Subcontractor Report

Biodiesel Analytical Methods

August 2002–January 2004

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1. Introduction to Biodiesel

Biodiesel is an alternative fuel for diesel engines that is receiving great attention world wide. Although it attracts the most attention because it is renewable, it can be used either pure or in blends with diesel fuel in unmodified diesel engines, and it reduces some exhaust pollutants. It is also attractive because it can be produced easily from common feedstocks. However, the relative simplicity of biodiesel production can disguise the importance of maintaining high quality standards for any fuel supplied to a modern diesel engine. It is essential to the growth of the biodiesel industry that all fuel produced and sold meet these quality standards.

The material contained in this book is intended to provide the reader with information about biodiesel in three basic areas:
1. Background about diesel engines and fuels to explain what engines need and what properties are used to characterize fuel quality.
2. The Analytical Methods used to measure fuel properties.
3. Specifications for biodiesel quality control and methods to monitor and maintain quality in the chemical plant.

What is biodiesel?

Biodiesel is defined as the mono-alkyl esters of fatty acids derived from vegetable oils or animal fats. In simple terms, biodiesel is the product obtained when a vegetable oil or animal fat is chemically reacted with an alcohol to produce fatty acid alkyl esters. A catalyst such as sodium or potassium hydroxide is required. Glycerol is produced as a co-product. The approximate proportions of the reaction are:

100 lbs of oil + 10 lbs of methanol $\rightarrow$ 100 lbs of biodiesel + 10 lbs of glycerol

Soybean oil is the most popular feedstock in the U.S.. Soybeans are a major U.S. crop and government subsidies are available that make the fuel economically attractive to consumers who need or want to use a nonpetroleum-based fuel. Biodiesel from soybeans is sometimes called soydiesel, methyl soyate, or soy methyl esters (SME). In Europe, most biodiesel is made from rapeseed oil and it is known as rapeseed methyl esters (RME). The University of Idaho has done considerable work with rapeseed to produce rapeseed ethyl esters (REE). Website: http://www.uidaho.edu/bae/biodiesel

Biodiesel can also be made from other feedstocks:
- Other vegetable oils such as corn oil, canola (an edible variety of rapeseed) oil, cottonseed oil, mustard oil, palm oil, etc.
- Restaurant waste oils such as frying oils
- Animal fats such as beef tallow or lard
- Trap grease (from restaurant grease traps), float grease (from waste water treatment plants), etc.

All vegetable oils and animal fats consist primarily of *triglyceride* molecules such as that shown schematically below.

$$
\begin{array}{l}
\quad\quad\quad\;\; O \\
\quad\quad\quad\;\; \| \\
CH_2 - O - C - R_1 \\
| \\
| \quad\quad\quad\; O \\
| \quad\quad\quad\; \| \\
CH\; - O - C - R_2 \quad\quad\quad\quad \text{Triglyceride} \\
| \\
| \quad\quad\quad\; O \\
| \quad\quad\quad\; \| \\
CH_2 - O - C - R_3
\end{array}
$$
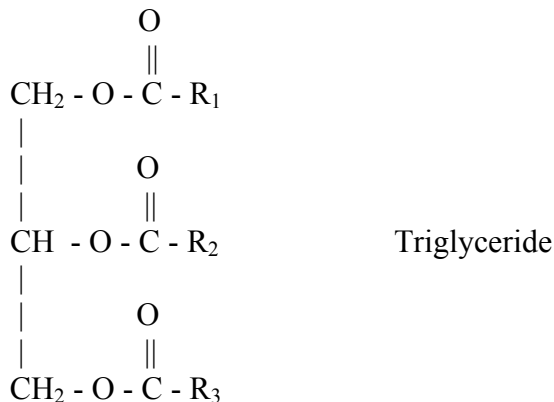
Figure 1.

R_1, R_2, and R_3 represent the hydrocarbon chains of the fatty acyl groups of the triglyceride. In their free form, fatty acids have the configuration shown below where R is a hydrocarbon chain $\geq$ 10 carbon atoms.

$$
\begin{array}{l}
\quad\;\; O \\
\quad\;\; \| \\
R - C - OH
\end{array}
$$
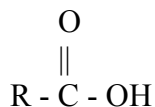
Figure 2.

Transesterification is the process of reacting a triglyceride molecule with an excess of alcohol in the presence of a catalyst (KOH, NaOH, $NaOCH_3$, etc.) to produce glycerol and fatty esters. The chemical reaction with methanol is shown schematically below.

$$
\begin{array}{lll}
\quad\quad\;\; O & & \quad\quad\;\; O \\
\quad\quad\;\; \| & & \quad\quad\;\; \| \\
CH_2 - O - C - R_1 & & CH_3 - O - C - R_1 \\
| & & \\
| \quad\quad\; O & & \quad\; O \quad\quad\quad CH_2 - OH \\
| \quad\quad\; \| & & \quad\; \| \quad\quad\quad\quad\; | \\
CH\; - O - C - R_2 \;+\; 3\,CH_3OH & \rightarrow & CH_3 - O - C - R_2 \;+\; CH - OH \\
| & \text{(catalyst)} & \\
| \quad\quad\; O & & \quad\; O \quad\quad\quad CH_2 - OH \\
| \quad\quad\; \| & & \quad\; \| \\
CH_2 - O - C - R_3 & & CH_3 - O - C - R_3
\end{array}
$$

Triglyceride   methanol   mixture of fatty esters   glycerol

Figure 3.

2

The mixture of fatty esters produced by this reaction is referred to as *biodiesel*. Other terms commonly associated with biodiesel are "soydiesel", which is biodiesel produced from soybean oil and "methyl soyate" which designates the esters produced from soybean oil and methanol. At the present time, a large portion of the biodiesel sold in the U.S. is produced from the methyl esters of soybean oil, so biodiesel, soydiesel and methyl soyate are often used interchangeably. In general, biodiesel may also include fatty esters derived from other vegetable or animal sources. Other alcohols besides methanol may be used so it will be necessary to distinguish between the three terms.

The fuel properties of biodiesel are determined by the amounts of each fatty acid in the feedstock used to produce the esters. Fatty acids are designated by two numbers: the first number denotes the total number of carbon atoms in the fatty acid chain and the second is the number of double bonds present in the chain. For example, 18:1 designates oleic acid, which has 18 carbon atoms and one double bond. Table 1 lists the fatty acid profiles of a number of common vegetable oils and animal fats.

Table 1. Composition of Various Oils and Fats.

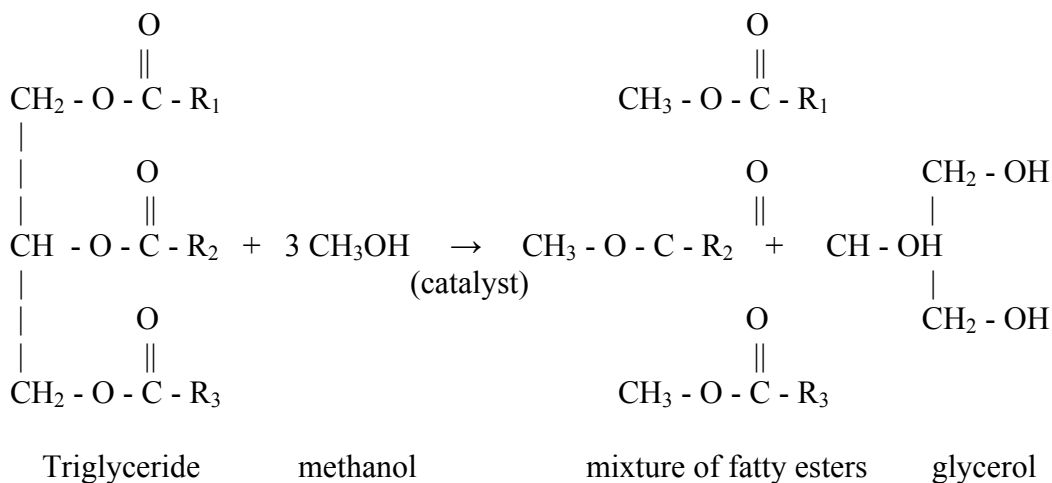| Oil or fat	14:0	16:0	18:0	18:1	18:2	18:3	20:0	22:1
Soybean		6-10	2-5	20-30	50-60	5-11		
Corn	1-2	8-12	2-5	19-49	34-62	trace		
Peanut		8-9	2-3	50-65	20-30			
Olive		9-10	2-3	73-84	10-12	trace		
Cottonseed	0-2	20-25	1-2	23-35	40-50	trace		
Hi linoleic Safflower		5.9	1.5	8.8	83.8			
Hi Oleic Safflower		4.8	1.4	74.1	19.7			
Hi Oleic Rapeseed		4.3	1.3	59.9	21.1	13.2		
Hi Erucic Rapeseed		3.0	0.8	13.1	14.1	9.7	7.4	50.7
Butter	7-10	24-26	10-13	28-31	1-2.5	.2-.5		
Lard	1-2	28-30	12-18	40-50	7-13	0-1		
Tallow	3-6	24-32	20-25	37-43	2-3			
Linseed Oil		4-7	2-4	25-40	35-40	25-60		
Tung Oil		3-4	0-1	4-15		75-90[**]		
Yellow Grease*	1.3	17.4	12.4	54.7	8.0	0.7	0.3	0.5

Peterson, C.L., "Vegetable Oil as a Diesel Fuel: Status and Research Priorities," ASAE Transactions, V. 29, No. 5, Sep.-Oct. 1986, pp. 1413-1422.

Linstromberg, W.W., Organic Chemistry, Second Edition, D.C. Heath and Company, Lexington, Mass., 1970.

* Typical analysis: listed in Tat, M.E. and J.H. Van Gerpen, "Fuel Property Effects on Biodiesel," ASAE Paper 036034, American Society of Agricultural Engineering Annual Meeting, Las Vegas, NV, July 27-30, 2003.

[**] The dominant fatty acid in tung oil is a conjugated isomer of linolenic acid called eleostearic acid. The three double bonds in eleostearic acid are located at 9:10, 11:12, and 13:14 instead of at 9:10, 12:13 and 15:16 as in linolenic acid.

The common names of the fatty acids given in Table 1 are as follows:
14:0   Myristic Acid (tetradecanoic acid)
16:0   Palmitic Acid (hexadecanoic acid)

18:0	Stearic Acid	(octadecanoic acid)
18:1	Oleic Acid	
18:2	Linoleic Acid	
18:3	Linolenic Acid	
20:0	Arachidic Acid	(eicosanoic acid)
22:1	Erucic Acid	

How much biodiesel can be made?

It is sometimes claimed that biodiesel could be the answer to the world's dependence on fossil fuels. It is enlightening to look at the potential impact of biodiesel on diesel fuel consumption.

Using the rough guideline that a pound of oil or fat will give a pound of biodiesel, we can use the total production of fats and oils in the U.S. to estimate the impact of biodiesel on total diesel consumption. Table 2 lists the annual U.S. production figures for vegetable oils and animal fats.

Table 2. Total Annual Production of US Fats and Oils.
[from Pearl, G.G., "Animal Fat Potential for Bioenergy Use," Bioenergy 2002, The Tenth Biennial Bioenergy Conference, Boise, ID, Sept. 22-26, 2002.]

Vegetable Oil Production (Billion pounds/yr)		Animal Fats (Billion pounds/yr)	
Soybean	18.340	Edible Tallow	1.625
Peanuts	0.220	Inedible tallow	3.859
Sunflower	1.000	Lard & Grease	1.306
Cottonseed	1.010	Yellow Grease	2.633
Corn	2.420	Poultry Fat	2.215
Others	0.669	Total Animal Fat	11.638
Total Veg. Oil	23.659		

The combined vegetable oil and animal fat production is 35.3 billion pounds per year in the U.S. Soybean oil dominates the vegetable oil market comprising over 75% of the total vegetable oil volume. Animal fats total almost 50% of the vegetable oil market. At about 7.6 pounds per gallon of oil, total fat and oil production would equal 4.64 billion gallons of biodiesel. Table 3 lists the total on-highway consumption of diesel fuel from 1996 to 2000.

Table 3. Sales of On-highway Diesel Fuel
[data from Energy Information Administration, www.eia.doe.gov]

	On-highway Diesel	
	(billion gallons/yr)	(billion pounds/yr)
1996	26.96	191.1
1997	28.61	202.9
1998	30.15	213.8

1999	32.06	227.3
2000	33.13	234.9

It is obvious that biodiesel is not going to completely replace petroleum-based diesel fuel in the near future. If all of the vegetable oil and animal fat were used to produce biodiesel, we could only replace about 15% of the current demand for on-highway diesel fuel. So, why bother with biodiesel?

There are five primary reasons for encouraging the development of biodiesel in the U.S.

1. It provides a market for excess production of vegetable oils and animal fats. There is increasing demand around the world for soybean meal to provide protein for human and animal consumption. If new markets are not found for the soybean oil, then the price of soy beans will be low and farmers will have even more difficulty producing a profit. The animal by-products industry also has a problem with more supply than the current market demands. This is compounded by the potential for even greater restrictions on the use of animal fats in animal feeds because of concerns about the spread of BSE (Bovine Spongiform Encephalopathy - Mad Cow Disease).

2. It decreases the country's dependence on imported petroleum. Obviously, this reason should not be overemphasized since the percentage of the country's fuel supply that can be replaced with biodiesel will be small. However, petroleum markets tend to be sensitive to small fluctuations in supply so an additional source of fuel can have a surprising impact on stabilizing fuel prices.

3. Biodiesel is renewable and does not contribute to global warming due to its closed carbon cycle. Because the primary feedstock for biodiesel is a biologically-based oil or fat that can be grown season after season, biodiesel is renewable. And, since the carbon in the fuel was originally removed from the air by plants, there is no net increase in carbon dioxide levels. Again, this reason should not be overemphasized because biodiesel does not have the potential to make a major impact on total carbon dioxide production. It should also be noted that the primary alcohol used to produce biodiesel is methanol. Methanol makes up about 10% of the feed stock input and since most methanol is currently produced from natural gas, biodiesel is not completely renewable.

4. The exhaust emissions from biodiesel are lower than with regular diesel fuel. Biodiesel provides substantial reductions in carbon monoxide, unburned hydrocarbons, and particulate emissions from diesel engines. While the carbon monoxide and unburned hydrocarbons from diesels are already low compared with gasoline engines, biodiesel reduces them further. Particulate emissions, especially the black soot portion, are greatly reduced with biodiesel. Unfortunately, most emissions tests have shown a slight oxides of nitrogen (NOx) increase with biodiesel. This increase in NOx can be eliminated with a small adjustment to the engine's injection timing while still retaining a particulate reduction.

5. Biodiesel has excellent lubricating properties. Even when added to regular diesel fuel in an amount equal to 1-2% (volume %), it can convert fuel with poor lubricating properties, such as ultra-low-sulfur diesel fuel, into an acceptable fuel.

2. Diesel Engine Fuel Requirements

Background on Diesel Combustion

Diesel combustion is the process that occurs when a hydrocarbon fuel, chosen for its ability to auto-ignite, is injected into a volume of air that has been compressed to a high temperature and pressure. When fuel is injected into the turbulent compressed air inside the engine cylinder, it does not ignite immediately. There is a time period called the *ignition delay*, during which the fuel heats up, vaporizes, mixes with air, and undergoes chemical precombustion reactions that produce the radicals necessary for spontaneous ignition or *autoignition*. The classical notion of ignition delay calls the heating, vaporization and mixing processes the "physical delay" and the pre-reactions the "chemical delay". This can be deceptive in that both processes can be, and probably are, occurring simultaneously.

After sufficient time has elapsed, ignition will occur spontaneously at multiple locations. Ignition occurs in regions of fuel-air mixture that have fuel-air ratios close to the chemically correct ratio or the *stoichiometric* ratio. Combustion proceeds very rapidly due to the backlog of prepared or nearly prepared fuel-air mixtures formed during the ignition delay period. The rapidly rising temperatures and pressure in the cylinder accelerate the combustion in an uncontrolled manner until the backlog is depleted. This portion of the combustion process is usually called *premixed combustion*. The remainder of the fuel in the spray core is still too rich to burn, so combustion slows down and is controlled by the rate at which the air is entrained and a combustible mixture formed. This portion of the combustion process is called *mixing controlled* or *diffusion* burning. Thus, while chemical kinetics dominates the ignition delay, the high temperatures and pressures of the post-ignition gases promote very fast reaction rates that make fuel-air mixing the rate determining process.

The Fuel Must Ignite in the Engine

One of the most important properties of a diesel fuel is its readiness to autoignite at the temperatures and pressures present in the cylinder when the fuel is injected. The laboratory test that is used to measure this tendency is the Cetane Number Test (ASTM D 613). Fuels with a high *cetane number* will have short ignition delays and a small amount of premixed combustion since little time is available to prepare the fuel for combustion. The cetane number has been criticized in recent years for not accurately reflecting the autoignition conditions in modern turbocharged engines, particularly with alternative fuels.

The Fuel Must Release Energy When It Burns

The energy content of a fuel is characterized by the amount of heat released when the fuel, starting at ambient conditions, is burned and the products are cooled to ambient conditions. This is defined as the enthalpy of combustion (or the heat of combustion) since the combustion process produces water and energy will be different depending on

whether the water is liquid or vapor. Two separate cases are considered. First, if all of the water in the exhaust products is assumed to be liquid, the heat extracted will be the *higher heating value* or *the gross heating value.* If all of the water is considered to be vapor, then the heat extracted is the lower heating value or the net heating value. Since engines do not have the ability to condense water in the exhaust, the lower heating value is the most commonly used measure of fuel energy content.

The energy content of the fuel is not controlled during manufacturing. The actual heating value for diesel fuel will vary depending on the refinery in which it was produced, the time of year, and the source of the petroleum feedstock. Beyond these differences, the heating value will depend on the composition of the fuel. Diesel fuels with high percentages of aromatics tend to have high energy contents per gallon even though the aromatics tend to have low heating values per pound. Their higher density more than compensates for their lower energy content on a weight basis. This is of special importance for diesel engines because fuel is metered to the engine volumetrically. A fuel with lower energy content per gallon will cause the engine to produce less power.

Biodiesel fuels do not contain aromatics but they contain fatty acids with different levels of unsaturation. Fuels with more unsaturation tend to have slightly lower energy contents (on a weight basis) while those with greater saturation tend to have higher energy content.

As can be seen in the table below, biodiesel has a lower energy content (lower heating value) than No. 2 diesel fuel. On a weight basis, the energy level is 12.5% less. Since biodiesel is more dense than the diesel fuel, the energy content is only 8% less on a per gallon basis.

Table 4. Lower Energy Content

	Btu/lb	Btu/gal
No. 2 Diesel	18,300	129,050
Biodiesel (soybean)	16,000	118,170
	(12.5% less)	(8% less)

Since diesel engines will inject equal volumes of fuel, most diesel engine operators see a power loss of about 8%. In some cases, the power loss may be even less than this since biodiesel's higher viscosity can decrease the amount of fuel that leaks past the plungers in the diesel fuel injection pump.

Tests have shown that the actual efficiency at which the energy in the fuel is converted to power is the same for biodiesel and petroleum-based diesel fuel reference. Therefore, the brake specific fuel consumption (BSFC), the parameter most often used by engine manufacturers to characterize fuel economy will be at least 12.5% higher for biodiesel.

$$BSFC = \frac{\dot{m}_{fuel}}{P_b}$$

The BSFC is similar to efficiency in that it measures how much fuel may be required to do a certain quantity of work. The smaller the BSFC, the more efficient the engine. However, it does not contain information about the amount of energy that may be available from the fuel, so it cannot be used to make comparisons between engines burning different fuels. The prefix "brake" designates that the power is measured directly at the engine's output shaft.

The thermal efficiency of a fuel is usually defined as the ratio of the power produced by the engine to the energy in the fuel consumed, as indicated by the lower heating value (LHV) of the fuel. When the brake power is used, the thermal efficiency can be defined as:

$$Brake\,Thermal\,Efficiency = \eta_{bt} = \frac{P_b}{\dot{m}_{fuel}(LHV)}$$

The lower heating value (LHV) can be measured by calorimetry or it can be estimated from equations based on the fuel composition.

There is some ambiguity in the definition of the thermal efficiency based on whether the higher or lower heating value should be used. Furnace efficiencies tend to be based on the higher heating value. Natural gas is sold on the basis of higher heating value. However, for engines, the normal procedure is to use the lower heating value since the engine does not condense the water vapor in the exhaust gases.

Example: An engine produces 230.4 kW of brake power while burning 50 kg/hr of fuel. The lower heating value of the fuel is 42,567 kJ/kg. What are the BSFC and brake thermal efficiency?

$$BSFC = \frac{\dot{m}_{fuel}}{P_b} = \frac{50\,^{kg}/_{hr}}{230.4\,kW} \times \frac{1000\,g}{kg} = 217.0\,^{g}/_{kW-hr}$$

$$\eta_{bt} = \frac{P_b}{\dot{m}_{fuel}(LHV)} = \frac{230.4\,kW}{50\,^{kg}/_{hr} \times 42,567\,^{kJ}/_{kg}} \times \frac{1\,kJ}{1\,kW-s} \times \frac{3600\,s}{hr} = 0.390\ (39.0\%)$$

The Fuel Must Provide A Large Amount of Energy Per Gallon

The density of the fuel is not itself an important parameter for the diesel engine but it is generally related to the fuel's energy content. As a first approximation, hydrocarbon diesel fuels all have about the same energy content per pound. The differences between fuels relate mostly to the density. More dense fuels provide greater energy per gallon and since fuel is sold volumetrically, the higher the density, the greater the potential energy. As mentioned earlier, since biodiesel has a higher density than diesel fuel (0.87-0.88 g/cc compared with 0.84-0.85 g/cc for No. 2 diesel fuel and 0.81 – 0.815 g/cc for No. 1 diesel

fuel), biodiesel's 12% lower energy content per pound becomes only 8% less on a gallon basis.

The Fuel Must Not Limit The Operability of the Engine at Low Temperatures

Diesel fuel contains small amounts of long chain hydrocarbons, called waxes, that crystallize at temperatures within the normal diesel engine operating range. If temperatures are low enough, these wax crystals will agglomerate and plug fuel filters and prevent engine operation. At a low enough temperature, the fuel will actually solidify.

Additives, known as pour point depressants, are used to inhibit the agglomeration of the wax crystals, which then lowers the point at which fuel filter plugging occurs. It is also common to add No. 1 diesel fuel to No. 2 diesel fuel to lower its pour point. No. 1 diesel fuel has a very low level of waxes and dilutes the waxes in No. 2 diesel fuel and thereby lowers the pour point.

