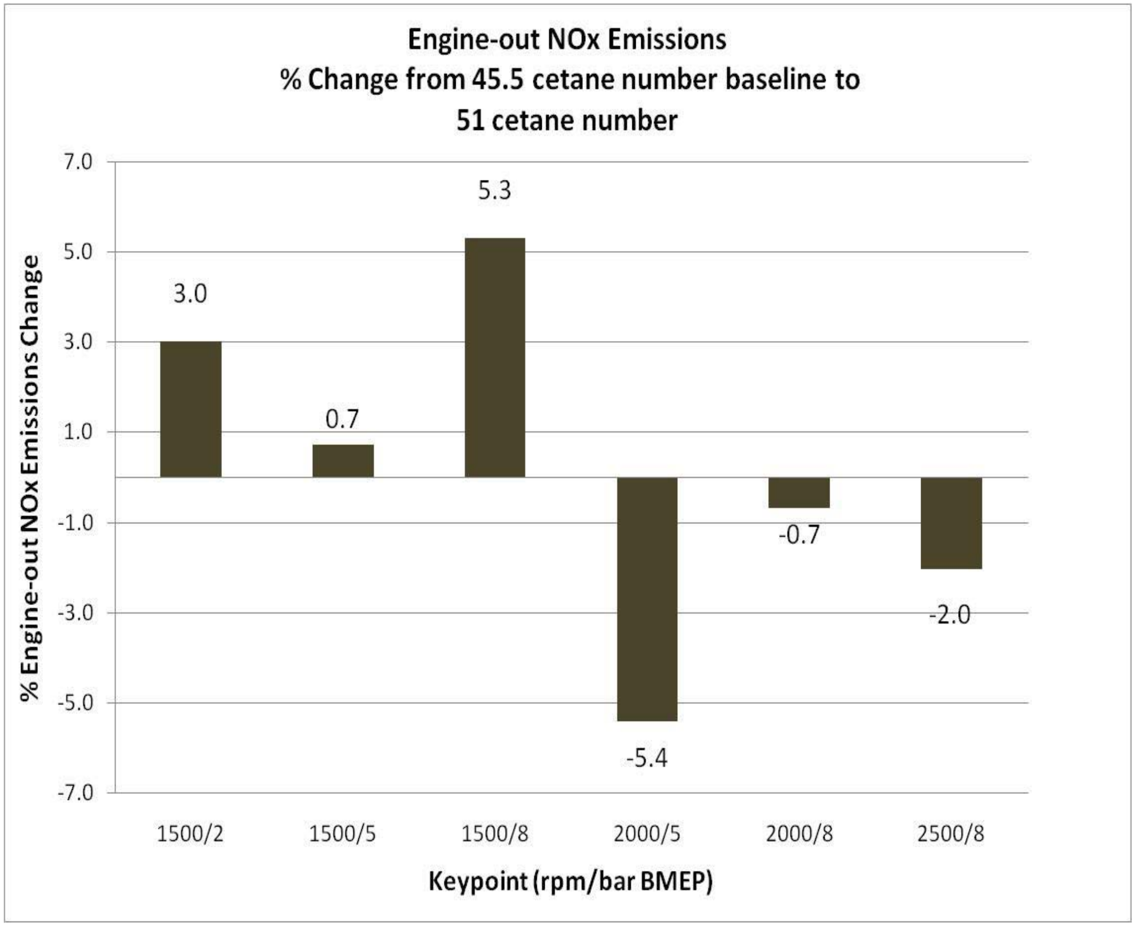
Fix RPM/BMEP keypoints, Normal Mode of engine operation
Coolant @ 90C, EGR ON, Constant combustion phasing, Constant EU5 NOx target

Impact on Emissions: NOx

~ 2 %

Estimated engine-out NOx emissions increase in the whole FTP Cycle with 51 cetane fuel

Matched engine calibration can potentially mitigate this difference for equal NOx emissions performance