ASTM D 2500 and D 97 are used to determine the Cloud Point and Pour Points of the fuels, respectively. Other tests are used to measure the tendency of the fuel to plug fuel filters.

The Fuel Must Not Contribute to Corrosion

Many of the parts in the diesel fuel injection system are made of high-carbon steels and thus are prone to corrosion when in contact with water. Water damage is the leading cause of premature failure of fuel injection systems. Many diesel engines are equipped with water separators that cause small water droplets to coalesce until they are large enough to drop out of the fuel flow where they can be removed. Diesel fuel containing excessive water that enters the injection system can cause irreversible damage in a very short time.

ASTM D 2709 is used to measure the total amount of water and sediment in a diesel fuel sample. The method uses a centrifuge to collect the water and limits the amount of water and sediment to 0.05%.

Some compounds in diesel fuel, especially sulfur compounds, can be corrosive. Since copper compounds are particularly susceptible to this type of corrosion, copper is used as an indicator of the tendency of the fuel to cause corrosion. ASTM D 130 uses polished copper strips soaked in the fuel to characterize the tendency to corrode metals. Some tarnish is typically allowed, but corrosion causes the fuel to fail the test.

The Fuel Must Not Contain Sediment That Could Plug Orifices or Cause Wear

Diesel fuel filters are designed to capture particles that are larger than 10 microns in size. Some newer engines are even equipped with filters that capture particles as small as 2 microns. These filters should stop foreign materials from entering the fuel injection

system. However, when fuels are exposed to high temperatures and the oxygen in air, they can undergo chemical changes that form compounds that are insoluble in the fuel. These compounds form varnish deposits and sediments that can plug orifices and coat moving parts causing them to stick. Several test procedures have been developed that attempt to measure the tendency of diesel fuels to produce these sediments, such as ASTM D 2274, but none have gained the acceptance needed to be included in the diesel fuel specification (ASTM D 975).

When diesel fuel burns, it should be converted entirely to carbon dioxide and water vapor. Inorganic materials present in the fuel may produce ash that can be abrasive and contribute to wear between the piston and cylinder. ASTM D 482 is used to characterize ash from diesel fuels. The ASTM specification for biodiesel, D 6751, requires that ASTM D 874 be used. This method measures sulfated ash, which is specified because it is more sensitive to ash from sodium and potassium. These metals are likely to be the main sources for ash in biodiesel.

When fuel is exposed to high temperatures in the absence of oxygen, it can pyrolyze to a carbon-rich residue. While this should not occur in the cylinder of a properly operating engine, some injection systems have the potential to create a region within the injection nozzle where this residue can collect and limit the range of motion of moving parts. Various test procedures such as ASTM D 189, D 524, and D 4530 have been developed as an attempt to predict the tendency of a fuel to form in-cylinder carbon deposits. Unfortunately, it is very difficult to reproduce in-cylinder conditions in a test, so the correlation of these procedures to actual engine deposits is limited.

Diesel fuel injection systems have very closely fitting parts that are subjected to high loads. These parts require lubrication to prevent rapid wear. All diesel injection systems rely on the fuel itself to provide this lubrication. While the mechanism is not fully understood, it is known that as refiners reduce the sulfur content of diesel fuel the ability of the fuel to provide the necessary lubrication decreases. The property that characterizes the ability of the fuel to lubricate is the *lubricity*. Several tests are commonly used to measure lubricity but they have not been accepted or required as part of the ASTM specification for diesel fuel.

The Fuel Should Not Cause Excessive Pollution

Under ideal circumstances, all of the carbon in the diesel fuel will burn to carbon dioxide and all of the hydrogen will burn to water vapor. In most cases, virtually all of the fuel does follow this path. However, if sulfur is present in the fuel, it will be oxidized to sulfur dioxide and sulfur trioxide. These oxides of sulfur can react with water vapor to form sulfuric acid and other sulfate compounds. The sulfates can form particles in the exhaust and elevate the exhaust particulate level. In 1993, the Environmental Protection Agency mandated that diesel fuel should contain no more than 500 ppm of sulfur. This was a factor of 10 reduction in sulfur level and greatly reduced sulfur as a source of exhaust particulate. In 2006, the EPA has mandated a new reduction in sulfur to 15 ppm. This will eliminate sulfur as a component of exhaust particulate and allow the introduction of

catalytic aftertreatment on diesel engines. Sulfur is a powerful catalyst poison and limits the options available for controlling emissions on future engines.

Aromatics are a class of hydrocarbon compounds that are characterized by stable chemical structures. They are usually present in diesel fuel at levels between 30 to 35%. They are desired by diesel engine operators because they provide greater energy per gallon of fuel but they are believed to contribute to higher particulate and NOx emissions, and tend to have lower cetane values. In the early 1990s, CARB implemented standards that limited the aromatic content of diesel fuels sold in California to 10%. CARB later allowed the aromatic content to be higher if fuel producers could show that their fuels produced equivalent or lower emissions than the low aromatic fuel.

Biodiesel contains no aromatics. It is also naturally low in sulfur. Biodiesel from soybean oil and most vegetable oils contain essentially no sulfur but some sulfur has been found in biodiesel produced from animal fats.

The Fuel Properties Should Not Deviate from the Design Specifications

Fuel viscosity is specified in the standard for diesel fuel within a fairly narrow range. Hydrocarbon fuels in the diesel boiling range easily meet this viscosity requirement. Most diesel fuel injection systems compress the fuel for injection using a simple piston and cylinder pump called the plunger and barrel. In order to develop the high pressures needed in modern injection systems, the clearances between the plunger and barrel are approximately one ten-thousandth of an inch. In spite of this small clearance, a substantial fraction of the fuel leaks past the plunger during compression. If fuel viscosity is low, the leakage will be enough to cause a significant power loss for the engine. If fuel viscosity is high, the injection pump will be unable to supply sufficient fuel to fill the pumping chamber. Again, the effect will be a loss in power. If fuel viscosity is extremely excessive, as is the case with vegetable oils that have not been transesterified, there will be a degradation of the spray in the cylinder causing poor atomization and the production of black smoke.

The Fuel Should be Intrinsically Safe

Diesel engine operators are accustomed to treating diesel fuel as is it were nonflammable. The volatility of both No. 1 and No. 2 diesel fuel are low enough that the air-vapor mixture above the fuel is below the flammability limit. The property that characterizes this behavior is the flashpoint. The temperature at which the fuel will give off enough vapor to produce a flammable mixture is the flashpoint. This temperature is 125°F to 150°F for diesel fuel and below -40°F for gasoline. This has been a concern for mixtures of ethanol and diesel fuel because ethanol reduces the flash point of diesel fuel to the point where it needs to be treated in the same manner as gasoline.

To ensure that diesel fuels meet the requirements imposed by the engine, engine manufacturers and fuel suppliers have cooperatively developed fuel standards. The group that has facilitated this cooperative effort is the American Society for Testing and Materials (ASTM). The standard for diesel fuel is ASTM D975 and is described in the following section.

3. Diesel Fuel Specification

ASTM Specifications for Diesel Fuel Oils (D975-97)

Diesel fuel is characterized in the United States by the ASTM standard D 975. This standard identifies five grades of diesel fuel described below.

Grade No. 1-D and Low Sulfur 1-D: A light distillate fuel for applications requiring a higher volatility fuel for rapidly fluctuating loads and speeds as in light trucks and buses. The specification for this grade of diesel fuel overlaps with kerosene and jet fuel and all three are commonly produced from the same base stock. One major use for No. 1-D diesel fuel is to blend with No. 2-D during winter to provide improved cold flow properties. Low sulfur fuel is required for on-highway use with sulfur level < 0.05%.

Grade No. 2-D and Low Sulfur 2-D: A middle distillate fuel for applications that do not require a high volatility fuel. Typical applications are high-speed engines that operate for sustained periods at high load. Low sulfur fuel is required for on-highway use with sulfur level < 0.05%. 2-D, or No. 2 diesel fuel, is more dense than 1-D and so it provides more energy per gallon. This makes it the preferred fuel for on-highway trucks.

Grade No. 4-D: A heavy distillate fuel that is viscous and may require fuel heating for proper atomization of the fuel. It is used primarily in low and medium speed engines.

ASTM D975 specifies the property values shown in Table 5 for these grades of diesel fuel. The surprising aspect about ASTM D 975 is how few requirements are actually included. The standard says nothing about the composition of the fuel or its source. It only defines some of the property values needed to provide acceptable engine operation and safe storage and transportation. Each of the properties has an ASTM standard that defines the methods used to measure the property. So, the individual standards define the measurement methods and ASTM D 975 defines the allowable value. The individual properties that are defined for diesel fuel are described below along with some properties that perhaps should be included. The next chapter will describe the actual test procedures for the measurement of each property.

Flash point – Diesel fuel flashpoints are measured with ASTM D93. The flash point is the lowest temperature at which a combustible mixture can be formed above the liquid fuel. It is dependent on both the lean flammability limit of the fuel as well as the vapor pressure of the fuel constituents. The flash point is determined by heating a sample of the fuel in a stirred container and passing a flame over the surface of the liquid. If the temperature is at or above the flash point, the vapor will ignite and an easily detectable flash can be observed. Number 2 diesel fuel is required to have a flash point above 52°C (125°F) and Number 1 diesel fuel must have a flashpoint above 38°C (100°F). Some special applications, such as marine fuels, may require higher flash points. Biodiesel's flash point is usually well above 150°C.

Table 5. Requirements for Diesel Fuel Oils (ASTM D 975-97)

Grade Property	Grade LS #1	Grade LS #2	Grade No. 1-D	Grade No. 2-D	No. 4-D
Flash point °C, min	38	52	38	52	55
Water and sediment, % vol, max.	0.05	0.05	0.05	0.05	0.50
Distillation temp., °C, 90%					
Min.	--	282	--	282	--
Max.	288	338	288	338	--
Kinematic Viscosity, mm^2/s at 40°C					
Min.	1.3	1.9	1.3	1.9	5.5
Max.	2.4	4.1	2.4	4.1	24.0
Ramsbottom carbon residue, on 10%, %mass, max.	0.15	0.35	0.15	0.35	--
Ash, % mass, max.	0.01	0.01	0.01	0.01	0.10
Sulfur, % mass, max	0.05	0.05	0.50	0.50	2.00
Copper strip corrosion, Max 3 hours at 50°C	No. 3	No. 3	No. 3	No. 3	--
Cetane Number, min.	40	40	40	40	30
One of the following Properties must be met:					
(1) cetane index	40	40	--	--	--
(2) Aromaticity, % vol, max	35	35	--	--	--
Cloud point, °C, max.					

Cloud point, °C, max.   Determined by local climate
Should be 6°C higher than the tenth percentile minimum ambient temperature for the region. For Iowa:

Month	10th % minimum temp
Oct	-2°C
Nov	-13
Dec	-23
Jan	-26
Feb	-22
Mar	-16

Water and Sediment – Water and sediment in diesel fuel are measured using ASTM D 2709. This method used to measure water and sediment is only sensitive to free water. It uses a centrifuge to separate small water droplets and particles to be sure they do not exceed 0.05% (500 ppm). An earlier method (D 1796) specified that a solvent should be added to allow the measurement to include dissolved water but since diesel fuel will only dissolve about 50 ppm of water, this has little impact on whether the fuel exceeds the specification value. This test is particularly important when working with biodiesel

because biodiesel is usually water-washed to remove traces of soap and free glycerol. Vacuum drying is usually needed to remove residual water following the washing process.

Distillation Curve - The distillation curve is determined by relating the fraction of a fuel sample that is removing by heating a fuel sample to progressively higher temperatures. The procedure is specified in ASTM Standard D 86. Typically, the curve is characterized by the initial point, the temperature at which the first drop of liquid leaves the condenser, the temperatures at each 10% of the liquid, and the end point. ASTM D 975 indicates that No. 1 diesel fuel should have a 90% point (90% of the fuel components boil below this temperature) that is no higher than 288°C. No lower limit is specified for No. 1 fuel. Number 2 diesel fuel has a lower limit of 282°C for the 90% point and an upper limit of 338°C. Since diesel fuel consists of hundreds of different compounds, a distillation curve provides important information about the composition of the fuel. However, biodiesel usually only contains 4 to 5 major compounds that all boil at about the same temperature. In addition, the boiling temperature is so high at atmospheric pressure that the biodiesel compounds usually decompose (crack) during the distillation test. Distillation tests following ASTM D 86 are not appropriate for biodiesel. The ASTM standard D 6751 specifies a distillation test although it recommends ASTM D 1160, which is conducted under vacuum. While this test will allow the biodiesel to be distilled without decomposing, the procedure specified in the technique for converting the distillation curve back to atmospheric pressure is only valid for petroleum products and should be used with caution for biodiesel.

Kinematic Viscosity - Viscosity is a measure of a fluid's resistance to flow. The greater the viscosity, the less readily the liquid flows. The viscosity of petroleum oils is a strong function of temperature with the viscosity decreasing as the temperature increases. ASTM D 445 is a standard test procedure for determining the kinematic viscosity of liquids. Biodiesel is more viscous than No. 2 diesel fuel but only by a small amount. Depending on feedstock and amount of oxidation, biodiesel viscosity will vary between 4.0 and 6.2, while No. 2 diesel fuels tend to fall in the a narrower range of 2.4 to 2.6.

Ash – Ash consists of the residue left when the fuel is heated to a sufficiently high temperature that combustible material burns and leaves as CO_2 and H_2O. The procedure is described in ASTM D 482. It primarily consists of inorganic compounds and their oxides. These materials can be abrasive and contribute to engine wear. Diesel fuels are generally very low in ash and ASTM D 975 allows no more than 0.01%, by weight.

Sulfur – Before 1993, No. 2 diesel fuel was allowed to contain up to 0.5% (5000 ppm) sulfur. This level is still acceptable for off-highway fuels, but after 1993, on-highway fuels were required to contain less than 0.05% (500 ppm) sulfur. In 2006, the sulfur specification for on-highway fuels will be lowered to 15 ppm. This is an extremely low level of sulfur and will be difficult to measure. The current method, D 2622, will need to be changed to a new method when the sulfur level drops.

Copper Strip Corrosion – Many of the compounds in diesel fuel can be corrosive. Copper and copper compounds tend to be particularly susceptible to chemical attack. As an indicator of the tendency of a fuel to cause corrosion, ASTM D 130 describes placing polished copper strips in the fuel for 3 hours at 50°C. Then the strips are washed in a solvent and compared to standard descriptions of tarnish and corrosion.

Cetane Number – The cetane number is an engine-based test defined by ASTM D 613. It is based on a special engine produced by Waukesha Engine Company that is similar to the Octane Test Engine used for rating gasoline. The cetane number relates to the readiness of the fuel to self-ignite when exposed to the high temperatures and pressure in the diesel engine combustion chamber. It is not directly related to the energy content of the fuel. On-highway diesel fuels in the U.S. are required to have cetane numbers of 40 or higher. Most will be in the range of 40 to 45. In Europe, cetane numbers are higher and tend to be in the 50-55 range.

Cloud Point – The cloud point is the temperature at which a cloud of wax crystals first appears in a fuel sample that is cooled under conditions described by ASTM D2500.

ASTM D 975 does not specify a specific value for the cold flow requirements of diesel fuel. Instead, it suggests that the cloud point be no more than 6°C higher than the 10th percentile minimum ambient temperature for the month the fuel will be used. The 10th percentile temperature corresponds to the minimum temperature that would be reached no more than 3 days out of 30 for the month. Figure 4 shows the values of 10th percentile temperatures during the month of January in the U.S.. ASTM D 975 contains similar maps for other low temperature months.
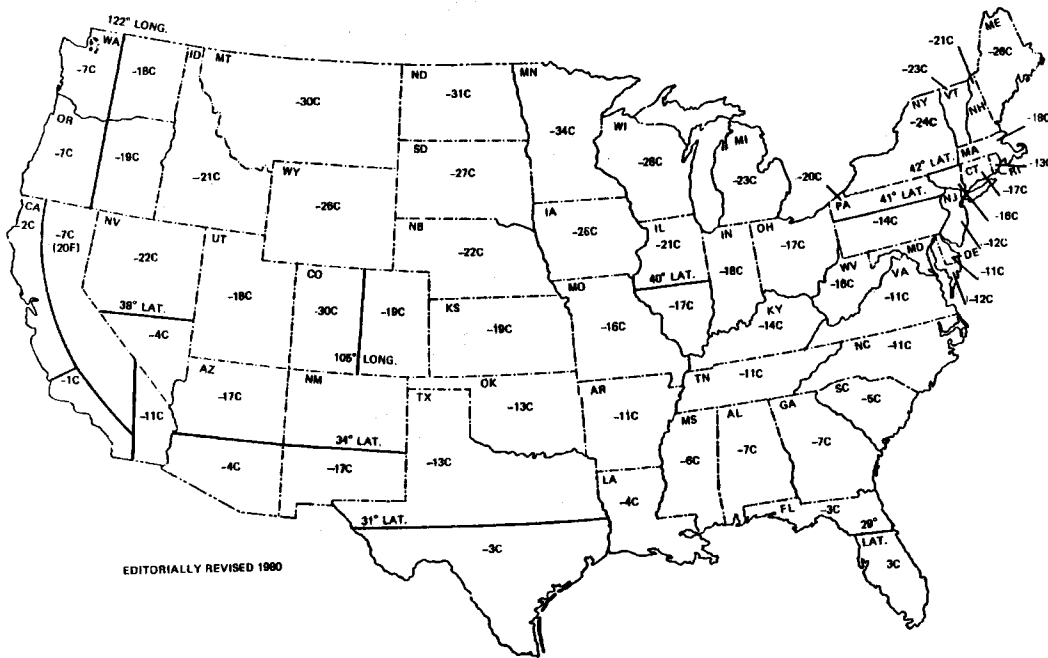

Figure 4. 10th Percentile Minimum Air Temperatures for January (ASTM D975-97)

Other important fuel properties that are not included in ASTM D 975 (but maybe should be)

Fuel Stability

A fuel is considered unstable when it undergoes chemical changes that produce undesirable consequences such as deposits, acidity, or a bad smell. There are three different types of stability commonly described in the technical literature. *Thermal stability* addresses fuel changes that occur due to elevated temperature. These changes may occur at conditions encountered in modern fuel injection systems as fuel is recirculated through the engine cylinder head and back to the fuel tank. *Oxidative stability* refers to the tendency of fuels to react with oxygen at temperatures near ambient. These reactions are much slower than those that would occur at combustion temperatures, and they produce varnish deposits and sediments. *Storage stability* is also a frequently used term and refers to the stability of the fuel while it is in long-term storage. These terms are not necessarily exclusive terms. For example, oxidative attack is probably one of the primary concerns of storage stability but storage stability might also involve issues of water contamination and microbial growth. While there is no stability test procedure specified in ASTM D 975, ASTM D 2274 is included in some private purchase requirements.

Heating value, net and gross

There are actually two heating values in common use, the higher, or gross, heating value and the lower, or net, heating value. Both quantities are measured using a calorimeter where the heat transfer from the hot gases resulting from combustion of the fuel with air is measured as the gases are cooled to the initial temperature of the reactants. The procedure is described in ASTM D 240. The higher heating value assumes that all of the water in the products is condensed liquid while the lower heating value assumes all of the water is present as vapor, even though the product temperature may be below the dew point temperature. The lower heating value is the most common value used for engine applications. It is used as an indicator of the energy content of the fuel. In general, the higher the heating value of the fuel, the less fuel that will be required to do a given amount of work. Biodiesel generally has a lower heating value that is 12% less than No. 2 diesel fuel on a weight basis. Since the biodiesel has a higher density, the lower heating value is only 8% less on a volume basis.

Lubricity

The need for diesel fuel lubricity has been recognized for many years. Most early concern focused on the use of #1 diesel fuel in place of #2 diesel fuel under cold weather conditions. Higher wear rates with #1 diesel fuel would be aggravated by #1 diesel fuel's lower viscosity. However, when the U.S. Environmental Protection Agency mandated that the sulfur content of on-highway diesel fuel be lowered from 5000 ppm to 500 ppm in 1993, fuel lubricity captured national attention. There is still disagreement about what specific fuel changes are caused by the sulfur reduction that result in lubricity reduction. Some have suggested that sulfur compounds themselves provide lubricity, others have

suggested that nitrogen compounds or naphthenic hydrocarbons are responsible. In any case, there is general agreement that the severe hydrotreating process used by petroleum refineries to remove sulfur results in lower fuel lubricity. Recent EPA regulations will lower the sulfur content of diesel fuel to 15 ppm by 2007. This change is expected to worsen fuel lubricity. The addition of small amounts of biodiesel (0.25% to 2%) to diesel fuel has a dramatic effect on the lubricity of that fuel. Pure biodiesel and high level blends have excellent lubricity.

Lubricity can be defined as: "The property of a lubricant that causes a difference in friction under conditions of boundary lubrication when all the known factors except the lubricant itself are the same. The lower the friction the higher the lubricity." [Kajdas, C., S.S.K. Harvey, and E. Wilusz, *Encyclopedia of Tribology*, Elsevier, New York, 1990.]

Laboratory Exercises

Specific Gravity

Use the specific gravity balance and the hydrometers to measure the density of the 5 fuels provided:

1. No. 1 diesel fuel
2. No. 2 diesel fuel
3. Biodiesel from soybean oil
4. Biodiesel from yellow grease
5. B20 from soy biodiesel and No. 2 diesel fuel

Apply temperature correction factors (ASTM D 1250) to convert the measured specific gravities to the reference temperature of 15°C.

Fuel	Measured Sp. Grav.	Measured Temp. (°C)	Corrected Sp. Grav.
#1D			
#2D			
B100-Soy			
B100-YG			
B20			

Viscosity

Use the viscometer to measure the viscosity (at 40°C) of the 5 fuels provided:

1. No. 1 diesel fuel
2. No. 2 diesel fuel
3. Biodiesel from soybean oil
4. Biodiesel from yellow grease
5. B20 from soy biodiesel and No. 2 diesel fuel

Fuel	Measured Time (sec)	Measured Temp. (°C)	Kinematic Viscosity (cSt)
#1D			
#2D			
B100-Soy			
B100-YG			
B20			

Flashpoint

Use the Pensky-Martens Closed Cup Tester to measure the flashpoint of the 3 fuels provided:

1. No. 1 diesel fuel
2. No. 2 diesel fuel
3. Biodiesel from soybean oil

Fuel	Flashpoint (°C)
#1D	
#2D	
B100-Soy	

Water and Sediment

The centrifuge will be demonstrated as a means to measure the water and sediment content of the fuels. However, the centrifuge can only determine the free water. A second technique, the Karl-Fisher titrator can be used to measure the dissolved water in a sample. This is particularly useful for monitoring drying operations. Use the Karl-Fisher Titrator to measure the water content of the 4 fuels provided:

1. No. 1 diesel fuel
2. No. 2 diesel fuel
3. Biodiesel from soybean oil
4. Biodiesel from yellow grease

Fuel	Water (PPM)
#1D	
#2D	
B100-Soy	
B100-YG	

Fuel Distillation

Use the fuel distillation apparatus to measure the atmospheric distillation profile for <u>one</u> of the 5 fuels provided:

1. No. 1 diesel fuel
2. No. 2 diesel fuel
3. Biodiesel from soybean oil
4. Biodiesel from yellow grease
5. B20 from soy biodiesel and No. 2 diesel fuel

Fuel Type =	Measured Temp. (°C)
IBP	
5%	
10%	
20%	
30%	
40%	
50%	
60%	
70%	
80%	
90%	
95%	

Laboratory Safety

Rules:

1. Everyone must wear safety glasses or goggles while working in the laboratory or conducting experiments elsewhere.
2. Lab coats or aprons will be supplied for those involved with pouring or mixing chemicals.
3. If a fire occurs, leave the building immediately. Do not try to fight it!
4. Absolutely no smoking in Iowa State University buildings.
5. Be aware of the closest eye-wash station. If you aren't sure how to use it, ASK!

4. Fuel Property Measurement

The development of internal combustion engines over the past century has resulted from the complimentary refinement of the engine design and fuel properties. As such, engines have been developed to utilize the properties of the fuels that were available. Replacement of existing fuels with new fuel formulations requires understanding the critical fuel properties to insure that the new fuels can be used. Discussed in this section will be some key fuel properties as well as the methods to measure these properties. The properties discussed will be specific gravity, kinematic viscosity, flash point, boiling point (distillation test), cetane number, cloud point, pour point, and copper strip corrosion.

Specific Gravity

The specific gravity is a relative measure of the density of a substance. It is defined as the ratio of the density of the substance, ρ, to a reference density, ρ_{ref}. The equation for the specific gravity (SG) is SG = ρ/ρ_{ref}. The most common reference density used in the measurement of specific gravity is the density of water at 4˚C, which corresponds to a reference density of 1 g/cc. The specific gravity of conventional No. 2 diesel fuel is about 0.85 while a typical density of biodiesel is 0.88, which means that biodiesel is more dense than conventional diesel fuel. Figure 5 shows a hydrometer for measuring specific gravity. Other methods are also in common use.
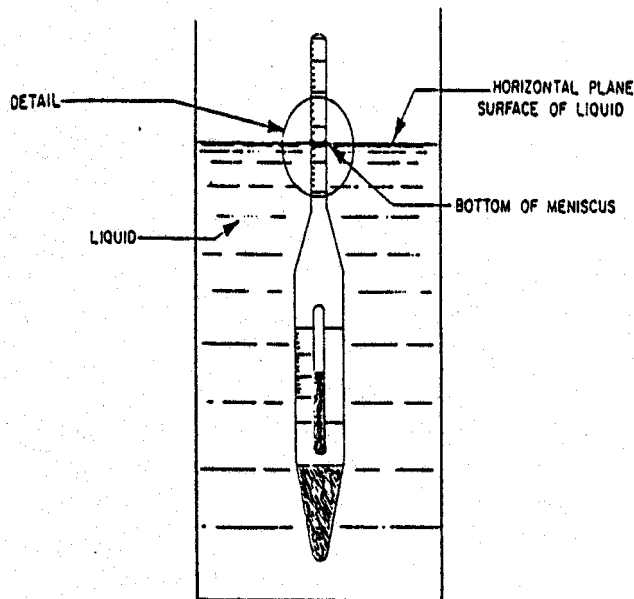

Figure 5. Hydrometer for measuring specific gravity

Kinematic Viscosity

To define kinematic viscosity it is useful to begin with the definition of viscosity. Simply stated, viscosity, which is also called dynamic viscosity (η), is the ease with which a fluid will flow. We intuitively understand viscosity as evidenced by the fact that we know, for example, honey is more viscous than water. There is a hydrodynamic definition of viscosity as well. Technically it is the ratio of the shear stress to the shear rate for a fluid. In contrast, the kinematic viscosity (ν) is the resistance to flow of a fluid under gravity. Therefore, the kinematic viscosity of a fluid is related to the dynamic viscosity through the density (ρ), i.e., $\nu = \eta/\rho$. The standard procedure for measuring kinematic viscosity in diesel or biodiesel fuels is ASTM D 445. The summary of the test method as presented in the standard is "The time is measured for a fixed volume of liquid to flow under gravity through the capillary of a calibrated viscometer under a reproducible driving head and at a closely controlled and known temperature." The repeatability of the test is within 0.5-1.0%, while the reproducibility is 1-2%. The test is usually conducted by measuring the time required for a volume of liquid to flow under gravity through a calibrated glass capillary tube. The kinematic viscosity is then equal to the product of this time and a calibration constant for the tube. Figure 6 shows a Cannon-Fenske style glass capillary tube that is commonly used for ASTM D 445.

Biodiesel is more viscous than No. 2 diesel fuel, but only by a small amount. Depending on feedstock and the amount of oxidation, biodiesel's viscosity will vary between 4.0 and 6.2, while No. 2 diesel fuels tend to fall in the a narrower range of 2.4 to 2.6.
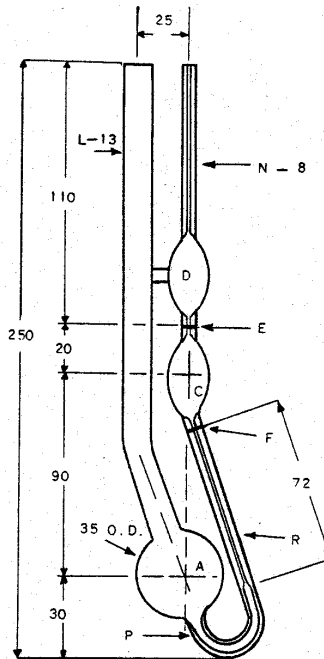

Figure 6. Cannon-Fenske Capillary Viscometer Tube

Flash Point

A key property determining the flammability of a fuel is the flash point. The flash point is the lowest temperature at which an applied ignition source will cause the vapors of a sample to ignite. Therefore, it is a measure of the tendency of a sample to form a flammable mixture with air. As a side note, the value of the flash point is used for the classification of *flammable* and *combustible* materials needed for safety and shipping regulations. The standard procedure for measuring the flash point for diesel and biodiesel fuels is ASTM D 93. The flash point is determined by heating a sample of the fuel in a stirred container and passing a flame over the surface of the liquid. If the temperature is at or above the flash point, the vapor will ignite and an easily detectable flash can be observed. The flash need not correspond to a sustained flame. The "fire point" is sometimes used to designate the fuel temperature that will produce sufficient vapor to maintain a continuous flame.

The equipment shown in Figures 7 and 8 are used to measure the flashpoint. Figure 7 shows the test cup for the apparatus. The cup is filled with fuel and heated with an external heater. The agitator ensures that the fuel temperature is uniform. A small open flame is maintained from an external supply of natural gas. Periodically, the stirrer is stopped and the flame is pivoted down to an opening in the top of the cup to see if the fuel vapors will ignite. The ignition source is shown in this position in Figure 7. When the flash point has been reached, there will be a small flash that is sometimes accompanied by an audible popping sound. Occasionally, the flash may actually extinguish the flame on the ignition source. Figure 8 shows the test cup with its heat source and a heat shield that ensures uniform heating. The repeatability of the test is within 2˚C and the reproducibility is 5˚C.
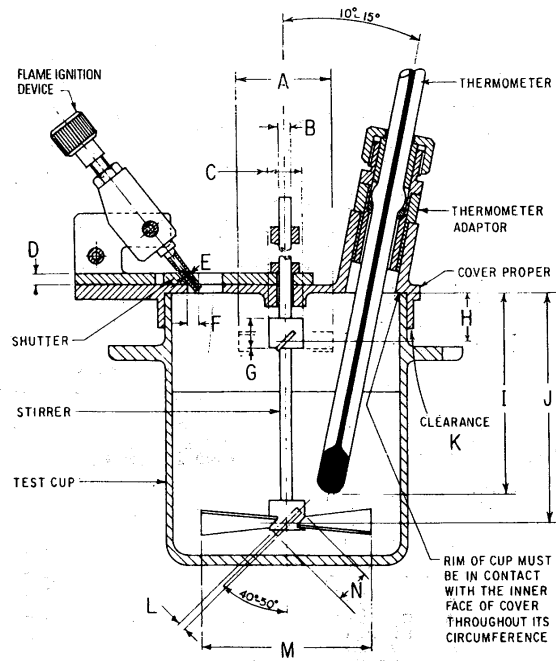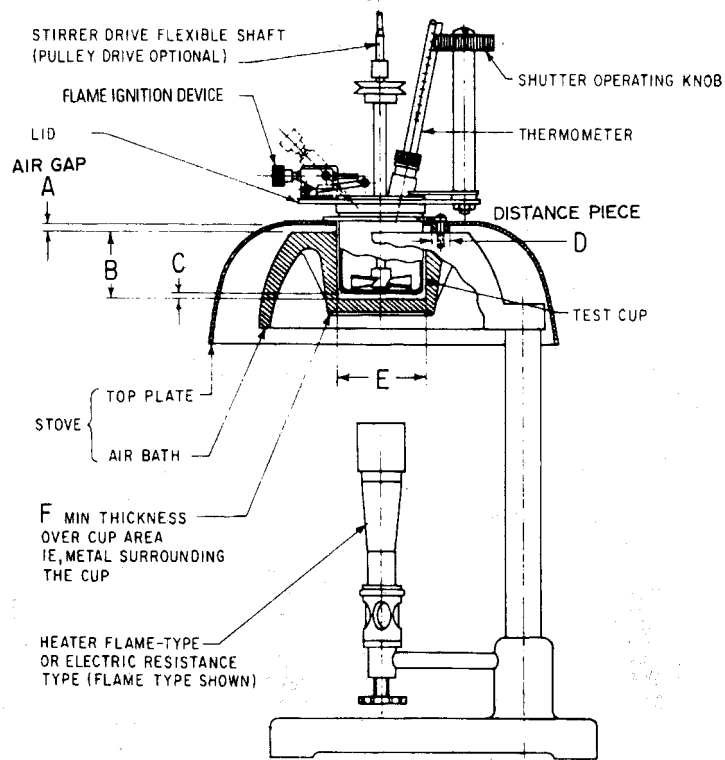
Figure 7. Test cup for ASTM D 93 Flashpoint Test

Figure 8. ASTM D 93 Pensky-Martens Flashpoint Apparatus

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Distillation Temperature

A property related to the flash point is the boiling point, which is the temperature at which a liquid transitions to a gas. For a pure substance the boiling point is a single temperature value. However, for a mixture of hydrocarbons as exists in diesel fuel there is a range of boiling points for the different constituent chemical species. The distillation test is used to determine the boiling range characteristics of a hydrocarbon sample. As one would expect, the distillation characteristics, i.e., the boiling point range, have an important effect on the performance, storage, and safety of fuels. Distillation limits are commonly included in petroleum product specifications due to the number of chemicals species that can be present. The standard procedure for measuring the boiling point range for diesel fuels is the distillation test, which is ASTM D 86. The simple distillation apparatus used for this test is shown in Figure 9.

To run the test, a simple batch distillation process is conducted on a sample of the fuel and boiling point data are collected. These data include the initial boiling point, the final boiling point, and the boiling temperature corresponding to increments of the volume of fuel distilled (5%, 10%, 20%, etc.).

Unfortunately, the boiling temperatures of the compounds in biodiesel are so high at atmospheric pressure that the compounds may decompose (crack) during the distillation test. When this happens, the distillation information no longer corresponds to the original fuel. Distillation tests following ASTM D 86 are not appropriate for biodiesel. The ASTM standard D 6751 specifies a distillation test although it recommends ASTM D 1160, which is conducted under vacuum. The equipment used for the vacuum distillation test is shown in Figure 10. While this test will allow the biodiesel to be distilled without decomposing, the procedure specified in the technique for converting the distillation curve back to atmospheric pressure is only valid for petroleum products and should be used with caution for biodiesel.
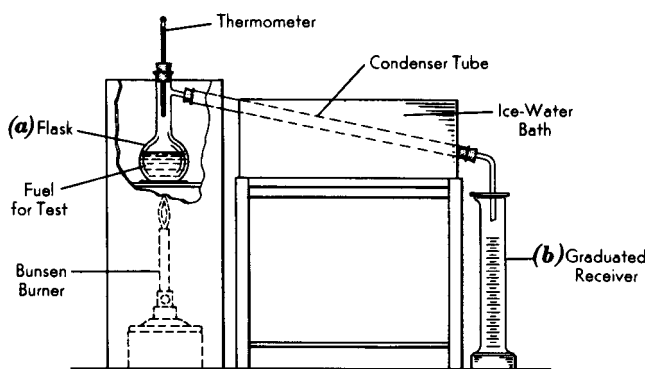

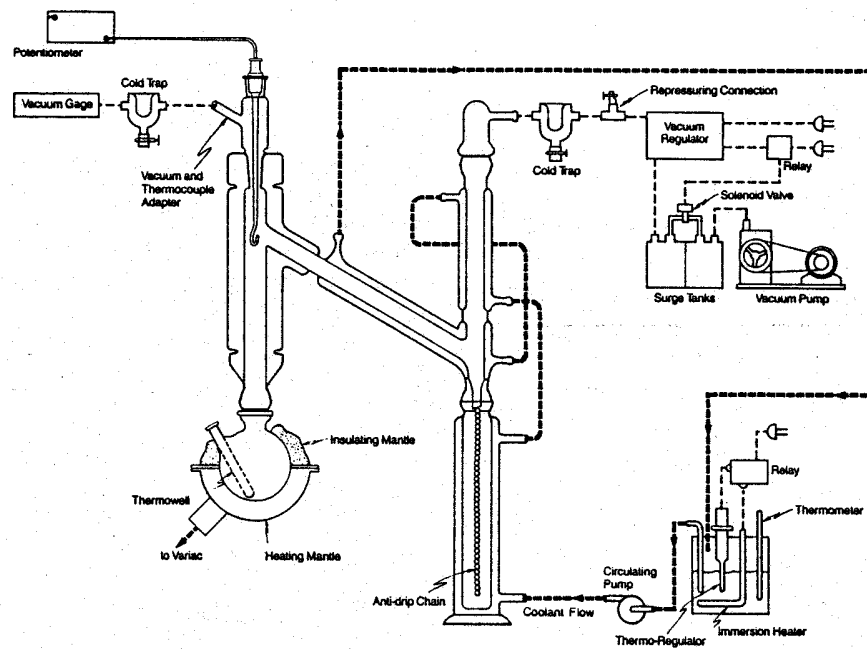**Figure 9. Distillation apparatus for ASTM D 86**

Figure 10. Vacuum distillation apparatus for ASTM D 1160

Cetane Number

Perhaps the most important measure of ignition characteristics of diesel and/or biodiesel fuels is the cetane number, since it directly pertains to ignition within compression ignition engines. The analog of cetane number in gasoline is the octane number.
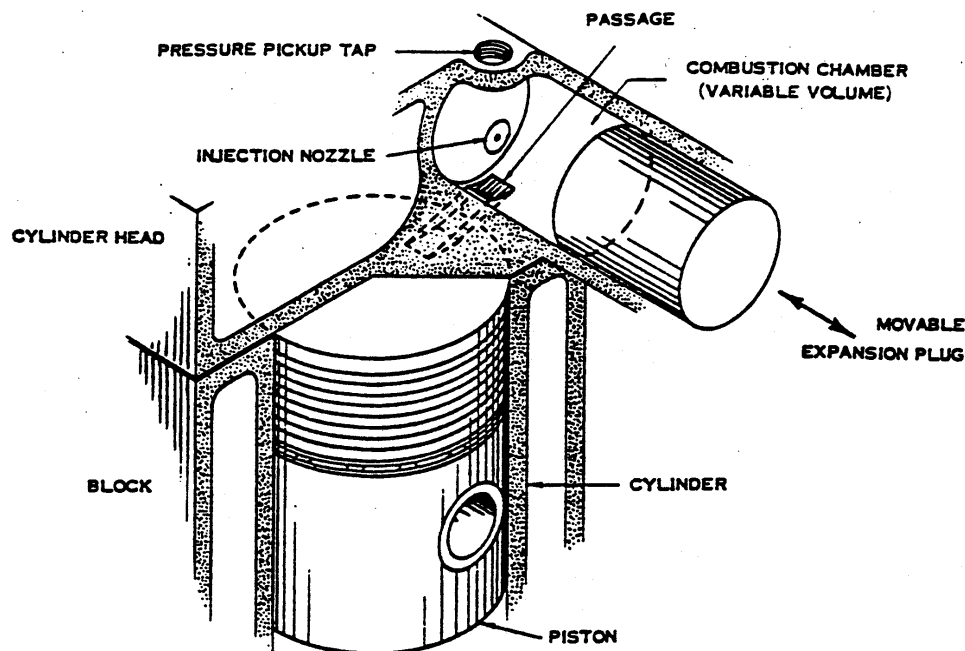
Figure 11. Cetane Test Engine Combustion Chamber
(ASTM D 613 Test Method for Cetane Number of Diesel Fuel Oil)

The cetane number is the primary specification measurement used to match fuels and engines. It is commonly used by refiners, marketers and engine manufacturers to describe diesel fuels. Nonetheless, cetane number is really a value that is the manifestation of a specific test, ASTM D 613.

The cetane number is an engine-based test. It is based on a special engine produced by the Waukesha Engine Company that is similar to the Octane Test Engine used for rating gasolines. The engine is a single cylinder, indirect injection diesel engine. The combustion chamber is shown in Figure 11. The engine speed is fixed at 900 rpm and while the engine is naturally aspirated, the intake air temperature is held at $150°F$. The test is based on a careful adjustment of the fuel/air ratio and the compression ratio to produce a standard ignition delay (the period between the start of fuel injection and the start of combustion) of 13 degrees while operating on the test fuel. Then the engine is switched to operate on a blend of two reference fuels. Different blends are tested until a formulation is found that restores the ignition delay to 13 degrees. The primary reference fuels are n-cetane (n-hexadecane), which has a cetane number of 100 and heptamethylnonane (HMN), which has a cetane number of 15. When the ignition delay is restored to 13 degrees, the cetane number is computed from the following relationship:

Cetane Number = % n-cetane + 0.15 (%HMN)

Since the price of the primary reference fuels is quite high, most commercial cetane testing is done with secondary reference fuels that have been calibrated to known cetane values. Phillips Petroleum supplies these secondary reference fuels.

It is important to note that if a 50/50 blend is made of fuels with cetane numbers of 40 and 50, respectively, the blended fuel will likely not have a cetane number of 45. This phenomenon is due to the fact that the cetane number of a blend is not directly proportional to the cetane numbers of its constituents. The cetane number of biodiesel is typically higher than standard diesel fuel and its addition to a standard diesel fuel will generally increase the cetane number of the subsequent blended fuel. For diesel fuel, the repeatability of the cetane number test is within 1 cetane number and the reproducibility is within 4 cetane numbers.

Cetane Index – (ASTM D 976 or D 4737) The cetane index is a calculated quantity that is intended to approximate the cetane number. It is much cheaper to determine than the engine-based cetane number but its accuracy is limited to the type of fuel on which the equation is based. It generally does not provide an accurate indication of cetane number if the fuel contains cetane improving additives or for non-petroleum-based alternative fuels. Two ASTM methods are available for computing the cetane index.

ASTM standard D 976 gives the following empirical equation for the cetane index:

$$\text{Cetane Index} = 454.74 - 1641.416\,D + 774.74\,D^2 - 0.554\,T_{50} + 97.803[\log_{10}(T_{50})]^2$$

> where D = fuel density at 15°C in g/ml.
> and T_{50} = the temperature corresponding to the 50% point on the distillation
>   curve in degrees C.

ASTM standard D 4737 gives the cetane index according to the following four-variable equation:

$$\text{Cetane Index} = 45.2 + 0.0892(T_{10}N) + 0.131(T_{50}N) + 0.0523(T_{90}N)$$
$$+ 0.901B(T_{50}N) - 0.420B(T_{90}N) + 4.9\times10^{-4}(T_{10}N)^2$$
$$-4.9\times10^{-4}(T_{90}N)^2 + 107B + 60\,B^2$$

> where $T_{10}N = T_{10} - 215$
> $T_{50}N = T_{50} - 260$
> $T_{90}N = T_{90} - 310$
> when T_{10}, T_{50}, and T_{90} are temperatures at 10%, 50%, and 90% volume
> distilled in degrees C
> and $B = [\exp(-3.5DN)] - 1$
> when DN = density at 15°C (kg/liter) - 0.85

Example Calculation

The following data were obtained from a commercial fuel testing laboratory for a sample of #2 diesel fuel.

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API Gravity	34.1
T_{10}	413°F (212.0°C)
T_{50}	502°F (261.4°C)
T_{90}	592°F (311.4°C)

Calculate and compare the calculated cetane indices using the two equations given above with the measured values shown.

Preliminary calculations:

$$S.G. = \frac{141.5}{API + 131.5} = 0.8545$$

$$\rho = 0.8545(999.1 g / ml) = 0.8537 g / ml$$

ASTM D976:

$$\text{Cetane Index} = 454.74 - 1641.416 \, (0.8537) + 774.74 \, (0.8537)^2$$
$$- 0.554 \, (261.4) + 97.803 \, [\log_{10}(261.4)]^2$$
$$= \mathbf{44.8}$$

ASTM D4737:

$$DN = 0.8537 - 0.85 = 0.0037$$
$$B = \exp(-3.5 \times 0.0037) - 1 = -0.0129$$
$$\text{Cetane Index} = 45.2 + 0.0892 \, (-3.0) + 0.131 \, (1.4) + 0.0523 \, (1.4)$$
$$+ 0.901 \, (-0.0129) \, (1.4) - 0.42 \, (-0.0129) \, (1.4) + 4.9 \times 10^{-4} \, (-3)^2$$
$$- 4.9 \times 10^{-4} \, (1.4)^2 + 107 \, (-0.0129) + 60 \, (-0.0129)^2$$
$$= \mathbf{43.8}$$

The cetane number for this fuel was measured by ASTM D 613 on two occasions and found to be 47.8 and 45.7. Note that the two measured cetane numbers are 2.1 apart. ASTM standard D 613 states that the repeatability of the measurement (in this cetane number range) is such that two measurements taken on the same material by the same operator with the same equipment at identical operating conditions will be within 0.7, 95% of the time. However, the reproducibility, which is the difference between two measurements taken by different operators in different laboratories may be as large as 2.6. Since the two cetane number measurements in this case were taken one month apart, the reproducibility specification is probably more applicable.