Additional Benefits for higher CN in applications

- Cold-Start
  - Shorter crank-to-run time (less unburned fuel in the exhaust)
  - Lower HC, CO and smoke
  - Improve NVH
  - Allows for glow-plug strategy refinement
  - Lower compression ratio base engine designs (CR ~16:1 or lower)
    - Lowers blow-by, heat-transfer, lower-heat release rates.
    - Tends to improve the NOx/PM tradeoff.
    - Lowers peak cylinder pressures (to be balanced back by boost control) and allows for more charge dilution at part-load(lowers combustion temps)
    - Smoother operation – especially on 4 cylinders

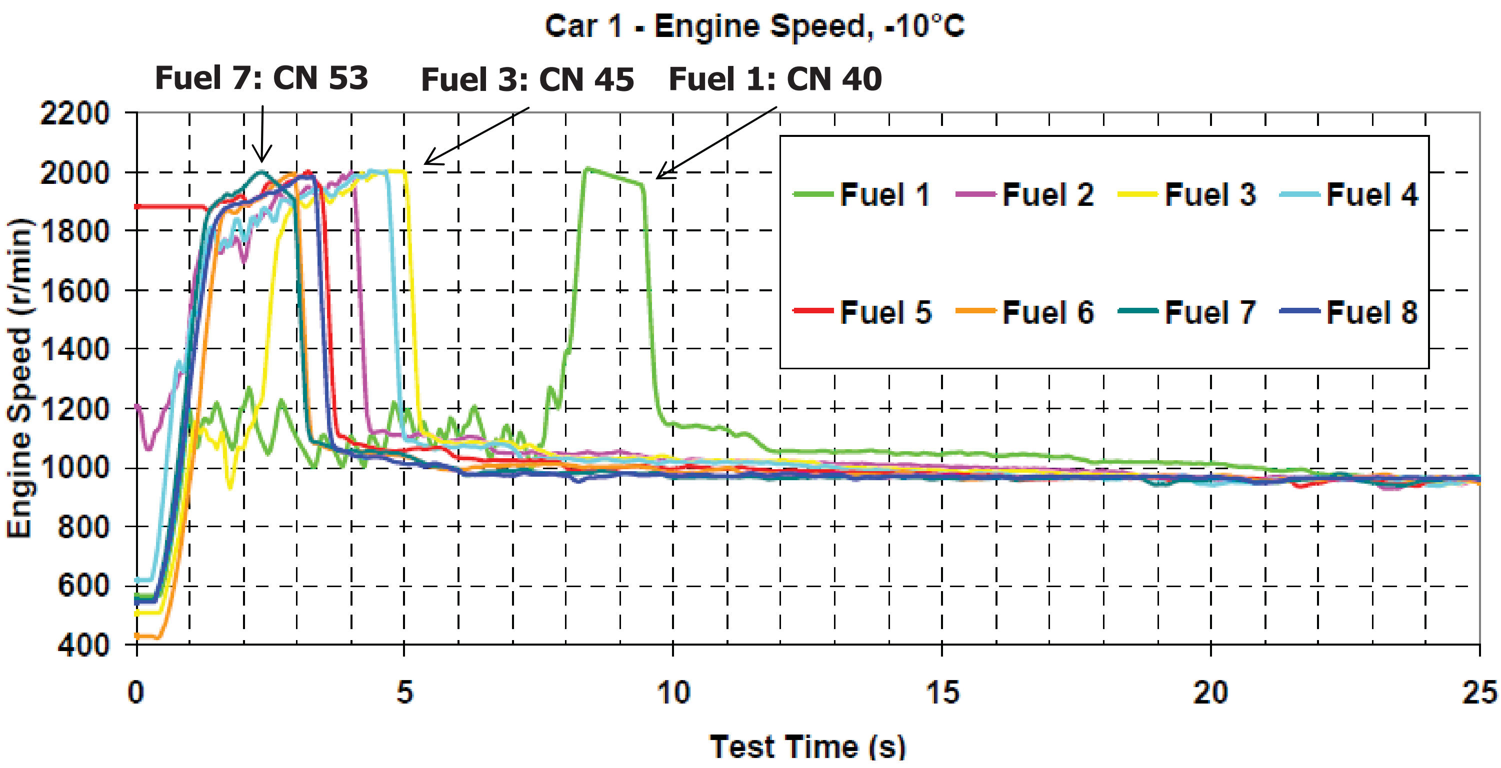
2004 CRC investigations:

- In 2004 The Coordinating Research Council (CNC) commissioned a Cetane Number (CN) assessment to understand its impact on European light duty diesel applications.
- Study focused on 8 fuels from CN 40 to 55 assessing cold start performance. (-10; 0; 10˚C equal to 14; 32; 50F).
- Vehicle assessed were 3 “Euro 3” and one “Euro 4”
- Compression ratio were higher than 17.5:1
- Simple EGR systems, and EGR rate were lower that 30% to meet European emission targets

Fuel Number	Cetane number Target (Measured, ASTM D613)	Natural or EHN	Fuel Identifier
1	40 (40.7)	Natural	DBR 0216 Low CN (4c)
2	44 (43.2)	EHN	DBR 0219 Boosted 45 CN
3	45 (44.7)	Natural	DBR 0222 45 CN Base
4	48 (46.8)	EHN	DBR 0220 Boosted 48 CN
5	49 (48.9)	EHN	DBR 0223 Boosted 50 CN
6	50 (52.3)	Natural	DBR 0221 50 CN Base
7	53 (53.2)	EHN	DBR 0224 Boosted 54 CN
8	55 (57.7)	Natural	DBR 0218 High CN (4c)

Type	Cylinders / displacement (l)	Max. Power (kW)	Fuel Injection System	Emissions Specification	Model Year	Odometer reading at start of test (miles)
Toyota Avensis D-4D	4/2.0	85	Common Rail	Euro IV	2003	5580
Mazda 6 TS	4/2.0	100	Common rail	Euro III/D4	2003	13934
VW Lupo TDi PD	3/1.2	45	Unit Injector	Euro III/D4	2003	8330
VW Golf TDI PD	4/1.9	74	Unit injector	Euro III/D4	2003	9345

Main results from the 2004 CRC investigations (1/2):