The calculated values of cetane index are about 2-3 numbers below the average of the two measured cetane numbers. ASTM standard D 976 says that the first equation will be within +/- 2 cetane numbers for 75% of typical distillate fuels. No precision estimates are given for D4737, the four variable equation. Both cetane index equations are based on data from petroleum-based fuels and should <u>not</u> be used for biodiesel

Cloud Point

A fuel property that is particularly important for the low temperature operability of diesel fuel is the cloud point. The cloud point is the temperature at which a cloud of wax crystals first appears in a liquid upon cooling. Therefore, it is an index of the lowest temperature of the fuel's utility under certain applications. Operating at temperatures below the cloud point for a diesel fuel can result in fuel filter clogging due to the wax crystals. As described in ASTM D 2500, the cloud point is determined by visually inspecting for a haze in the normally clear fuel, while the fuel is cooled under carefully controlled conditions. The apparatus used for this test is shown in Figure 12. The cloud point is an important property for biodiesel since biodiesel fuels typically have higher cloud points, i.e., crystals begin to form at higher temperature, than standard diesel fuel. This feature has implications on the use of biodiesel in cold weather applications.

An alternative procedure for measuring the cloud point of diesel/biodiesel fuels is ASTM D 5773. A summary of the procedure steps is 1) the sample is cooled in a Peltier device at a constant rate, 2) the sample is continuously monitored by optical detectors, and 3) the temperature is recorded that corresponds to the first formation of a cloud in the fuel. The repeatability of the cloud point test is <0.5˚C and the reproducibility is <2.6˚C.
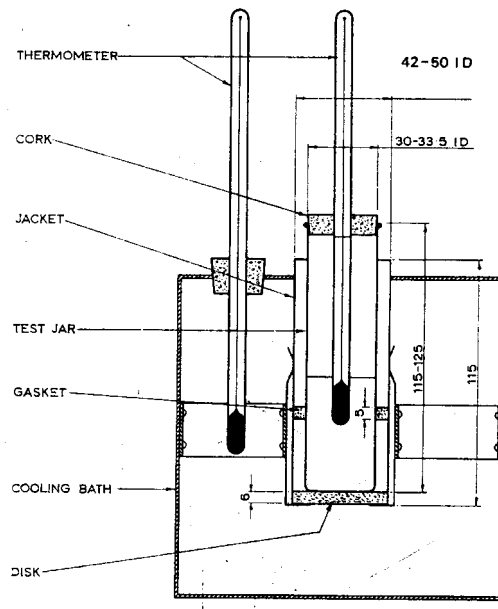

Figure 12. Cloud Point Apparatus

Pour Point

A second measure of the low temperature performance of diesel/biodiesel fuels is the pour point. The pour point is the lowest temperature at which a fuel sample will flow. Therefore, the pour point provides an index of the lowest temperature of the fuel's utility for certain applications. The pour point also has implications for the handling of fuels during cold temperatures. The standard procedure for measuring the pour point of fuels is ASTM D 97. A summary of the procedure steps is 1) the sample is cooled at a specified rate, 2) the sample is examined at 3°C intervals for flow, and 3) the lowest temperature at which sample movement is observed is noted. The repeatability of the pour point test is < 3°C and the reproducibility is < 6°C.

Copper Strip Corrosion

Many of the compounds in diesel fuel can be corrosive. The corrosiveness of a fuel is measured using the copper strip corrosion test, which is ASTM D 130. Copper and copper compounds tend to be particularly susceptible to chemical attack. The corrosivity of a fuel has implications on storage and use of the fuel. As an indicator of the tendency of a fuel to cause corrosion, polished copper strips are placed in the fuel for 3 hours at 50°C. Then the strips are washed in a solvent and compared to the descriptions in Table 6. The test results are given as a number followed by a letter. For example, a strip that was slightly tarnished with a dark orange color would be designated as "1b."

Table 6. Copper Strip Classifications

Classification	Designation	Description
1	Slight Tarnish	a. Light orange, almost the same as freshly polished strip b. Dark orange
2	Moderate Tarnish	a. Claret red b. Lavender c. Multicolored with lavender blue or silver, or both, overlaid on claret red d. Silvery e. Brassy or gold
3	Dark Tarnish	a. Magenta overcast on brassy strip b. Multicolored with red and green showing (peacock), but no gray
4	Corrosion	a. Transparent black, dark gray or brown with peacock green barely showing b. Graphite or lusterless black c. Glossy or jet black

<u>Fuel Stability Measurement</u>

Figure 13 shows part of the apparatus used for ASTM D 2274. Oxygen is bubbled through the fuel for 16 hours while the fuel is held at 95°C. Then, the fuel is filtered to measure the amount of any insolubles that are formed.
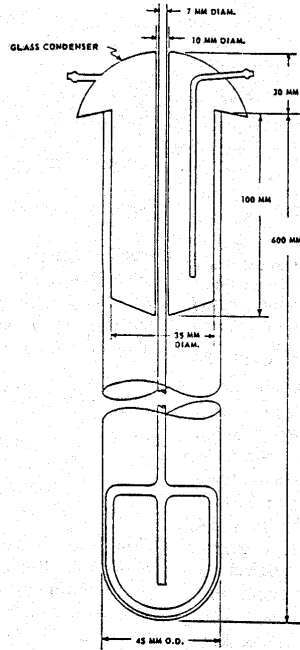

Figure 13. Glassware for ASTM D 2274

Lubricity is actually a very difficult property to characterize. In spite of the definition's attempt to separate the lubricity as a fluid property, it is also strongly dependent on the method used to measure it and on the characteristics of the solid surfaces being lubricated. For example, as friction occurs, small particles of the solid material may be removed and entrained in the lubricant. In some applications, these particles will be swept away by a flow of lubricant while in others, the particles stay in the vicinity of the surface contact. Particles that are present in the area of surface contact may act very differently. In some cases, they may act as an abrasive to increase wear while in other cases, the particles may shield the surface from further wear. When trying to characterize lubricity, it is important to use a measurement technique that correlates well with the actual lubrication situation. In the case of diesel fuel, the fuel acts as a lubricant for the finely fitting parts in the diesel fuel injection system. While all diesel fuel injection systems depend on the fuel to act as a lubricant, rotary pump style injection systems seem to be the most sensitive to fuel lubricity.

There are two methods that are commonly used to measure lubricity, the Scuffing Load Ball On Cylinder Lubricity Evaluator (SLBOCLE - ASTM D 6078-99) and the High

Frequency Reciprocating Rig (HFRR - ASTM D 6079-99). The apparatus used for the SLBOCLE test is shown in Figure 13. This test involves placing a steel ball bearing against a rotating steel ring whose lower edge is immersed in the test fluid. Weight is gradually applied to the ball until a "scuff" mark is seen on the rotating ring. The tangential force is also measured and the point of scuffing is indicated by a large increase in the friction coefficient. The EMA has indicated that a weight of 3150 grams is representative of an acceptable lubricity level. The higher this number, the better the fuel lubricity.
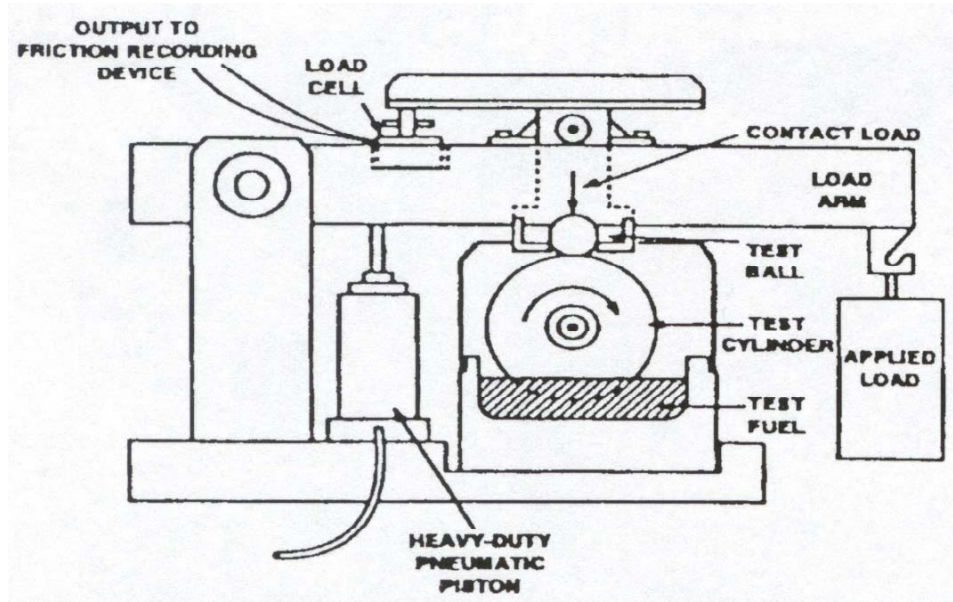

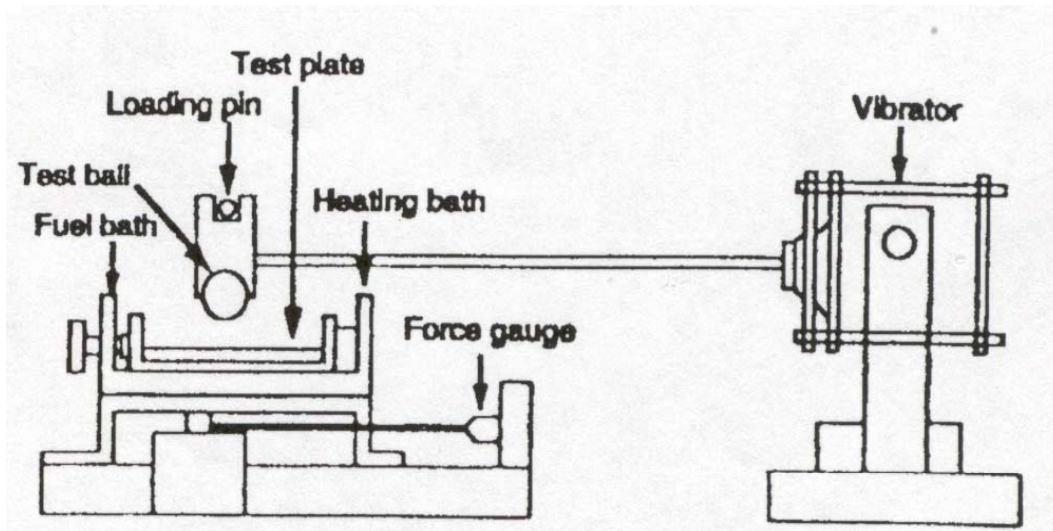**Figure 14. Scuffing Load Ball On Cylinder Lubricity Evaluator (SLBOCLE - ASTM D 6078-99)**

Figure 15. High Frequency Reciprocating Rig (HFRR - ASTM D 6079-99)

The HFRR test also uses a steel ball but in this case the ball is held against a stationary disk and the ball is reciprocated back and forth across the disk with a frequency of 50 hertz. This apparatus is shown in Figure 15. The applied load is 200g and the test duration is 75 minutes. The wear scar produced on the disk is measured and a scar diameter of less than 450 micron is considered to be acceptable.

Measurements of Lubricity

Schumacher and Adams [10th Biennial Bioenergy Conference – Bioenergy 2002, Boise, Idaho, Sept. 22-26, 2002] have measured the effect of low-level blends of soybean-based biodiesel on biodiesel that has been produced to meet 15 ppm sulfur levels. Figure 16 shows SLBOCLE results for No. 2 diesel fuel with small amounts of biodiesel. As little as 1% biodiesel could change the diesel fuel from an unacceptable level to an acceptable level.

Figure 17 shows the same effect for No. 1 diesel fuel that has also been treated to lower the sulfur contain to less than 15 ppm. In this case, the lubricity of the original No. 1 diesel fuel was so low that even 2% biodiesel was not able to bring the lubricity back up to the acceptable level of 3150 grams. However, the lubricity was greatly improved and it is unlikely that the engine would suffer damage from short term use at a lubricity level of 2880 grams.

	Diesel 2004 Tier	1/2% Biodiesel	1% Biodiesel	2% Biodiesel	100% Biodiesel
Grams	2100	2600	3400	3500	5450
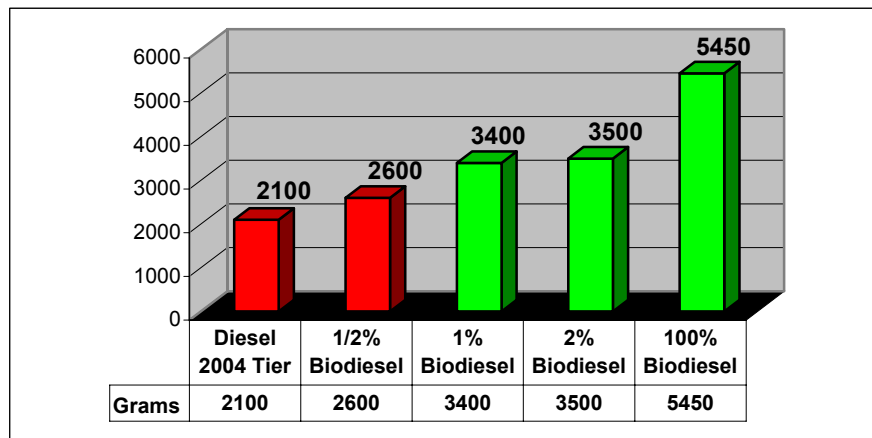
Figure 16. SLBOCLE for #2 Diesel 2004 Tier 2 Fuel, Biodiesel, and Biodiesel Blends
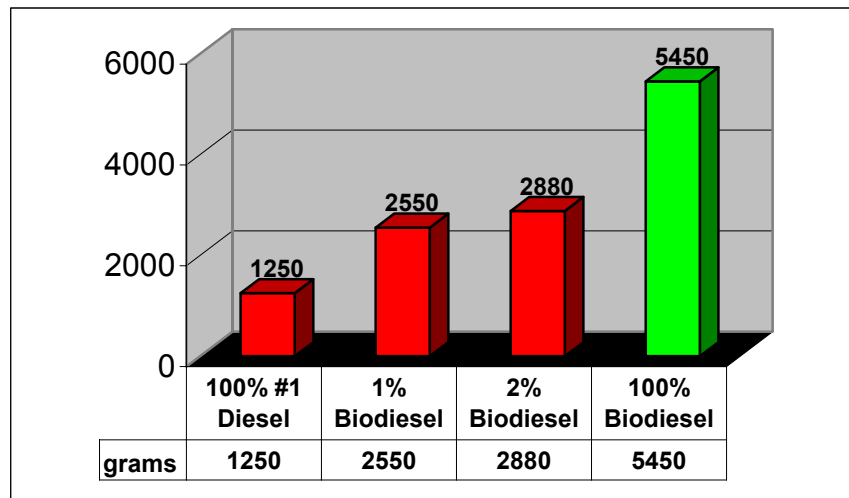
| grams | 1250 | 2550 | 2880 | 5450 |

Figure 17. SLBOCLE for #1 Diesel Fuel, Biodiesel, and Biodiesel Blends

5. Soap and Catalyst Measurement

Production of biodiesel using an alkali catalyst always produces some amount of soap. There will be more soap with recycled restaurant waste and animal fats and less with refined vegetable oils.

After the transesterification reaction is complete, the leftover catalyst and soap tend to concentrate in the glycerol phase. However, some soap and a small amount of catalyst may be left in the biodiesel phase. During process development, it can be useful to know the amount of soap formed, where the catalyst resides, and how effective the washing process is in removing these two compounds.

A simple titration procedure can be used to measure the amount of soap and catalyst. The basic procedure consists of titrating a sample of the phase to be analyzed, such as glycerol, ester, wash water, etc., with a 0.1 N solution of HCl to the phenolphthalein end point. This gives an estimate of the amount of catalyst. Then, a few drops of bromophenol blue indicator are added and the titration continued to the color change for that indicator. This gives an indication of the amount of soap.

In the first titration, the HCl neutralizes the alkali catalyst, so when the phenolphthalein indicates that the solution has become neutral, then all of the catalyst has been counted. Then, if the titration is continued, the HCl, as a strong acid, begins to split the soap molecules to free fatty acids and salt. When the pH reaches about 4.6, where the bromophenol blue changes color, then this indicates that the HCl has split all of the soap. It is now lowering the pH, so it has protons to donate since the soap has all been split.

The following procedure is a modified version of AOCS method Cc 17-79, soap in Oil.

1. Dissolve sample in 100 ml of acetone containing 2% distilled water. The amount of sample will depend on the expected level of catalyst and soap. Use 0.5 g of sample for crude glycerol, 5 g of sample for unwashed methyl esters, and 100 g of sample for washed methyl esters.
2. Add 2 ml of 1% phenolphthalein indicator (in isopropyl alcohol).
3. Titrate with 0.01 N hydrochloric acid until you get the phenolphthalein color change (red to clear). This indicates that you have neutralized the free catalyst in the sample. Designate this amount of solution as "A".
4. Add 1 ml of bromophenol blue indicator (0.4% in water). This indicator changes color at about pH = 4.5.
5. Titrate until the bromophenol changes from blue to yellow. This indicates that the pH is low enough that all of the soap should have been split into FFA and salt. The strong acid that we are adding (hydrochloric) is more strongly attracted to the metal ion on the soap than the fatty acid chain. So, the metal ion combines with the Cl from the hydrochloric acid to produce NaCl, and the hydrogen freed from the hydrochloric acid converts the fatty acid chain to a free fatty acid. Designate this quantity of solution as "B".

Now, the amount of HCl added during the first titration tells us how much free catalyst is in the sample and the amount added during the second titration tells us the amount of soap.

If you take the ml of HCl added for the first titration and do the following calculation:
["A" ml of 0.1 N HCl] x [1 liter/1000 ml] x [0.1 moles of HCl/liter] x [1 mole of KOH/mole of HCl] x [56.1 g/mole KOH] / [grams of sample] = grams of KOH/gram of sample

or

$$\frac{A \times 0.1 \times 56.1}{1000 \times W} = \text{grams of KOH catalyst/gram of sample}$$

This gives the amount of free catalyst in the sample, done here assuming the catalyst was KOH. You can substitute the appropriate molecular weight for other catalysts (KOH = 56.1, NaOH = 40.0, NaOCH$_3$ = 54.0).

If you take the ml of HCl for the second titration and do the following calculation:
["B" ml of additional 0.1N HCl added] x [1 liter/1000ml] x [0.1 moles of HCl/liter] x [1 mole of soap/mole of HCl] x [320.56 g/mole of soap] / [grams of sample] = grams of soap (as sodium oleate) per gram of sample.

Or

$$\frac{B \times 0.1 \times 320.56}{1000 \times W} = \text{grams of soap (as potassium oleate)/gram of sample}$$

This often expressed as ppm, so this number should be multiplied by one million. This calculation assumed the soap was potassium oleate. When using sodium catalysts, the molecular weight of sodium oleate is 304.4 g/mole. Oleic acid is a pretty good average compound for soybean oil but you might want to change it for rapeseed oil.

When the level of catalyst and soap are small, it is a good idea to use blank samples.. Just prepare a second beaker of the acetone-water solution but don't add any sample. Titrate the blank at the same time as the sample and subtract the quantities for the blank from the numbers from the sample.

6. Fatty acid composition, and total and free glycerol

Fatty acid composition. The most common fatty acids (and their methyl esters) are listed in Tables 7 and 8. There are numerous other fatty acids, but, the ones given here comprise the vast majority of those contained in biodiesel.

Table 7. Chemical Structure of Fatty Acids

Fatty acid (trivial name/rational name)	Structure	Common acronym	Methyl Ester (trivial name/rational name)
Palmitic acid / Hexadecanoic acid;	$R\text{-}(CH_2)_{14}\text{-}CH_3$	C16:0	*Methyl palmitate / Methyl hexadecanoate*
Stearic acid / Octadecanoic acid	$R\text{-}(CH_2)_{16}\text{-}CH_3$	C18:0	*Methyl stearate / Methyl octadecanoate*
Oleic acid / 9(Z)-octadecenoic acid	$R\text{-}(CH_2)_7\text{-}CH{=}CH\text{-}(CH_2)_7\text{-}CH_3$	C18:1	*Methyl oleate / Methyl 9(Z)-octadecenoate*
Linoleic acid / 9(Z),12(Z)-octadecadienoic acid;	$R\text{-}(CH_2)_7\text{-}CH{=}CH\text{-}CH_2\text{-}CH{=}CH\text{-}(CH_2)_4\text{-}CH_3$	C18:2	*Methyl linoleate / Methyl 9(Z),12(Z)-octadecadienoate*
Linolenic acid / 9(Z),12(Z),15(Z)-octadecatrienoic acid;	$R\text{-}(CH_2)_7\text{-}(CH{=}CH\text{-}CH_2)_3\text{-}CH_3$	C18:3	*Methyl linolenate / Methyl 9(Z),12(Z),15(Z)-octadecadienoate*

Table 8. Formula, Molecular Weight, and Properties of Fatty Acids and Their Methyl Esters

Fatty acid _Methyl ester_	Formula	Acronym	Molecular weight	Melting point (°C)	Cetane number
Palmitic acid _Methyl palmitate_	$C_{16}H_{32}O_2$ $C_{17}H_{34}O_2$	C16:0	256.428 _270.457_	63-64 _30.5_	— _74.5_
Stearic acid _Methyl stearate_	$C_{18}H_{36}O_2$ $C_{19}H_{38}O_2$	C18:0	284.481 _298.511_	70 _39_	— _86.9_
Oleic acid _Methyl oleate_	$C_{18}H_{34}O_2$ $C_{19}H_{36}O_2$	C18:1	282.465 _296.495_	16 _-20_	— _47.2; 55_
Linoleic acid _Methyl linoleate_	$C_{18}H_{32}O_2$ $C_{19}H_{34}O_2$	C18:2	280.450 _294.479_	-5°C _-35°C_	— _28.5; 42.2_
Linolenic acid _Methyl linolenate_	$C_{18}H_{30}O_2$ $C_{19}H_{32}O_2$	C18:3	278.434 _292.463_	-11 _-52 / -57_	— _20.6; 22.7_

The data in Table 8 indicates that two important properties of fatty compounds (melting point and cetane number) for fuel use vary with structure of the fatty acid or ester. For example, cetane numbers increase with increasing chain length and increasing saturation. Melting points also increase with increasing chain length and increasing saturation. Therefore, the fatty acid profile (composition) is the major factor influencing the fuel properties of a biodiesel fuel. Accordingly, analytical methods for its determination are of great significance.

The methyl esters are derived from the parent oil or fat by the _transesterification_ reaction. Note that triacylglycerols (the glycerol esters of fatty acids) are the major components of vegetable oils.

```
CH₂OOR                                                              CH₂OH
 |                               catalyst                             |
CHOOR       +      3 CH₃OH         →              CH₃OOCR    +      CHOH
 |                                                                    |
CH₂OOR                                                              CH₂OH
Triacylglycerol          Methanol                 Methyl ester       Glycerol
```
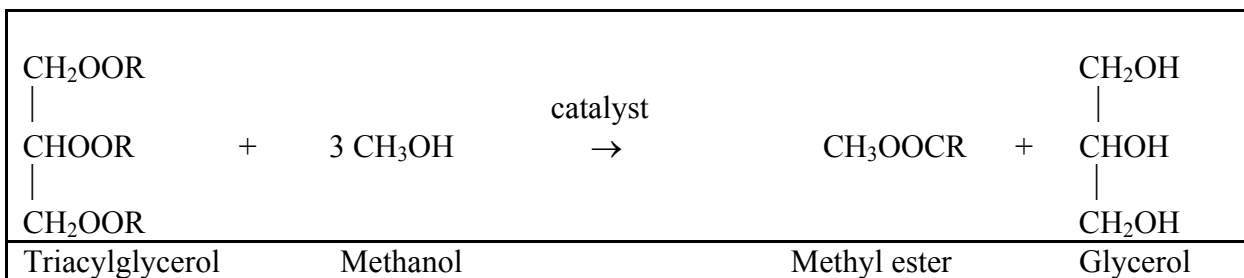
Figure 18.

The main reason why transesterification is conducted to produce biodiesel is that the viscosity of the parent vegetable oil or animal fat is an order of magnitude greater than that of the corresponding methyl esters (biodiesel). The high viscosity of triacylglycerols leads to operational problems such as engine deposits, etc. Other alcohols such as ethanol, propanol, or *iso*-propanol could be used for producing biodiesel, however, methanol is the least expensive alcohol and is therefore most commonly used for producing biodiesel. Therefore, this module will assume, unless mentioned otherwise, that methanol is the alcohol used in biodiesel production. Note that some analytical methods may require modification when using an alcohol other than methanol.

As in most chemical reactions, intermediates are formed during the course of the transesterification reaction. In case of vegetable oils or animal fats (triacylglycerols), it is probably not very surprising that *mono*- and *di*-acylglycerols are formed, i.e., partially reacted triacylglycerols.
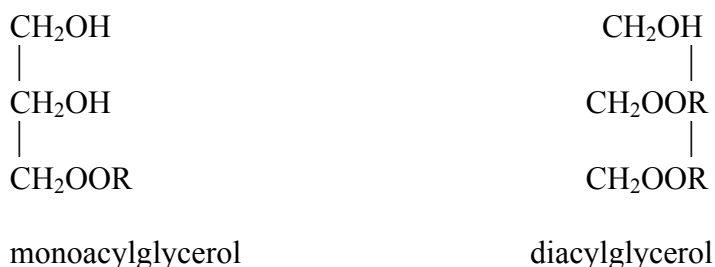
$$CH_2OH \qquad\qquad\qquad\qquad CH_2OH$$
$$| \qquad\qquad\qquad\qquad\qquad\quad |$$
$$CH_2OH \qquad\qquad\qquad\qquad CH_2OOR$$
$$| \qquad\qquad\qquad\qquad\qquad\quad |$$
$$CH_2OOR \qquad\qquad\qquad\qquad CH_2OOR$$

monoacylglycerol   diacylglycerol

Figure 19. Intermediate Products of Transesterification

Besides the acylglycerols, residual alcohol (methanol) and catalyst (usually KOH or NaOH) from the transesterification reaction can contaminate the final biodiesel product. Contaminants not resulting from the transesterification reaction, for example, non-fatty materials occcurring naturally in fats and oils, may also contaminate the final product.

This section will describe the analysis of biodiesel (fatty acid methyl esters) contaminated with glycerol and the various acylglycerols as free and total glycerine (the terms glycerine and glycerol can be used interchangeably in many cases although glycerol is preferable). The limiting values given in the ASTM standard for biodiesel, D 6751, are 0.02% (by wt.) for free glycerol, and 0.24% for total glycerol. Obviously, glycerol remaining in the biodiesel after purification is the free glycerin parameter. The three acylglycerols in combination with the free glycerol are the total glycerin parameter.

Generally, the analytical methods discussed in this module can be divided into three categories: chromatographic methods, spectroscopic methods, and physical-property-based methods. Chromatographic and spectroscopic methods can be combined (with a spectroscopic method automatically analyzing the effluent of chromatographic methods) to give what are often termed *hyphenated* methods. This term is a result of the fact that the names of the two methods are then combined through a hyphen.

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Chromatographic methods

Chromatographic methods are used to separate a mixture of compounds based on their physical properties. The major chromatographic methods are *gas chromatography* (GC) and *liquid chromatography* (LC), often termed *high-performance liquid chromatography* (HPLC).

In GC, the mixture is separated mainly by the boiling point and the structure (imparting a feature termed *polarity)* of the individual compounds. To carry out a GC analysis, the sample is usually dissolved in low concentrations in an organic solvent and then injected into the gas chromatograph. In some cases, a sample needs to be *derivatized* with a specific reagent in order to obtain a useful gas chromatogram. This is the case for biodiesel. Glycerol and the mono- and diacylglycerols contain free hydroxyl groups, causing these materials not to perform well in GC. Derivatization (in the case of biodiesel with a *silylating* reagent) improves their performance considerably. Derivatization can provide better resolution between compounds with similar properties.

After injection into the gas chromatograph, the sample is separated on a *column*. A column is a long, thin path (*capillary*) tube that contains a material with which the sample components interact more or less strongly depending on their structure (polarity!) while it is heated. Usually, the solvent used and, if applicable, residual derivatizing agent used for preparing the sample are the first materials to *elute* (i.e., come out) from the GC and will be registered by means of a *detector*. When the detector detects a material eluting from the column at a certain *retention time* (i.e., the time after which a compounds comes out from the column), this will be shown by a *peak* in the *chromatogram* (i.e, the record of the chromatographic analysis). Generally, the integrated value of the peak a amplitude over time is proportional to the amount of material causing them. This constitutes the usefulness of GC in quantifying the amounts of components in a mixture.

As indicated, the structure (polarity!) of the individual components and their boiling points are the major factors determining the retention time. Often, but not always, larger molecules will have longer retention times in GC.

Often *standards* are used in GC. They are known compounds which will indicate when compounds of a specific nature can be expected to elute. They are therefore very useful in establishing the nature of the compounds in a mixture.

For biodiesel, GC forms the basis of the standard ASTM D 6584, which is the prescribed method for measuring free and total glycerol. It determines the amount of glycerol (in derivatized form), mono- and diacylglycerols (both also in derivatized form), triacylglycerols, and methyl esters in a biodiesel sample. The derivatized glycerol is the first material to elute, followed sequentially by the methyl esters and the derivatized monoacylglycerols, diacylglycerols, and triacylglycerols. While many individual compounds can be separated by GC, often some overlap in elution time occurs in complex mixtures (see the chromatogram in ASTM D6584), especially when they are

major components with similar properties. On the other hand, to determine the amount of contaminants in biodiesel you actually do not need to know the complete fatty acid profile in form of the methyl esters. All that is required is the total amount of the specified contaminants relative to the methyl esters.

Details on the preparation of the samples and conducting the GC runs are given in the ASTM D 6584 standard. Manuals provided by the manufacturers provide information on how to operate a GC.

LC generally separates a mixture based on the solubility of its components in a solvent (or mixture of solvents) while passing the mixture through a column (similar to GC). It is usually conducted at room temperature. Since similar compounds have similar solubilities and interactions with column material, complex mixtures containing many different compounds will usually be separated by classes of compounds and not necessarily by individual compounds. There are modifications to LC to improve on this aspect but they will not concern us here. In the case of biodiesel, for example, methyl palmitate and methyl stearate (both being saturated long-chain methyl esters) will elute simultaneously in most systems. Many terms such as *detector*, *retention time*, etc. are also used in LC and have the same meaning as with GC.

LC can be as suitable as GC for determining the contaminants in biodiesel relative to the total amount of methyl esters. Free glycerol can be detected in fatty acid methyl esters by AOCS (American Oil Chemists' Society) Recommended Practice Ca 14b-96 entitled "Quantification of Free Glycerine in Selected Glycerides and Fatty Acid Methyl Esters by HPLC with Laser Light-Scattering Detection". However, it is not included in the standard ASTM D6751.

Spectroscopic methods

In contrast to chromatographic methods, spectroscopic methods analyze the intact sample at the same time, i.e., impurities contribute to the results and must be taken into consideration. However, when coupling spectroscopic methods to chromatographic methods, uncertainties remaining in the use of the latter are eliminated. The reason is that the (pure) compounds have obtained unique spectra. This information is related directly to the structure of the compound. Note that chromatographic methods only detect if a compound is eluting, not its identity or structure. The identity or structure needs to be established through the use of standards as far as possible. Thus, using a spectroscopic method of detection in combination with a chromatographic method yields more detailed information. However, it usually results in additional instrument costs and additional knowledge in interpreting the data.

The most common method in combination with chromatography is *mass spectrometry* (MS). The spectra in MS record how a compound is broken up into fragments by means of energy (usually a beam of electrons). The way a compound splits into fragments is characteristic of its structure. Any detailed discussion of this is beyond the scope of this course. It may be noted, however, that GC-MS, the combination of gas chromatography

with mass spectrometry, is currently the most commonly used hyphenated analytical technique in organic chemistry. Mass spectrometry can also be coupled to LC, yielding LC-MS.

Recently, stand-alone spectroscopic methods that have been used for biodiesel include *nuclear magnetic resonance* (NMR) and *near-infrared* (NIR) spectroscopy. In both cases, certain peaks characteristic for triacylglycerols and methyl esters in the spectra indicate how far the conversion of triacylglycerols to methyl esters (biodiesel) has progressed. NIR is especially easy to use and can give spectra in less than a minute. One of the advantages of these stand-alone methods is that no derivatization is needed.

Physical property-based methods

The difference in viscosity between the parent vegetable oil and the corresponding methyl esters can serve to monitor the progress of the transesterification reaction. Otherwise, physical property-based methods do not yield as much detailed analytical information as the other two categories of methods. It also appears that other physical properties may be suitable in a fashion similar to viscosity.

The following publication, prepared by one of the authors, provides an in-depth overview of biodiesel analytical methods. Knothe, G., "Analytical Methods Used in the Production and Fuel Quality Assessment of Biodiesel," ASAE Transactions, v. 44 (2), 2001, pp. 193-200.

Wet chemical methods

Fatty acid profile. The fatty acid profile can only be crudely determined by wet chemical methods. Wet chemical methods include the iodine and saponification values. The iodine value is based on the theoretical addition of iodine to the double bonds of fatty compounds. The iodine value is an indicator of the total amount of unsaturated fatty compounds in a sample. Otherwise, it does not give any information on the nature of the unsaturated compounds nor, of course, the saturated compounds. The saponification value is related to the average molecular weight of the sample of fatty compounds. It is probably best to use the iodine and saponification values in conjunction with each other. There are several wet chemical methods for each one, each having its advantages and limitations. Neither of these values is contained in the biodiesel standard ASTM D6751.

There are several wet-chemical AOCS methods for determining glycerol, for example, AOCS Official Method Ca 14-56 entitled "Total, Free and Combined Glycerol Iodometric - Periodic Acid Method". The LC method mentioned above appears preferable. Other methods deal with the determination of glycerol in specific products or under specific circumstances and are not applicable.

Generally, wet chemical methods are being replaced by the more sophisticated chromatographic, spectroscopic methods or hyphenated methods because of the superior information obtained. The wet chemical methods also are often more time-consuming as they can require complex sample preparation.

7. ASTM Methods for Determining The Chemical Properties of Biodiesel

Introduction

The instructional goals of this chapter are to provide an overview of the ASTM standard tests for determining:
      1. Acid value (or acid number)
      2. Phosphorus content
      3. Sulfur content
      4. Sulfated ash content, and
      5. Water and sediment

This presentation does not replace the need for a testing facility to have access to, and explicitly follow, the ASTM standard test methods for determining these properties.

Individual ASTM standards can be searched for, and purchased at, www.astm.org. They are also commonly found in a technical library reference section.

ASTM Methods for Key Biodiesel Properties:

Originally known as the American Society for Testing and Materials, ASTM International provides standards and methods that are accepted and used in research and development, product testing, quality control protocols, and commercial transactions. ASTM standard tests are explicit outlines of procedures and the apparatus necessary to carry out those procedures. In an effort to provide an accurate, yet concise module, these standards will be directly cited. The full titles of these ASTM standards are:

- <u>D 664</u> Standard Test Method for Acid Number of Petroleum Products by Potentiometric Titration
- <u>D 4951</u> Standard Test Method for Determination of Additive Elements in Lubricating Oils by Inductively Coupled Plasma Atomic Emission Spectrometry
- <u>D 5453</u> Standard Test Method for Determination of Total Sulfur in Light Hydrocarbons, Motor Fuels and Oils by Ultraviolet Fluorescence
- <u>D 874</u> Standard Test Method for Sulfated Ash from Lubricating Oils and Additives
- <u>D 2709</u> Standard Test Method for Water and Sediment in Middle Distillate Fuels by Centrifuge

All ASTM standards use a similar format. They are divided into sections that may or may not be present in all standards. Every section contained in each of these five standards is not covered, only those necessary to convey the general contents of the test method. These five standards all contain the following sections:
      <u>Scope</u> – discusses the materials and objects to which the test applies
      <u>Referenced Documents</u> – lists ASTM standards that are referred to in the standard
      <u>Summary of the Test Method</u> – brief discussion of test

> Significance and Use – discusses points pertaining to the test method
> Apparatus – detailed specifications for all equipment needed to perform the test
> Reagents – detailed specifications for all chemicals needed to perform the test
> Procedure – detailed instructions of performance of the test method
> Precision & Bias – discussion of the reliability and repeatability of the test
> Keywords – used in database searching

The standards also contain sections pertaining to concerns specific to each individual test.

ASTM D – 664 Determination of Acid Number by Potientiometric Titration (Biodiesel limit 0.80 mg of KOH/g sample)

Scope - This test method covers procedures for the determination of acidic constituents in petroleum products and lubricants that are soluble in mixtures of toluene and isopropanol. In B100 (biodiesel), the acid number is a measure of free fatty acids. The free fatty acids can lead to corrosion and are a symptom of water in the fuel or fuel oxidation.

Discussion - This test method determines the quantity of base that is required to titrate a sample from its initial reading to a reading corresponding to a basic buffer solution or an inflection point as specified in the test method. It also provides the additional information on the quantity of base required to titrate a sample from its initial reading to a reading corresponding to an acidic buffer solution or an inflection point, as specified in the test method. This quantity is reported as the *strong acid number*. The causes and effects of strong acids and the causes and effects of other acids can be very different. Therefore, this test method differentiates and reports the two values. Since biodiesel generally contains only weak acids, this distinction is not relevant. An alternative method that is simpler to perform and gives similar results is the American Oil Chemist's Society Official Method Cd 3a-63. This method uses phenolphthalein indicators to determine neutrality. However, since it is not included in ASTM D 6751, it should be used only for process development, not for verifying product quality.

Summary of test method - The sample is dissolved in a mixture of toluene and isopropanol that contains a small amount of water. The sample is titrated potentiometrically with alcoholic potassium hydroxide. The meter readings are plotted against the respective volumes of titrating solution and the end points are taken at well defined inflections in the resulting curve.

Terminology - Acid number is the quantity of base, expressed as milligrams KOH per gram of sample, required to titrate the sample to a specified end point.

Apparatus - Exacting specifications are given in the standard for the potentiometer, electrodes, stirrer, buret, titration beaker, and titration stand to be used. Specifications of an automatic titration apparatus accepted as an adequate substitute are also given.

Procedure for acid number and strong acid number - Small volumes of KOH are added to samples in alcohol solution while measuring the electrode potential in mV. A curve of KOH volume vs. potential is then plotted.

Detailed procedures for the manual and automatic titration methods are given, including blank titrations of solvent.

Calculations – The electrode potential curves are plotted as the volume of KOH needed to titrate the sample vs mV or pH. The end (inflection) point is chosen as the point at which the curve is most nearly vertical. A procedure is also given for curves without a definite inflection point. Figure 20 is an example of the titration curves that are produced using this method.

Acid number = 56.1M(A-B)/W
  where M = concentration of KOH (moles/L)
  A = volume of KOH used to reach end point corresponding to basic buffer (mL)
  B = volume corresponding to A for blank titration (mL)
  W = mass of sample (g)

Strong acid number = 56.1(CM + Dm)/W
  where C = volume of KOH used to reach end point corresponding to acidic buffer (mL)
  D = volume HCl used to reach end point corresponding to C (mL)
  m = concentration of HCl (moles/L)

The acid number and strong acid number are to be reported as follows:
  Acid number (Test Method D 664) = *result*
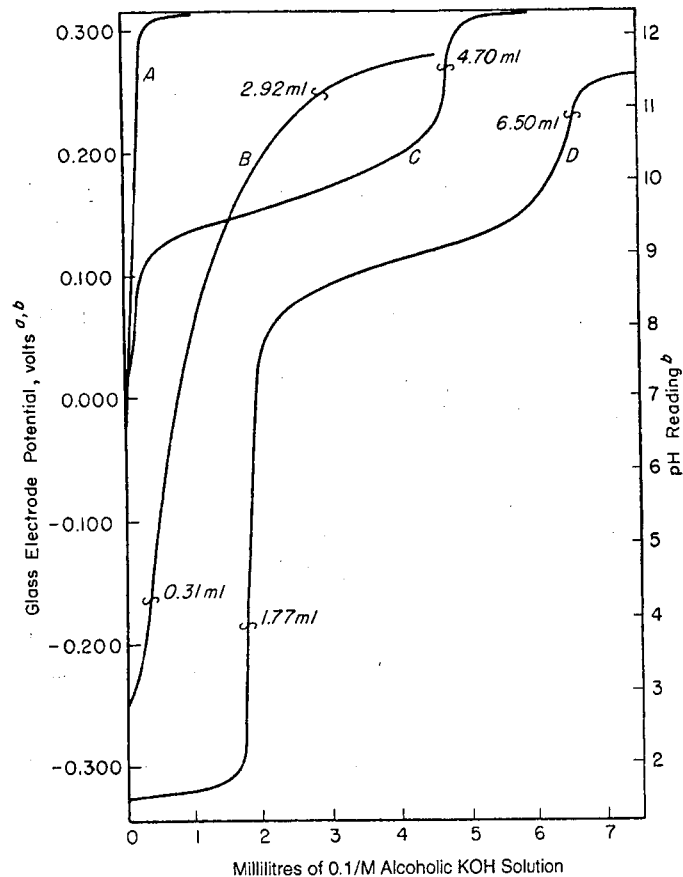 Strong acid number (Test Method D 664) = *result*

Figure 20. Sample Titration Curve for ASTM D 664

Curve A – Blank of 125 ml of titration solvent.

Curve B – 10.00 g of used crankcase oil, plus 125 ml of titration solvent. Since no sharp inflections are apparent, the end points are chosen at the meter readings obtained with the two non-aqueous buffer solutions.

Curve C – 10.00 g of oil containing a weak acid plus 125 ml of titration solvent. The end point is chosen as the point at which the curve is most nearly vertical.

Curve D – 10.00 g of oil containing weak and strong acids, plus 125 ml of titration solvent. The end points are chosen as the points at which the curve is most nearly vertical.

ASTM D – 4951: Standard Test Method for Determination of Additive Elements in Lubricating Oils by Inductively Coupled Plasma Atomic Emission Spectrometry (Biodiesel limit – 0.001 mass % phosphorus)

Scope - This test method covers the quantitative determination of barium, boron, calcium, copper, magnesium, phosphorus, sulfur and zinc in unused lubricating oils and additive packages.

Additive packages are blends of individual additives, which can act as detergents, antioxidants, antiwear agents, etc. Many additives contain one or more elements covered by this test, which was developed for testing oil additives to meet industry specifications. In biodiesel processing, this test is used primarily for the determination of phosphorus content. The presence of phosphorus may be due to the incomplete refining of vegetable oil or bone and proteins remaining from the rendering process in recovering animal fats.

This test can also be used to determine the presence of sulfur if the ICP instrument used can operate at a wavelength of 180 nm. However, this test is not the recommended method for sulfur determination when testing to meet the specifications of B100 biodiesel as outlined in ASTM D6751. That test method (D5453) is discussed later in this module.

Summary of method – A sample is diluted (1% to 5% by mass of oil in solvent) with mixed xylenes or kerosene. An internal standard is included in the solvent and calibration standards. The solutions are run through the ICP. By comparing emission intensities of the sample to those of the standards, concentrations of the elements present are determined.

Apparatus – Required and optional apparatus are listed in the apparatus section of the standard. The primary instrument is an atomic emission spectrometer that is equipped with a quartz inductively-coupled plasma (ICP) torch and r-f generator to form the plasma. Also needed are an analytical balance and solution containers. Optional equipment includes a peristaltic pump, solvent dispenser, vortexer and ultrasonic homogenizer. Mixed xylenes, o-xylene, or kerosene can be used as solvents. Base oil (U.S.P. white oil or a lubricating base oil free of analytes) is required for the internal standard solution (several possible internal standards are listed). Calibration standard solutions containing known concentrations of the elements being determined are prepared in accordance with the ASTM Practice D 4307.

Phosphorus is the only element of interest when this test method is applied to biodiesel production specifications.

Sampling – The objective of sampling is to obtain a test specimen that is representative of the entire quantity. Lab samples are recommended to be taken in accordance to ASTM D4057, which provides procedures for sampling petroleum products from a wide variety of containers. The specific sampling technique can affect the accuracy of this test.

Preparation of apparatus – Recommendations for the operation of the atomic emission spectrometer, ICP excitation source and peristaltic pump are given in this section of the test method. There are several different adequate instruments so the recommendation is to follow the manufacturer's instructions regarding operation of the ICP unit.

Preparation of test specimens – Procedures are given for the weighing out and dissolution of oil sample specimens

Preparation of calibration standards – The user is given freedom to determine the identity and concentration of calibration standards. Guidelines are given for solution preparation and instrument check standards are suggested.