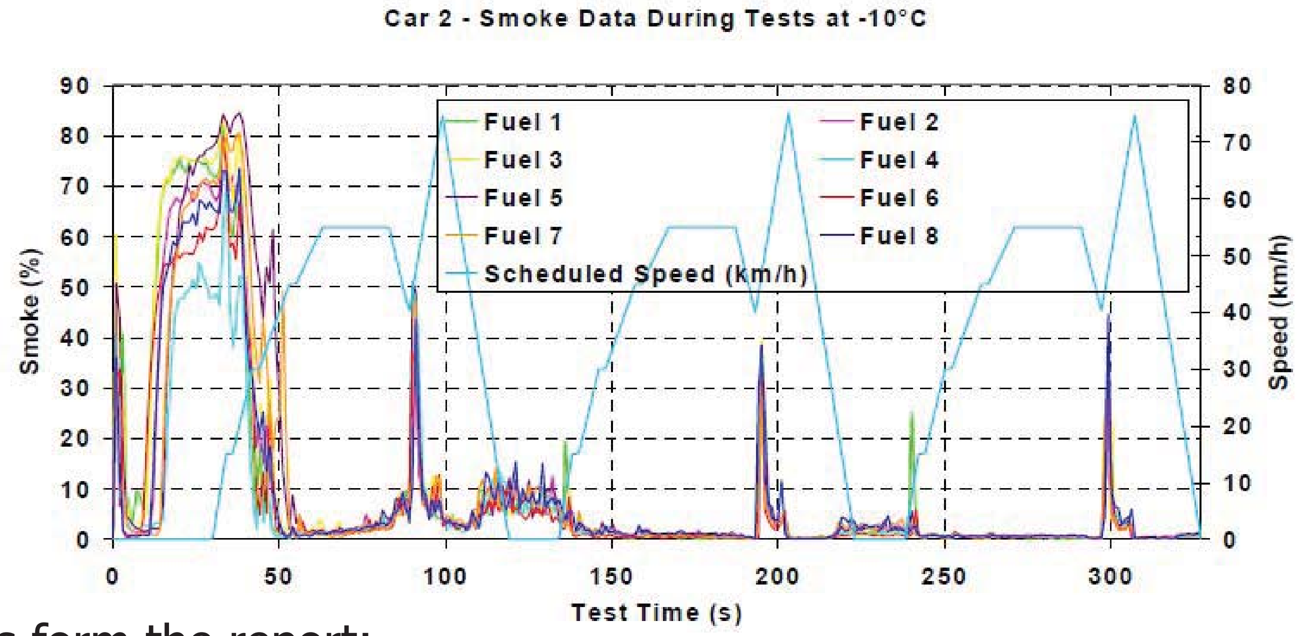


- Cold start at -10˚C (14F): the CN number 53 shows a very good acceleration to 2000 rpm in cold start. This is important to support the initial stage of the FTP cycle minimizing the generation HC during warm up.
- CRC Report highlights that high CN positive effects increase at lower temperatures,
- NO emission performance measured

Source: CRC project # AVFL-11

Main results from the 2004 CRC investigations (2/2):

- Smoke & CN correlation was measured in the NEUDC cycle.
  - CN number has a big impact in the very first portion of the test cycle increasingly at lower temperatures.



- Other results form the report:
  - Idle stability not tangibly dependent to CN of fuels
  - Noise and vibration performance varies with temperature and the Engine architecture.

    No tangible correlation between noise or vibration and CN has been reported

Source: CRC project # AVFL-11

BACK UP

North America Next generation emission requirements

Table 2

Tier 2 Emission Standards, FTP 75, g/mi

Bin#	Intermediate life (5 years / 50,000 mi)					Full useful life				
	NMOG*	CO	NOx	PM	HCHO	NMOG*	CO	NOx†	PM	HCHO
Temporary Bins										
11 MDPV[c]						0.280	7.3	0.9	0.12	0.032
10[a,b,d,f]	0.125 (0.160)	3.4 (4.4)	0.4	-	0.015 (0.018)	0.156 (0.230)	4.2 (6.4)	0.6	0.08	0.018 (0.027)
9[a,b,e,f]	0.075 (0.140)	3.4	0.2	-	0.015	0.090 (0.180)	4.2	0.3	0.06	0.018
Permanent Bins										
8[b]	0.100 (0.125)	3.4	0.14	-	0.015	0.125 (0.156)	4.2	0.20	0.02	0.018
7	0.075	3.4	0.11	-	0.015	0.090	4.2	0.15	0.02	0.018
6	0.075	3.4	0.08	-	0.015	0.090	4.2	0.10	0.01	0.018
5	0.075	3.4	0.05	-	0.015	0.090	4.2	0.07	0.01	0.018
4	-	-	-	-	-	0.070	2.1	0.04	0.01	0.011
3	-	-	-	-	-	0.055	2.1	0.03	0.01	0.011
2	-	-	-	-	-	0.010	2.1	0.02	0.01	0.004
1	-	-	-	-	-	0.000	0.0	0.00	0.00	0.000

* for diesel fueled vehicle, NMOG (non-methane organic gases) means NMHC (non-methane hydrocarbons)
† average manufacturer fleet NOx standard is 0.07 g/mi for Tier 2 vehicles

a - Bin deleted at end of 2006 model year (2008 for HLDTs)
b - The higher temporary NMOG, CO and HCHO values apply only to HLDTs and MDPVs and expire after 2008
c - An additional temporary bin restricted to MDPVs, expires after model year 2008
d - Optional temporary NMOG standard of 0.195 g/mi (50,000) and 0.280 g/mi (full useful life) applies for qualifying LDT4s and MDPVs only
e - Optional temporary NMOG standard of 0.100 g/mi (50,000) and 0.130 g/mi (full useful life) applies for qualifying LDT2s only
f - 50,000 mile standard optional for diesels certified to bins 9 or 10