Internal Standardization – This section of the test method outlines the required use of internal standards.

Calibration – A comprehensive discussion of calibration curves and the application of internal standards to those curves in ICP spectrometry is provided in this section. After compensating for the internal standard, the calibration curve is a plot of the intensity of emission for the analyte vs. analyte concentration.

Analysis – Samples should be analyzed using the same procedure as the calibration standards. An instrument check standard should be run after every fifth test specimen to ensure that the instrument is still calibrated.

Quality assurance – QA/QC is required by this standard. When QA/QC protocols are already established in the testing facility, these may be followed. If no QA/QC protocols exist, the appendix to this standard (Appendix X1) can be used. Appendix X1 discusses the use of quality control charts to determine if the procedure is under statistical control.

Calculations –
$$C = S(W_1+W_2+W_3)/W_1$$
where C = analyte concentration in sample (mass %)
S = analyte concentration in test specimen (mass %)
W_1 = sample mass (g)
W_2 = diluent mass (g)
W_3 = base oil mass (g)

Generally, ICP software performs this calculation automatically.

Reporting – Report mass % to three significant figures.

ASTM D – 5453: Standard Test Method for Determination of Total Sulfur in Light Hydrocarbons, Motor Fuels and Oils by Ultraviolet Fluorescense
(Biodiesel limit – 0.05 mass %)

Scope – This test method covers the determination of total sulfur in liquid hydrocarbons. It is applicable to naphthas, distillates, oils, gasoline, diesel, biodiesel and jet fuel.

Some process catalysts used in petroleum and chemical refining can be poisoned when trace amounts of sulfur are present. Biodiesel feedstocks typically have very little sulfur, but this test is an indicator of contamination of protein material and/or carryover catalyst or neutralization material.

Summary of method – The sample is inserted into a high temperature combustion tube where sulfur is oxidized to sulfur dioxide (SO_2) in an oxygen rich atmosphere. Sample combustion gases are next exposed to UV light. The SO_2 is excited, from which fluorescence is emitted as it returns to its stable state. The fluorescence is detected by a photomultiplier tube and the resulting signal is a measure of the amount of sulfur contained in the sample.

Apparatus – Required and optional apparatus are discussed in this section of the standard. Primary pieces of equipment include a Quartz Combustion Tube and a UV Fluorescence Detector. Sample input systems can either be a boat inlet system or a direct injection design. Another necessity for this test is a furnace capable of holding a temperature (1075±25°C) sufficient to pyrolyze all of the sample and oxidize sulfur to SO_2.

Also required is a dryer tube or permeation dryer to remove water vapor that is produced in the pyrolysis tube. Water must be removed prior to the fluorescence measurement by the detector. The test method allows the option of using a self calibrating analyzer.

Reagents – High purity, dry oxygen is used in the pyrolysis tube. Solvents such as toluene, xylene, isooctane are needed to prepare standards and dilute samples. A sulfur-containing compound such as dibenzothiophene, butyl sulfide, or benzothiophene can be used for calibration standards.

Procedures for mixing appropriate standard are provided. QC samples, representative of the samples of interest, can be used to check the validity of the testing process.

Sampling – The objective of sampling is to obtain a test specimen that is representative of the entire quantity. Lab samples should be taken in accordance with ASTM D4057, which provides procedures for sampling petroleum products from a wide variety of containers. The specific sampling technique can affect the accuracy of this test.

Preparation of Apparatus – This section of the standard test method discusses the typical operating conditions including sample inlet rate, furnace temperature, oxygen flow rate, and carrier gas flow rate.

Calibration and Standardization – This section provides the procedure for preparation of a calibration curve. Three different suggestions for curve preparation are given, based on the anticipated sulfur concentration in the sample. Again, procedures for both direct injection and inlet boat delivery into the apparatus are provided.

Procedure – The procedure allows for either gravimetric or volumetric dilution of samples and either direct injection or inlet boat delivery into the apparatus. It requires repeat instrument calibration prior to reanalysis of the sample. Also, each test specimen must be measured three times and the average response must be calculated.

Calculation – Either analyzers calibrated using a standard curve or analyzers using a self calibration routine are accepted. Sulfur content can be calculated using either the mass or volume of the test sample for either type of analyzer used.

> Using analyzer with standard curve:
> (using sample mass)   Sulfur (ppm) = $(I-Y)/SMK_g$
> > I = integrated detector response (counts)
> > Y = y-intercept of standard curve (counts)
> > S = slope of standard curve (counts/µg Sulfur)
> > M = mass of test specimen (g)
> > K_g = gravimetric dilution factor;mass sample/mass sample+solvent (g/g)
>
> (using sample volume) Sulfur (ppm) = $(I-1000Y)/SVK_V$
> > V = volume of test specimen (g)
> > K_V = volumetric dilution factor; mass sample/volume sample+solvent (g/mL)
>
> Using self calibrating analyzer:
> (using sample mass) Sulfur (ppm) = $1000G/MK_g$
> G = sulfur found in test specimen (µg)
> > M = mass of sample solution injected (mg)
> (using sample volume) Sulfur (ppm) = $1000G/VD$
> > D = density of sample in solution (mg/µL)
> > V = volume of sample solution injected (µL)

Quality Control – Required confirmation of the performance of the test procedure is performed by analyzing a quality control sample. When QA/QC protocols are already established in the testing facility, these may be followed. If no QA/QC protocols exist, the appendix to this standard (Appendix X1) can be used. Appendix X1 discusses the use of quality control charts to determine if the procedure is under statistical control.

Appendices – As stated above, App. X1 discusses QA/QC techniques. App. X2 discusses direct injection system input. App. X3 discusses boat inlet system input.

ASTM D – 874: Standard Test Method for Sulfated Ash from Lubricating Oils and Additives (Biodiesel limit – 0.02 mass %)

Scope – This test method determines the amount of mineral ash remaining after a fuel is burned. For biodiesel, this test is an important indicator of the quantity of residual metals in the fuel that could come from the catalyst used in the esterification process. The lower limit of this test is 0.005 mass% sulfated ash.

Terminology – Sulfated ash is the residue remaining after the sample has been carbonized, and the residue subsequently treated with sulfuric acid and heated to constant weight.

Summary of the Test Method – 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 oxidation of carbon is complete. The ash is then cooled, re-treated with the sulfuric acid, and heated at 775°C to constant weight.

Apparatus – Necessary for the test method are a furnace capable of maintaining 775±25°C and evaporating dishes or crucibles. A 50 or 100 mL crucible is recommended for samples containing more than 0.02 mass% sulfated ash. A 120 or 150 mL crucible is recommended for samples containing less than 0.02 mass% sulfated ash.

Reagents – Required reagents include concentrated sulfuric acid and 50 volume% sulfuric acid in water. Isopropanol and toluene may be needed if the sample contains sufficient moisture to cause foaming and loss of material from the dish/crucible.

Sampling – It is recommended to follow the instructions in ASTM Standard Practice D4057.

Procedure – The general steps required to complete this test are:
- Prepare the sample dish by heating at 775 C for at least 10 min, cooling, and weighing;
- Weigh in the sample to be determined;
- Heat the sample until the contents will sustain a flame and burn the sample until there is no further smoke or fumes;
- If the sample has sufficient moisture to foam, discard the sample, and follow procedures given to reduct the moisture content before proceeding;
- Cool the sample, add water and sulfuric acid, and heat until no further fumes are evolved;
- Place the dish in a furnace and heat at 775 C until oxidation of the carbon is complete. Continue the cooling, acidification and heating process until successive weighings differ by no more than 1.0 mg.

Calculation – Sulfated ash is calculated as a percentage of the original sample.

Sulfated Ash (mass%) = w/W*100
w = mass of sulfated ash (g)
W = mass of sample used in test (g)

Report – Report the result to the nearest 0.001 mass% for samples below 0.02 mass% and to the nearest 0.01 mass% for higher levels.

ASTM D 2709 Standard Test Method for Water and Sediment in Middle Distillate Fuels by Centrifuge (Biodiesel limit – 0.05 volume %)

Scope – This test method covers the determination of the volume of free water and sediment in middle distillate fuels having viscosities at 40°C in the range of 1.0 to 4.1 mm^2/s and densities in the range of 770 to 900 kg/m^3. This test is a measure of cleanliness of the fuel. For B100 biodiesel it is particularly important because water can react with the esters to make free fatty acids and can support microbial growth in storage tanks.

Summary of Test Method – A 100 mL sample of undiluted fuel is centrifuged in a tube readable to 0.005 mL. After centrifugation, the volume of water and sediment which has settled into the tip of the centrifuge tube is read to the nearest 0.005 mL and recorded as the volumetric percent water and sediment by centrifuge.

Apparatus – Centrifuge which can be controlled to give a relative centrifugal force (rcf) of 800±60 at the tip of the tubes. A table is provided that relates centrifuge diameter and rpm to rcf. Specifications and suggested suppliers for centrifuge tubes are listed.

Sampling - It is recommended to follow the sampling instructions in ASTM Standard Practice D4057. The sample for a laboratory test will normally be an aliquot of a much larger sample taken for full or partial specification testing.

Procedure – 100 mL of a well-shaken sample is poured into a centrifuge tube and spun at 800±60 rcf for 10 minutes. The volume of combined water and sediment present at the bottom of the tube is recorded to the nearest 0.005 mL.

Report – Report the volume of the combined water and sediment read from the tube as a percentage of the total sample, since 100 mL of sample was used. Results lower than 0.005% may be reported as either 0 or 0.005 volume%.

Apparatus – Centrifuge which can be controlled to give a relative centrifugal force (rcf) of 800±60 at the tip of the tubes. A table is provided that relates centrifuge diameter and rpm to rcf. Specifications and suggested suppliers for centrifuge tubes are listed.

<u>Sampling</u> - It is recommended to follow the sampling instructions in ASTM Standard Practice D4057. The sample for a laboratory test will normally be an aliquot of a much larger sample taken for full or partial specification testing.

<u>Procedure</u> – 100 mL of a well-shaken sample is poured into a centrifuge tube and spun at 800±60 rcf for 10 minutes. The volume of combined water and sediment present at the bottom of the tube is recorded to the nearest 0.005 mL.

<u>Report</u> – Report the volume of the combined water and sediment read from the tube as a percentage of the total sample, since 100 mL of sample was used. Results lower than 0.005% may be reported as either 0 or 0.005 volume%.

Summary:

This module discusses accepted ASTM Standard Test Methods for five B100 biodiesel specifications. It did not seek to give a fully detailed description or in any way replace the actual standards as published by ASTM.

This module provided an overview of the following ASTM standard tests, emphasizing their application to B100 biodiesel specifications:

1. determining acid value (or acid number) of sample
2. phosphorus content in sample
3. sulfur content in sample
4. sulfated ash content in sample
5. water and sediment present in sample

Laboratory Exercises

Measurement of Acid Value, Soap, AOCS Total Glycerol, Cloud Point and Pour Point

Acid Value

We will be using the American Oil Chemists' Society method to measure acid value. It is equivalent to the method prescribed in the ASTM standard and easier to perform. The laboratory instructor will demonstrate the titration technique used for acid value. Use the technique to measure the Acid Value of the 3 oils provided.

1. Crude Soybean Oil
2. Restaurant waste oil
3. Yellow grease from animal fat

Fuel	Acid Value (mg KOH/g)
Crude Soy Oil	
Restaurant waste oil	
Yellow grease from animal fat	

Soap and Catalyst Content

We will be using a modification of the American Oil Chemists' Society method to measure soap content. The modification allows us to measure residual catalyst, also. It should be noted that neither the catalyst or soap content of the biodiesel is limited in the ASTM specification. However, if significant amounts of these substances are present, the biodiesel will not meet the sulfated ash specification. The laboratory instructor will demonstrate the titration technique used for catalyst and soap level. Use the technique to measure the residual catalyst and soap content of the 3 fuels provided.

1. Unwashed biodiesel from crude Soybean Oil
2. Unwashed biodiesel from restaurant waste oil
3. Unwashed biodiesel from yellow grease from animal fat

Fuel	Catalyst amount (ppm)	Soap amount (ppm)
Unwashed biodiesel from C S O		
Unwashed biodiesel from Restaurant waste		
Unwashed biodiesel from Yellow grease		

AOCS Total Glycerol Measurement

Ordinarily, measurement of total glycerol remaining in a sample of biodiesel requires a gas chromatograph, and this is the technique specified in the ASTM Standard for biodiesel. However, a so-called "wet-chemical" technique is available that can give accurate values of the total glycerol. This technique takes more time and requires a higher level of care and attention from the technician, but it does not require any expensive pieces of equipment. While verification that a given sample of biodiesel meets the ASTM specification requires a GC analysis, this technique provides data that is very suitable for process development and quality control. The laboratory instructor will demonstrate the technique used for measuring the total glycerol. Use the technique to measure the total glycerol of the 3 fuels provided.

1. Unwashed biodiesel from crude Soybean Oil
2. Unwashed biodiesel from restaurant waste oil
3. Unwashed biodiesel from yellow grease from animal fat

Fuel	Total glycerol (%)
Unwashed biodiesel from C S O	
Unwashed biodiesel from Restaurant waste	
Unwashed biodiesel from Yellow grease	

Cloud Point and Pour Point

The Cloud Point and Pour Point are standard ASTM test procedures for determining the cold flow properties of fuels. The laboratory instructor will demonstrate the measurement of these two properties using the temperature-controlled bath and a sample of biodiesel. Use the technique to measure the Cloud Point and Pour Point of the 3 fuels provided.

1. Biodiesel from crude Soybean Oil
2. Biodiesel from restaurant waste oil
3. Biodiesel from yellow grease from animal fat

Fuel	Cloud Point, ºC	Pour Point, ºC
Biodiesel from C S O		
Biodiesel from Restaurant waste		
Biodiesel from Yellow grease		

8. Review of Biodiesel Production Techniques

This module provides an overview of the steps in the production of biodiesel from preparation of the feedstock to the recovery and purification of the fatty acid esters (biodiesel) and the co-product glycerol (also called glycerin). We will review several chemistries used for esterification and different approaches to product purification. The emphasis throughout the module will be the quality control issues at each process step and the effects of off-specification materials and process changes on the final product. The analytical laboratory will be involved in feedstock characterization and acceptance, determination if the final product meets ASTM D-6751, monitoring of the quality of the glycerol co-product, and monitoring of process effluent streams. Detailed analytical results are critical for creating process material balances, verifying product quality, and resolving any operating problems in the process. The analytical person for the plant is a monitor, process assistant, and, occasionally, a detective, ensuring top quality products and error-free operation.

Specifically, this section will review feedstock requirements, transesterification processes, and glycerol separation and recovery.

Feedstocks Used in Biodiesel Production

The reaction to produce biodiesel consumes the following reactants in the approximate amounts shown:
- Triglygeride (triacylglycerol) or fats and oils (e.g. 100 kg soybean oil)
- Primary alcohol (e.g. 10 kg methanol)
- Catalyst (e.g. 0.3 kg sodium hydroxide)
- Neutralizer (e.g. 0.25 kg sulfuric acid)

The choice of the fat or oil to be used in producing biodiesel is both a process chemistry decision and an economic decision. With respect to process chemistry, the greatest difference among the choices of fats and oils is the amount of free fatty acids that are associated with the triglycerides. Most vegetable oils have a low percentage of associated free fatty acids, while animal tallows and yellow grease can have as much as 15 percent free fatty acids. Some of the recovered waste materials can have in excess of 40 percent free fatty acid content. The free fatty acid content affects the amount and extent of feedstock preparation necessary to use a particular reaction chemistry.

Triglycerides for biodiesel can come from a wide variety of sources including the following:
- Vegetable oils such as soybean, canola, palm, etc.
- Rendered animal fats such as beef tallow, lard, chicken fat
- Rendered greases such as yellow grease (multiple sources)
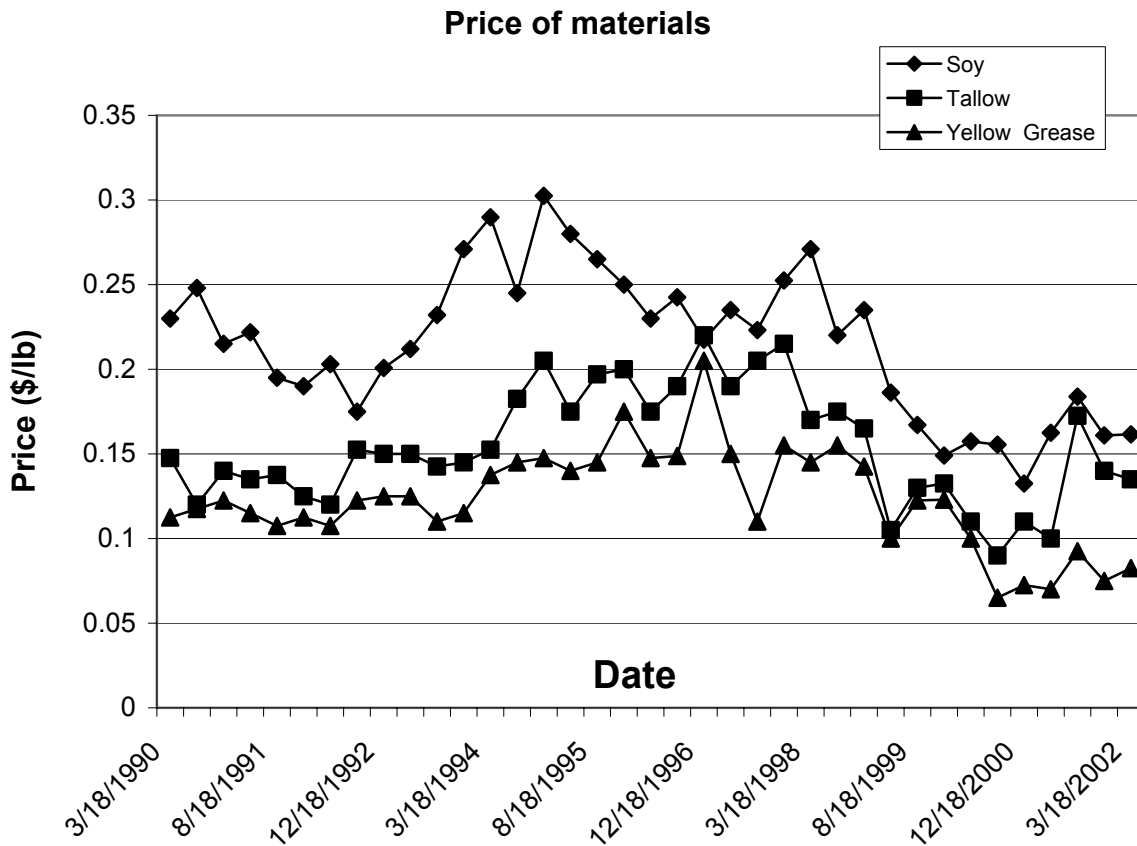- Recovered materials such as brown grease, soapstock, etc.

Price of materials

Figure 21. Price of biodiesel feedstocks.

Suitable feedstocks for a base-catalyzed process require FFA < 1 % and preferably < 0.05 %. The feedstock must be dry, preferably < 0.5 % moisture.

The most commonly used alcohol for biodiesel production is methanol, although ethanol also is used. A key quality factor for the alcohol is water content. Water affects the extent and rate of the esterification reaction. Unfortunately, all the lower alcohols are hygroscopic to some degree.

Catalysts may be either base, acid, or enzyme materials. The most commonly used catalyst material used at this time is sodium hydroxide. Acid catalysts are more commonly used for the esterification of free fatty acids. The base catalysts are highly hygroscopic and they form chemical water when dissolved in the alcohol reactant. Neutralizers are used to remove the base or acid catalyst from the product biodiesel and glycerol, prior to a water wash.

Price Patterns for Biodiesel Sources

The price of the triglyceride raw material accounts for 70 to 85 percent of the final cost of the biodiesel product. This is the dominant component in biodiesel economics. The price differential between the most common feedstocks is relatively constant, but the prices for all of the materials show considerable variability over time as shown in Figure 21. In addition, there are an increasing number of incentive programs to aid in establishing the biodiesel industry that have the effect of lowering the effective cost of one or more of the raw materials for a limited time. An average price of $ 0.15 per pound of triglyceride is recommended as a base cost for evaluating a proposed venture.

Table 9. Properties of primary alcohols

Alcohol	Molecular Weight	Density g/cc	Boiling Point °C
Methanol	32.04	0.792	64.7
Ethanol	46.07	0.789	78.4

Primary Alcohol Sources

Both methanol and ethanol have been used to make biodiesel. As long as the product esters meet ASTM 6751, it does not make any chemical difference which alcohol is used in the process. However, since the reaction to form the esters is on a molar basis, but we purchase these reactants on a volume basis, their properties make a significant difference in raw material price.

It takes three moles of alcohol to react completely with one mole of triglyceride. Today (December 2002), one gallon of methanol costs $ 0.61. That gallon contains 93.56 gram-moles of methanol; at a cost of $ 0.00652 per gram-mole. By contrast, a gallon of ethanol, at the current price of $ 1.45 per gallon for fuel-grade ethanol, costs $ 0.02237 per gram-mole. In addition, a base catalyzed process typically uses an operating mole ratio of 6:1 mole of alcohol rather than the 3:1 ratio required by the reaction stoichiometry. This means that the excess alcohol must be recovered to minimize operating costs and environmental impacts. The difference in boiling point between the two alcohols makes the methanol considerably easier to recover than the ethanol. These two factors are the reason that even though methanol is more toxic, it is the preferred alcohol for producing biodiesel. Methanol has a flash point of 10 °C, while the flash point of ethanol is 8 °C, so both are considered highly flammable. Methanol does have a somewhat variable pricing structure. When the production of MTBE was mandated for the reduction of emissions from gasoline engines in the winter, there was a significant expansion in world capacity for methanol. The excess capacity and crash in demand led to methanol prices of $ 0.31 per gallon in early 2002. However, in late July, 2002, the production/consumption levels regained equilibrium and the methanol price doubled back to the more typical value of $ 0.60 per gallon.

The alcohol quality requirements are that it be un-denatured and anhydrous.

Catalyst Options

A number of approaches are available for ensuring the transesterification reaction occurs quickly enough to be practical. These options can be classified into the following groups:
•Base Catalysts such as NaOH, KOH, and NaMeO
•Acid Catalysts such as H_2SO_4, H_3PO_4, and $CaCO_3$
•Lipase Enzymes (activity depends on source).
•Non-catalyst options such as supercritical proceeses, and co-solvent systems.

Base catalysts are used for essentially all vegetable oil biodiesel production. The initial free fatty acid content is generally low and the water content is also generally low. Tallows, and greases with a free fatty acid content greater than about 1 % must be pretreated to either remove the FFA or convert the FFA to esters before beginning the base catalyzed reaction. Otherwise, the base catalyst will react with the free fatty acids to form soap and water. The soap formation reaction is very fast and goes to completion before any esterification begins. Base catalyzed reactions are relatively fast, with residence times from about 5 minutes to about 1 hour, depending on temperature, concentration, mixing and alcohol:triglyceride ratio.

Acid catalyst systems are characterized by slow reaction rates and high alcohol:TG requirements (20:1 and more). Generally, acid catalyzed reactions are used to convert FFAs to esters, or soaps to esters as a pretreatment step for high FFA feedstocks. Residence times from 10 minutes to about 2 hours are reported.

Lipase catalyzed reactions have the advantage of producing only esters and pure glycerol. The enzyme reactions are highly specific and chemically clean. Because the alcohol can be inhibitory to the enzyme, a typical strategy is to feed the alcohol into the reactor in three steps of 1:1 mole ratio each. The reactions are very slow, with a three step sequence requiring from 4 to 40 hours, or more. The reaction conditions are modest, from 35 to 45 °C.

The non-catalyst options are designed to overcome the reaction initiation lag time caused by the extremely low solubility of the alcohol in the TG phase. One approach that is nearing commercialization is the use of a co-solvent, tetrahydrofuran, to solubilize the methanol. The result is a fast reaction, on the order of 5 to 10 minutes, and no catalyst residues in either the ester or the glycerol phase. The THF co-solvent is chosen, in part, because it has a boiling point very close to that of methanol. This system requires a rather low operating temperature, 30°C.

Another non-catalytic approach is the use of a high (42:1) alcohol to oil ratio. Under supercritical conditions (350 to 400 °C and > 80 atm or 1200 psi). The reaction is complete in about 4 minutes.

Each of these processes is described in more detail below.

Base Catalyzed Processes

Base catalyzed processes dominate current commercial production. These reactions are relatively fast but are sensitive to water content and free fatty acids. The typical alcohol used is methanol with a 6:1 molar ratio (100% excess). Typical base concentrations are 0.3 to 1.5% based on the weight of oil. When sodium methoxide is used, the concentration can be 0.5% or less.

Essentially all of the current commercial operations use base catalyzed reactions. Most use NaOH as the catalyst. There are some operations that use KOH, in spite of the higher cost, because the potassium can be precipitated as K3PO4, a fertilizer, when the products are neutralized using phosphoric acid. This can make meeting water effluent standards a bit more difficult because of limits on phosphate emissions.
The typical alcohol:TG mole ratio for batch reactions and sequential batch reactions is 6:1. There have been reports that continuous flow systems operate better with a ratio of 8:1.

Sodium methoxide, usually as a 25 % solution in methanol, is a more powerful catalyst on a weight basis than the mixture of NaOH and methanol. This appears to be, in part, the result of the negative effect of the chemical water produced *in situ* when NaOH and methanol react to form sodium methoxide.
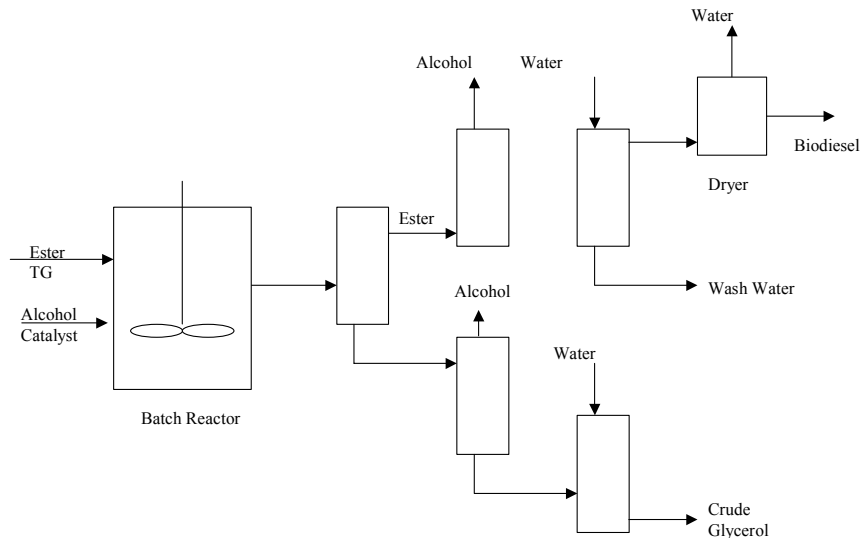

Figure 22. Batch processing of biodiesel

The classical method for producing alcohol esters in to use a batch, stirred tank reactor as shown in Figure 22. Alcohol to triglyceride ratios from 4:1 to 20:1 (mole:mole) have been reported, with a 6:1 ratio most common. The reactor may be sealed or equipped with a reflux condenser. The operating temperature is usually about 65 °C, although temperatures from 25 to 85 °C have been reported.

Thorough mixing is necessary at the beginning of the reaction to bring the oil, catalyst and alcohol into intimate contact. Towards the end of the reaction, less mixing can help increase the extent of reaction by allowing the inhibitory product, glycerol, to phase separate from the ester – oil phase. Completions of 85 to 94 % are reported. Some groups use a two-step reaction, with glycerol removal between steps, to increase the final reaction extent to 95+ percent. Higher temperatures and higher alcohol:oil ratios also can enhance the percent completion. Typical reaction times range from 20 minutes to more than one hour.

A popular variation of the batch process is the use of continuous stirred tank reactors (CSTRs) in series. The CSTRs can be varied in volume to allow for a longer residence time in CSTR 1 to achieve a greater extent of reaction. After the initial product glycerol is decanted, the reaction in CSTR 2 is rather rapid, with 98+ completion not uncommon.

An essential element in the design of a CSTR is sufficient mixing input to ensure that the composition throughout the reactor is essentially constant. This has the effect of increasing the dispersion of the glycerol product in the ester phase. The result is that the time required for phase separation is extended.
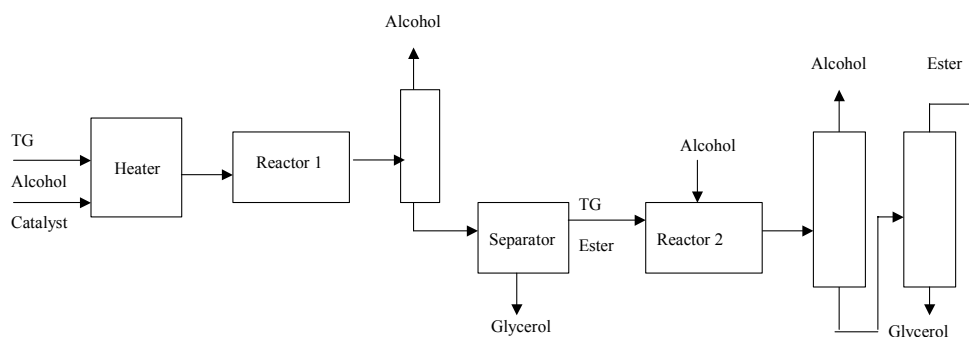

Figure 23. Plug flow reactor

There are several processes that use intense mixing, either from pumps or motionless mixers, to initiate the transesterification reaction. Instead of allowing time for the reaction in an agitated tank, the reactor is tubular. The reaction mixture moves through this type of reactor in a continuous plug, with little mixing in the axial direction. This type of reactor, called a plug-flow reactor (PFR), behaves as if it were a series of small CSTRs chained together.

The result is a continuous system that requires rather short residence times, as low as 6 to 10 minutes, for near completion of the reaction. The PFRs can be staged, as shown in Figure 23, to allow decanting of glycerol. Often this type of reactor is operated at an elevated temperature and pressure to increase the reaction rate.**Acid Catalyzed Processes**
Acid catalyzed processes are used for direct esterification of free fatty acids in a high FFA feedstock, or to make esters from soapstock. A typical flow diagram for pretreating high FFA feedstocks is prior to transesterification is shown in Figure 24. If the feedstock contains a high FFA content, the process requires water removal during the reaction.

Very high alcohol to fatty acid ratios, about 40:1, are required and acid amounts equal to 5 to 25% of the FFA level may be needed.
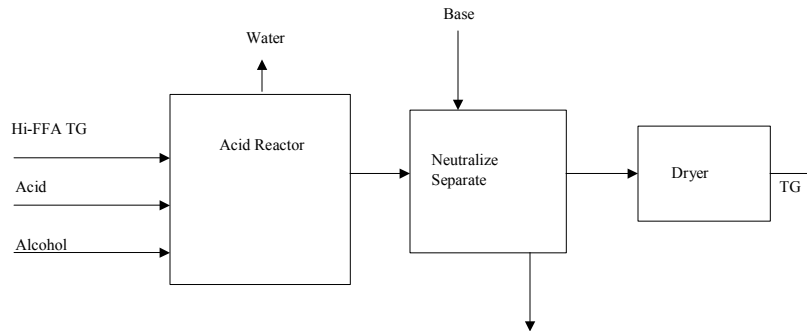

Figure 24. Acid catalyzed esterification

Base-High FFA Soapstock Removal

An alternative approach to utilization of high FFA feedstocks is to use a base catalyst to deliberately form soap from the FFAs. As shown in Figure 25, the soap is recovered, the oil dried, and then used in a conventional base catalyzed system.
This strategy can lead to a false sense of economy. If the soapstock is discarded, the effective price of the feedstock is increased in inverse proportion to the percentage of remaining oil. The soapstock can, however, be converted into esters by using an acid catalyzed reaction. The problem with this strategy is that the soapstock system contains a large amount of water that must be removed before the product esters can meet the biodiesel standard.
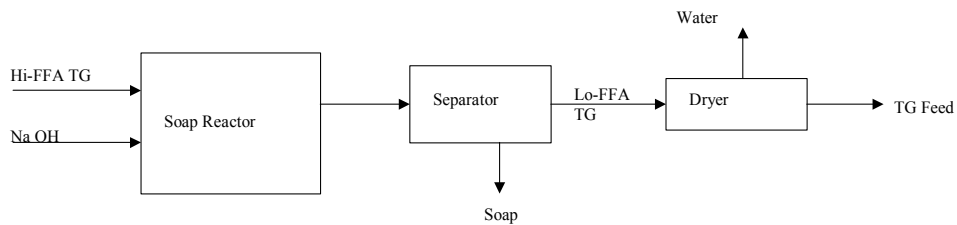

Figure 25. Removal of fatty acids with caustic

A variation of the base-catalyzed system that avoids the problem of high FFAs is the use of a fixed bed, insoluble base catalyst as shown in Figure 26. An example of this system, using calcium carbonate as the catalyst has been demonstrated at the bench-scale.
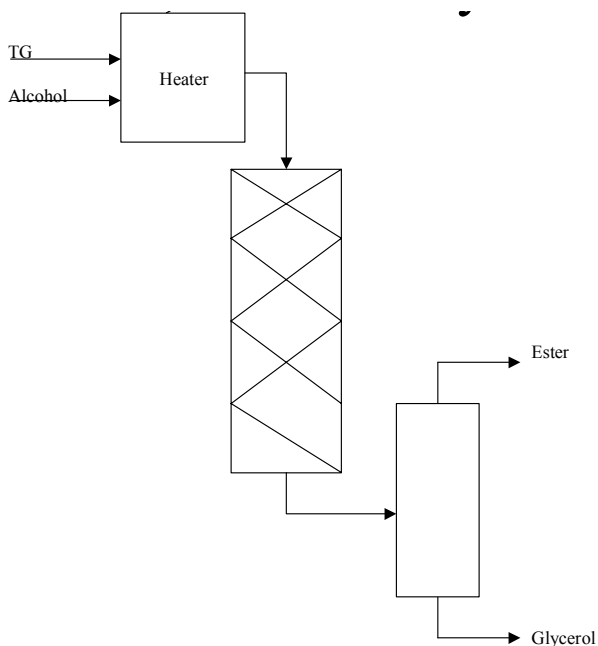
TG
Alcohol
Heater
Ester
Glycerol

Figure 26. Heterogeneous catalyzed process

Non-Catalytic Systems
Esterification is a three-step reaction sequence:
- Induction phase
- Rate limiting phase
- Glycerol inhibition phase

Base and acid catalysts serve as solubilizers to speed the induction reaction. Other approaches have been used to accelerate the reaction including cosolvents and supercritical systems.

The Biox Co-solvent Process, shown in Figure 27, uses an additional solvent that dissolves both in the alcohol and the oil to overcome the initial slow reaction rate caused by alcohol-oil immiscibility. Tetrahydrofuran was chosen as the co-solvent because it has a boiling point nearly identical to methanol. After the reaction is complete, the excess methanol and the tetrahydrofuran co-solvent is recovered in a single step.

The ester-glycerol phase separation is clean and the final products are catalyst- and water-free. The equipment volume has to be larger for the same quantity of final product because of the additional volume of the co-solvent.

Another approach to increasing the reaction rate is to use supercritical temperatures and pressures. When a solvent is subjected to temperatures and pressures in excess of its critical point, there are a number of unusual properties exhibited. There no longer is a distinct liquid and vapor phase, but a single, fluid phase present. Solvents containing a

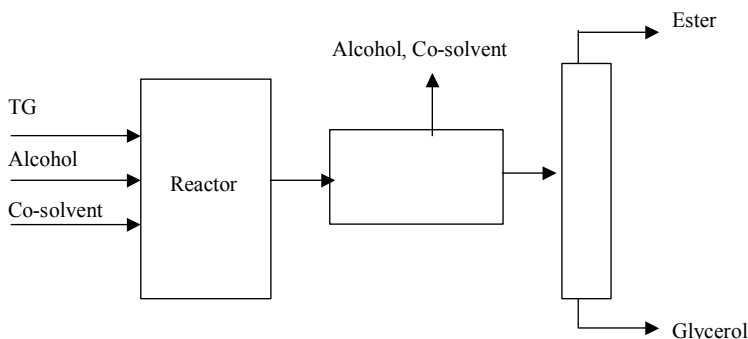hydroxyl (OH) group, such as water or primary alcohols, take on the properties of super-acids.

Figure 27. A typical cosolvent process

A schematic of how this process could be implemented in a biodiesel production system is shown in Figure 28.

An intriguing process has been demonstrated in Japan, where oils in a very large excess of methanol have been subjected to very high temperatures and pressures for a short period of time. The result is a very fast (3 to 5 minute) reaction to form esters and glycerol. The reaction must be quenched very rapidly so that the products do not decompose. The reactor used in the work to date is a 5 ml cylinder that is dropped into a bath of molten metal, and then quenched in water. Clearly, while the results are very interesting, the scale-up to a useful process may be quite difficult.

Glycerol Recovery Steps

To recover glycerol as a usable product requires separation from the esters phase. Although methanol has some activity as a cosolvent, the solubility of glycerol in the ester is very low. Usually the glycerol can be removed by gravity separation or by centrifugation. At this point the glycerol still contains most of the catalyst, soaps, and methanol. The soap and catalyst can be removed by acidulation, which produces salts, water and free fatty acids. The FFAs are insoluble and rise to the top of the glycerol where they can be removed. Ion exchange columns can also be used to remove this material.

Finally, the water and any other remaining impurities need to be removed. This can be accomplished by vacuum distillation followed by filtering with activated carbon.
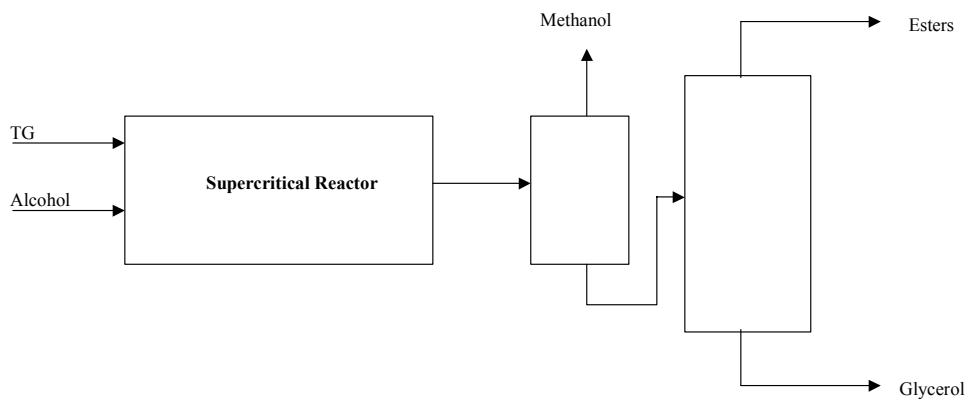
Figure 28. A supercritical biodiesel production system

Summary

There are multiple operating options available for making biodiesel. The technology choice is a function of desired capacity, feedstock type and quality, alcohol recovery, and catalyst recovery. The dominant factor in biodiesel production is the feedstock cost, with capital cost contributing only about 7 % of the product cost.

9. The ASTM Specification for Biodiesel Fuel

Introduction

The ASTM system is the basis for defining product specifications and measurement methods for most segments of the fuels and industrial products market in the U.S.. ASTM D 6751 – 02 sets forth the specifications that must be met for a fatty acid ester product to carry the designation "biodiesel fuel" or "B100". Products that meet the specification, by implication, will perform properly as a compression ignition fuel either as B100 or in blends with any petroleum-derived diesel fuel defined by ASTM Specification D 975 Grades 1-D, 2-D, and low sulfur 1-D and 2-D.

The instructional goals for this chapter are:

1. Become familiar with the structure of ASTM Specification and Methods documents.
2. Learn the Specifications for B100 fuel.
3. Introduce the methods used to measure the performance parameters for B100 fuel.

ASTM Specification Structure:

All ASTM Specifications have the same basic format. The "Scope" section describes the specific materials and applications that are covered by the Specification. The "Referenced Documents" section lists all of the ASTM Standards and Methods that are used in conducting the tests to verify that the material meets the specifications of the Standard. The methods provide detailed equipment requirements and experimental methodologies to be used for each parameter measured.

The "Terminology" section consists of a set of definitions explicit to the Standard. The methods to be used for obtaining and protecting samples, test methods, the required property values to meet the standard (typically in the form of limits), and the required units for reporting results are presented as "Requirements".

"Test Methods" is a listing of the required test methods specified for each property to be measured. Often a given test method will involve a number of additional ASTM Specifications and/or Methods to correctly carry out the procedure. In some cases, such as ASTM 6751, there will be appendices to the Standard that specify additional equipment requirements or methods that are not currently a part of the ASTM approved methods.

"Workmanship" describes additional precautions to be followed in conducting the testing. The "Key Words" are included as an aid to cross-referencing and for data-base searches.

Definition of Biodiesel

Biodiesel is defined in the standard as a fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats, designated B100.

A "mono-alkyl ester" is the product of the reaction of a straight chain alcohol, such as methanol or ethanol, with a fat or oil (triglyceride) to form glycerol (glycerin) and the esters of long chain fatty acids. Biodiesel can be used as B100 (neat) or in a blend with petroleum diesel. A blend of 20 % biodiesel with 80 % petrodiesel, by volume, is termed "B20". A blend of 2 % biodiesel with 98 % petrodiesel is " B2", and so on.

Table 10. ASTM D 6751 – 02 Requirements

Property	Method	Limits	Units
Flash point, closed cup	D 93	130 min	° C
Water and sediment	D 2709	0.050 max	% volume
Kinematic viscosity, 40 ° C	D 445	1.9 – 6.0	mm^2/s
Sulfated ash	D 874	0.020 max	wt. %
Total Sulfur	D 5453	0.05 max	wt. %
Copper strip corrosion	D 130	No. 3 max	
Cetane number	D 613	47 min	
Cloud point	D 2500	Report to customer	° C
Carbon residue	D 4530	0.050 max	wt. %
Acid number	D 664	0.80 max	mg KOH/g
Free glycerin	D 6584	0.020	wt. %
Total glycerin	D 6584	0.240	wt. %
Phosphorus	D 4951	0.0010	wt. %
Vacuum distillation end point	D 1160	360 °C max, at T-90	% distilled
Storage stability	To be determined	To be determined	To be determined

The flash point is defined as the "lowest temperature corrected to a barometric pressure of 101.3 kPa (760 mm Hg), at which application of an ignition source causes the vapors of a specimen to ignite under the specified conditions of test." This test, in part, is a measure of residual alcohol in the B100. The flash point is also a determinant for

flammability classification of materials. B100's typical flash point is > 200 ° C, classifying it as "non-flammable".

Water and sediment is a test that "determines the volume of free water and sediment in middle distillate fuels having viscosities at 40 °C in the range 1.0 to 4.1 mm^2/s and densities in the range of 700 to 900 kg/m^3." This test is a measure of cleanliness of the fuel. For B100 it is particularly important because water can react with the esters, making free fatty acids, and can support microbial growth in storage tanks.

Kinematic viscosity: "the resistance to flow of a fluid under gravity". [Equal to the dynamic viscosity/density.] The kinematic viscosity is a basic design specification for the fuel injectors used in diesel engines. Too high a viscosity, and the injectors do not perform properly.

Dynamic viscosity – 'ratio between applied shear stress and rate of shear of a liquid."

Density – "the mass per unit volume of a substance at a given temperature."

Sulfated ash – "The residue remaining after a sample has been carbonized, and the residue subsequently treated with sulfuric acid and heated to a constant weight." This test monitors the mineral ash residual when a fuel is burned. For biodiesel, this test is an important indicator of the quantity of residual metals in the fuel that came from the catalyst used in the esterification process.

Total sulfur – "This method covers the determination of total sulfur in liquid hydrocarbons, boiling in the range from approximately 25 to 400 ° C, with viscosities between approximately 0.2 and 20 cSt (mm^2/s) at room temperature." Vegetable oil feedstocks typically have very little sulfur, but this test is an indicator of contamination of protein material and/or carryover catalyst material or neutralization material from the production process.

Copper strip corrosion – " [for the] detection of the corrosiveness to copper of fuels and solvents." This test monitors the presence of acids in the fuel. For B100, the most likely source of a test failure would be excessive free fatty acids, which are determined in accordance with an additional specification.

Cetane number – "a measure of the ignition performance of a diesel fuel obtained by comparing it to reference fuels in a standardized engine test." Cetane for diesel engines is analogous to the octane rating in a spark ignition engine. It is a measure of how the fuel will ignite in the engine. For B100, the cetane number can be very accurately predicted using the ester's composition. It is unlikely that an individual producer will ever run cetane tests on-site.

Cloud point – "The temperature at which a cloud of wax crystals first appears in a liquid when it is cooled down under conditions prescribed in this test method." The cloud point is a critical factor in cold weather performance for all diesel fuels. The chemical

composition of some biodiesel feedstocks leads to a B100 that may have higher cloud points than desired. The cloud point, however, is another parameter that can be predicted accurately with knowledge of the esters composition, but producers are advised to be able to perform this test.

Carbon residue – "In petroleum products, the part remaining after a sample has been subjected to thermal decomposition." The carbon residue is a measure of how much residual carbon remains after combustion. This is particularly important in diesel engines because of the possibility of carbon residues clogging the fuel injectors. The most common cause of excess carbon residues in B100 is an excessive level of total glycerin. Total glycerin is also measured directly using an additional procedure specified in this Standard.

Acid number – "The quantity of base, expressed as milligrams of potassium hydroxide per gram of sample, required to titrate a sample to a specified end point." The acid number is a direct measure of free fatty acids in B100. The free fatty acids can lead to corrosion and may be a symptom of water in the fuel.

Free glycerin – glycerin present as molecular glycerin in the fuel. Free glycerin results from incomplete separation of the ester and glycerin products after the esterification reaction. This can be a result of incomplete washing and may be accompanied by incomplete alcohol removal and a lowered flash point. The free glycerin is a source of carbon deposits in the engine because of incomplete combustion.

Total glycerin – "is the sum of free and bonded glycerin." Bonded glycerin – "is the glycerin portion of the mono-, di-, and triglyceride molecules." Elevated total glycerin values are indicators of incomplete esterification reactions and predictors of excessive carbon deposits in the engine. The terms "glycerin" and "glycerol" are used interchangeably.

Phosphorus – "This test covers the quantitative determination of barium, calcium, copper, magnesium, phosphorus, sulfur, and zinc in unused lubricating oils and additive packages." In the case of B 100, phosphorus can come from incomplete refining of the vegetable oil and from bone and proteins encountered in the rendering process.

Vacuum distillation end-point – "This test covers the determination, at reduced pressures, of the range of boiling points for petroleum products that can be partially or completely vaporized at a maximum liquid temperature of 400 ° C." Petroleum fractions have tens to hundreds of individual compounds mixed together. The distillation curves are used to characterize the broad chemistry of a given crude oil source. In B100 there are at most ten different esters present, and they can be identified using gas or liquid chromatography. The same chromatograph that determines free and total glycerin can determine the esters composition in the B100. This composition allows calculation of the T-90 point for the fuel, without having to perform the testing for every batch of product. The "T-90" point is the temperature at which 90 percent of the liquid volume has been distilled.

Storage stability – All fuels are subject to degradation over time when they are stored. This degradation may be due to microbial action, water intrusion, air oxidation, etc. The standard and the test methods for determining storage stability for B 100 are still in the development stage within the ASTM process.

ASTM Testing Procedures

ASTM Standards are based upon the use of a number of ASTM Methods to perform the property measurements. The Methods provide very explicit directions with respect to the equipment, the measurements, and the data analysis. Standardization of procedure and reproducibility of results among laboratories is the goal of the process.
Each test method outlines a specific procedure to perform a property measurement, and specifies the equipment to be used and the data analysis techniques to be followed. The goal of the Methods is to define procedures that will give identical results for the same sample in any laboratory that follows the ASTM procedures in making the measurement.

It is common for a Method to reference a number of additional Standards and Methods. In order to conform with ASTM requirements, all elements incorporated into a given test must meet all of the Standards and Methods of that test.

Summary:

This module describes the key elements in ASTM Specifications and Standard Test Methods. ASTM Specification D 6751 – 02, the specification of B 100 (biodiesel) fuel is described in detail and key properties of B 100 are discussed in terms of their tests and specifications.

10. Lab Safety, MSDS and "Right to Know"

Introduction

A biodiesel production facility always involves handling hazardous materials such as methanol and strong bases. In most cases, the facility will include a quality control laboratory that will also handle hazardous materials depending on the analytical methods practiced in the laboratory. It is important that anyone considering entering the biodiesel industry be aware of the need for laboratory safety.

This chapter outlines general principles and Federal regulations concerning basic laboratory safety, Material Safety Data Sheets (MSDS) information sheets, and Right-to-Know requirements.

Most people who work in the laboratory setting find discussions of safety tedious, but definitely understand the need for them. All have heard general safety guidelines numerous times before. A safe lab environment is best achieved by the application of common sense, common courtesy, and keeping things as simple as possible. While some basic lab safety issues will be addressed, it is assumed that anyone working in the lab has been trained in basic safety measures previously.

Specific Federal regulations pertaining to an employer's obligation to laboratory personnel exist under OSHA regulations. These obligations will be outlined.

Laboratories or producers of chemical hazards or wastes also have to follow Community Right-to-Know regulations with regards to public notification of possible environmental concerns.

The instructional goals for this chapter are:
1. Review basic laboratory safety practices;
2. Present a synopsis of employer obligations for OSHA compliance and reporting; and,
3. Describe company requirements under the Community Right-to-Know regulations.

Due to the legal and technical nature of these topics, this presentation in no way will provide the basis for performing duties as a facility Safety Officer or Compliance Officer. Specialized training by a certified instructor is required.

OSHA Requirements

Lab safety is covered by the OSHA Occupational Exposure to Hazardous Chemicals in Laboratories Standard (Title 29, Code of Federal Regulations, Section 1910.1450). In the appendix of that section, noted as non-mandatory but widely accepted, reference is made to the National Research Council publication **Prudent Practices for Handling Hazardous Chemicals in Laboratories** concerning chemical hygiene in laboratories. The terms "chemical hygiene" and "lab safety" are essentially interchangeable.

OSHA Hazard Communication Standard (Title 29, Code of Federal Regulations, Section 1910.1200) requires Material Safety Data Sheets (MSDS) for all chemicals used in an industrial facility. MSDS's are provided by manufacturers when they ship chemicals. They contain information that allows users to be aware of the physical properties and possible hazards associated with the use a chemical.

Just as the OSHA HazCom requires employers to keep their employees informed, Right-to-Know requires users and producers of chemicals to keep the public informed of possible hazards. It is required under the Emergency Planning and Community Right-to-Know Act (EPCRA).

OSHA Definition of Hazardous Chemical

The OSHA Occupational Exposure to Hazardous Chemicals Standard applies to all employers engaged in the laboratory use of hazardous chemicals. "Hazardous chemical" means a chemical for which there is statistically significant evidence, based on at least one study conducted in accordance with established scientific principles, that acute or chronic health effects may occur in exposed employees.

OSHA standards as covered in other sections of 29CFR1910 obviously still apply, unless they are superceded by more specific requirements of this standard. This definition does not apply to uses of hazardous chemicals outside of the laboratory.

Specific requirements of the OSHA Lab Safety Standard include:
- Permissible Exposure Limit - PEL - For laboratory uses of OSHA regulated substances, the employer shall assure that laboratory employees' exposures to such substances do not exceed the permissible exposure limits specified.
- Employee exposure - Employers shall perform initial and periodic monitoring of PELs if there is reason to believe that exposure limits routinely exceed the action level. Employees must be notified of monitoring results.
- Respirators - Where the use of respirators is necessary to maintain exposure below permissible exposure limits, the employer shall provide, at no cost to the employee, the proper respiratory equipment.
- Medical consultation - The employer shall provide all employees who work with hazardous chemicals an opportunity to receive medical attention performed by or under the direct supervision of a licensed physician. This attention shall be provided without cost to the employee, without loss of pay and at a reasonable time and place.
- Records - The employer shall retain a written record of the physician's opinion concerning the exposure.
- Information and training - The employer shall provide employees with information and training to ensure that they are apprised of the hazards of chemicals present in their work area.
- Hazard identification - Hazards shall be labeled, and the MSDS shall be made available to employees.
- Chemical hygiene plan - A chemical hygiene plan (lab safety manual) is required to be developed specifically for each lab. Among its contents should be general safety

considerations, standard procedures involving the use of hazards, requirements for adequate ventilation, and designation of personnel responsible for the implementation of the plan. Recommendations for preparation of a hygiene plan are given by the NRC.

National Research Council Lab Safety Recommendations

<u>Prudent Practices for Handling Hazardous Chemicals in Laboratories</u> is listed as a non-mandatory recommended reference in the OSHA Lab Safety Standard. It is a publication of the National Research Council. The book is cited because of its wide distribution and acceptance and because of its preparation by members of the laboratory community through the sponsorship of the National Research Council.

However, none of the recommendations given modify any requirements of the lab safety standard. The publication deals with both safety and chemical hazards, while the laboratory standard is concerned primarily with chemical hazards. An outline of its contents, similar to that listed in following slides, is actually included in the OSHA Lab Safety Standard appendix.

General Principles
- <u>Exposures</u> - It is prudent to minimize all chemical exposures. Because few laboratory chemicals are without hazards, general precautions for handling all laboratory chemicals should be adopted, rather than specific guidelines for particular chemicals. As a rule, skin contact with chemicals should be avoided. Methanol, a primary ingredient in biodiesel, can enter the body through the skin and accumulate to toxic levels. Other compounds, such as the strong bases and acids used as catalysts, can cause burns or eye injury if contact occurs.
- <u>Avoid underestimation of risk</u> - For work with substances which present special hazards, special precautions should be taken. One should assume that any mixture will be more toxic than its most toxic component and that all substances of unknown toxicity are toxic.
- <u>Ventilation</u> - The best way to prevent exposure to airborne substances is to prevent their escape into the working atmosphere by use of hoods and other ventilation devices. Within the production facility, methanol vapors should be captured or contained and vents should be equipped with scrubbers.
- <u>Chemical hygiene plan</u> - A mandatory chemical hygiene plan (lab safety manual) designed to minimize exposures is needed. It should be a regular, continuing effort, not merely a standby or short-term activity. Its recommendations should be followed in academic teaching laboratories, as well as by full-time laboratory workers.
- <u>PEL and TLV</u> - The Permissible Exposure Limits (PEL) of OSHA and the Threshold Limit Values (TLV) of the American Conference of Governmental Industrial Hygienists should not be exceeded.

Responsibility

The Chief Executive Officer has ultimate responsibility for chemical hygiene within the institution and must, with other administrators, provide continuing support for institutional chemical hygiene. The Chemical Hygiene Officer works with administrators and other employees to develop and implement appropriate chemical hygiene policies and practices. The Laboratory Supervisor has overall responsibility for chemical hygiene in the laboratory. The laboratory worker is responsible for developing good personal chemical hygiene habits.

Laboratory Facility

The laboratory facility should be designed to function as a laboratory, with adequate ventilation, storage space, lab sinks, safety shower, and eye wash, in addition to appropriate fire safety apparatus. The facility should be kept clean and well maintained. Work conducted and its scale must be appropriate to the physical facilities available.

Chemical Hygiene Plan

The chemical hygiene plan (lab safety manual) should contain procedures covering the following topics:
- Chemical procurement and storage - Before a substance is received, information on proper handling, storage, and disposal should be known to those who will be involved. Chemical inventories should be separated into compatible groups and appropriate storage provided.
- Housekeeping, Maintenance, and Inspections - Formal housekeeping and chemical hygiene inspections should be held semiannually; informal inspections should be continual. Safety equipment should be inspected regularly. (e.g., every 3-6 months).
- Medical Program - Regular medical surveillance should be established to the extent required by regulations. Personnel trained in first aid should be available during working hours and an emergency room with medical personnel should be nearby.
- Protective Apparel and Equipment - Protective apparel compatible with the required degree of protection for substances being handled, an easily accessible drench-type safety shower, an eyewash fountain, fire extinguisher, respiratory protection, fire alarm and telephone for emergency use should be available nearby.

The chemical hygiene plan (lab safety manual) should contain procedures covering the following topics:
- Records - Accident and medical records should be kept. Chemical Hygiene Plan records should document that the facilities and precautions were compatible with current knowledge and regulations. Inventory and usage records for high-risk substances should be kept.
- Signs and Labels - Emergency telephone numbers, location signs for safety showers, eyewash stations, and exits should be posted. Identity labels, showing contents should be on all containers (including waste receptacles).

- Spills and Accidents - A written emergency plan and spill control policy should be established and communicated to all personnel. All accidents or near accidents should be carefully analyzed.
- Information and Training Program - Assure that all individuals at risk are adequately informed about the work in the laboratory, its risks, and what to do if an accident occurs.
- Waste Disposal Program - The waste disposal program should specify how waste is to be collected, segregated, stored, and transported and include consideration of what materials can be incinerated.

The chemical hygiene plan should also contain the obligatory list of common dos and don'ts:
- Avoid chemical with skin and eyes
- No food or drink in lab
- Wear appropriate personal protective equipment
- Use a ventilation hood when necessary
- Do not work alone
- Keep the work area clean
- Don't use damaged glassware
- Confine long hair and loose clothing
- Plan work well before beginning
- Pay attention to what you and others are doing
- Follow standard procedures carefully when using toxins or allergens

Material Safety Data Sheets (MSDS)
- Required by OSHA Hazard Communication Standard
- Provided by chemical supplier
- Must be made available to employees
- Must contain certain basic information

Information Required in MSDS
- Material manufacturer and identification - Name and address of manufacturer, name of chemical, Chemical Abstract Service number, date MSDS prepared
- Hazardous ingredients - Lists the product ingredients which are hazardous
- Physical and chemical data - Boiling point, freezing point, solubility, etc
- Fire and explosion data - Flash point, recommended extinguishing media, special protective equipment needed
- Reactivity data - Chemical compatibility information, product stability over time, light sensitivity
- Health hazard - Threshold Limit Value(TLV) is the recommended maximum exposure concentration. Respiratory or contact hazard information, exposure symptoms, carcinogen
- Precautions for safe handling and use - Disposal information, special procedures for spills or leaks
- Control measures - Personal Protective Equipment (PPE) recommended

Community Right-to-Know (EPCRA)

The Emergency Planning and Community Right-to-Know Act (1986) regulates property owners and businesses that are involved with hazardous chemicals. There are five basic reporting requirements under EPCRA. They are:

- Emergency planning - Required if an Extremely Hazardous Substance (EHS) becomes present at the facility in excess of a Threshold Planning Quantity (TPQ). If TPQ is exceeded, the State Emergency Response Commission (SERC) must be notified and an emergency response coordinator must be appointed at the facility.
- Emergency release reporting - If a Reportable Quantity (RQ), as determined by the EPA, of an EHS is released, the operator must report it to the SERC.
- Submission of MSDS and submission of inventory - If a Threshold Reporting Quantity (TRQ), as determined by the EPA, becomes present at the facility, the operator must give a copy of the MSDS and chemical inventory forms to the SERC. TRQ of most hazards is 10,000 lbs. TRQ of an EHS is 500 lbs.
- Submission of toxic chemical release forms - Operators that manufacture or process 25,000 lbs or otherwise use 10,000 lbs of a toxic chemical in year are subject to this requirement. They must submit to the EPA an estimate of the quantity of toxic chemicals released into the environment or transported offsite.

11. Property Prediction

Property Prediction Basics

Biodiesel is a simple fuel consisting of a blend of a few specific, naturally derived fatty acid esters. Each fatty acid source has a fairly consistent fatty acid profile and composition. Most physical properties of organic compounds can be empirically correlated using methods based on the Law of Corresponding States. These properties include: density, viscosity, heating value, cloud point, cetane number, and surface tension.

Density Prediction

The primary parameters for density estimation are the esters composition and temperature. Density can be estimated using values for the individual components, or based on measured densities for biodiesel from different feedstocks. Component densities can be estimated using the Rackett Equation (a corresponding states equation) to predict each ester density and Kay's Rule to calculate the mixture value. An easier component-based prediction uses empirical constants for each ester component and a Kay's Rule mixture expression. This approach gives accuracies of $\pm 0.7 \%$

Another approach used is to measure the specific gravity (SG) of the biodiesel as a function of temperature, and fit an expression of the form $SG = a + b\, t$, where a and b are empirical constants and t is temperature. This approach requires data for SG for each fat or oil source to be used. This approach gives accuracies of $\pm 0.3 \%$ for soy biodiesel. The effort of temperature on density should not be neglected. While biodiesel and petroleum-based diesel fuel behave similarly, the impact is much greater with this fuel than with other common fluids such as water. [Tat, M.E. and J. H. Van Gerpen, "The Specific Gravity of Biodiesel and Its Blends with Diesel Fuel," JAOCS, v. 77 (2), pp. 115-119, 2000.

Viscosity Prediction

The primary parameters for viscosity estimation are esters composition and temperature. Viscosity can be estimated using values for the individual components, or based on measured viscosities for biodiesel from different feedstocks.

The temperature dependence for the viscosity of organic liquids follows the general empirical expression

$$\ln \varsigma = A + (B/T) + (C/T^2)$$

where ç is the kinematic viscosity [cSt], T is temperature [K], and A, B, and C are empirical constants that depend on the material. Viscosities for soydiesel and biodiesel-diesel blends have been shown to follow the empirical temperature dependence shown above. [Tat, M.E. and J. H. Van Gerpen, "The Kinematic Viscosity of Biodiesel and Its Blends with Diesel Fuel," JAOCS, v. 76 (12), pp. 1511-1513, 1999.]

The viscosity of the soydiesel/diesel blends follow the mixing rule

$$\log \varsigma_B = m_1 \log \varsigma_1 + m_2 \log \varsigma_2$$

where m_i is mass fraction of component, i. Accuracies on the order of 0.5 % are reported. [Tat, M.E. and J. H. Van Gerpen, "The Kinematic Viscosity of Biodiesel and Its Blends with Diesel Fuel," JAOCS, v. 76 (12), pp. 1511-1513, 1999.]

The viscosity of biodiesel can also be estimated using the ester composition of a specific sample. The viscosity of each different ester can be estimated at a specific temperature using an empirical expression such as the temperature relation, or another empirical form.

When individual component viscosities are used to estimate the mixture (biodiesel) viscosity, the form of the mixing rule used is very important. A logarithmic rule has shown accuracies on the order of 2.8 %

$$\ln \varsigma_m = Ę \, m_i \ln \varsigma_i$$

Heating Value Prediction

The fuel heating value is a measure of the energy content available upon combustion. Individual methyl esters all have heating values of about 39.8 MJ/kg. Biodiesel heating values can be estimated using component compositions with Kay's mixing rule

$$P_{mix} = Ę \, x_i \, P_i$$

Accuracies reported for this method are on the order of $\pm$ 4 %.

Cloud Point Predictions

The cloud point is a measure of the temperature at which components in the biodiesel begin to solidify out of the solution. The fraction of unsaturates in the neat biodiesel mixture has been found to be an important parameter in estimating cloud point. The empirical expression

$$\ln (t + 10) = 2.2 - 1.57 \ln (E \, m_{unsat})$$

has been shown to estimate the cloud point $\pm$ 6 %. There has been considerable interest in developing additives to lower biodiesel cloud points.

Cetane Number Prediction

The cetane number is a measure of a diesel fuel's engine performance, compared to a standard fuel. ASTM D-6751 requires a minimum cetane number of 47 for B100.

One approach to estimating a biodiesel's cetane number is to use the blending cetane number (BCN) of each ester component determined from

$$BCN = [A - (1 - x) B]/x$$

where A is the measured CN of the blend, B is the CN of the base fuel, and x is the weight fraction of the component.

Blending cetane numbers (BCN) have been measured for a number of esters. Their accuracy is reported as CN ± 10 units. There are a number of measurements of the CN for individual esters available. [Van Gerpen, J., "Cetane Number Testing of Biodiesel," Proceedings of the Third Liquid Fuel Conference, American Society of Agricultural Engineers, Nashville, TN, September 15-17, 1996.] The use of Kay's rule for estimating the biodiesel CN using component CNs and the corresponding mass fractions give accuracies on the order of ± 10 %, or about ± 5 CN units.

Surface Tension Prediction

The surface tension of a diesel fuel is important, along with the viscosity, in determining the atomization characteristics of the fuel. Fuel atomization via the injectors is an essential step in the compression ignition process.

The surface tension of a liquid is a fundamental property that is related to the chemical structure of the molecule. Sugden expresses the surface tension in the form

$$\sigma^{1/4} = [P] \, ñ / M$$

where σ is the surface tension [mN/m], [P] is the "parachor", ñ is the liquid density [g/ml], and M is the molecular weight [g/mol].

The parachor is a temperature independent parameter that is based on the chemical structure of the compound. The parachor is estimated using generalized group contributions. Surface tension estimates using this method have a reported accuracy of ± 5 %.

Summary

Most of the important physical properties of biodiesel fuel can be estimated with reasonable accuracy using values, or estimates for the component esters and appropriate mixing rules. Contaminants, such as moisture, glycerol, etc. can only be determined from using the quality control measurements in ASTM D-6751.

12. Biodiesel Blend Detection

In the biodiesel industry, there is a need for determining the blend level of mixtures of biodiesel and diesel fuel. This can be accomplished quire readily in the laboratory by running a test to determine the Saponification Value of the mixture and then converting this to a percentage of biodiesel. The saponification value simply determines the fraction of a mixture that can be reacted with potassium hydroxide to form soap (or saponified). Measurement of the blend level in the field, and providing an output that can be used to control a process, is a much more difficult problem. The following abstract of a technical paper describes a sensor that is based on measurements of the dielectric constant of the fuel and which can determine the blend level very accurately if samples of the two primary fuels are available. It is also accurate enough for engine control purposes even if the primary fuels are not available.

Abstract. Biodiesel is an alternative diesel fuel consisting of the alkyl monoesters of fatty acids from vegetable oils and animal fats. Biodiesel can be used in diesel engines as a pure fuel or in blends with petroleum-based diesel fuel. To maintain optimum performance and meet emission regulations, it may be necessary to measure the composition of blended fuels and adjust the fuel injection timing and other injection parameters during operation. The objective of this study was to investigate the suitability of using a commercial Flexible Fuel Composition Sensor for the detection of biodiesel composition in biodiesel/diesel fuel blends. Twelve different biodiesel fuel samples were tested including pure esters and esters from soybean oil, tallow, lard, canola oil, and yellow grease. The sensor produced a frequency output between 58.75 and 60.23 Hz for all of the biodiesel samples. Six different diesel fuel samples were also tested including commercial No.1 diesel fuel and EPA emission certification fuel. All of the diesel fuel samples gave frequencies between 51.84 and 52.62 Hz. The frequency output of the sensor was observed to be linearly proportional to the percentage of biodiesel in the blend. The 7.14 Hz average difference from diesel fuel to biodiesel is sufficient to use this fuel composition sensor for blend detection of biodiesel blended fuels.

In this paper, a Ford Motor Company dielectric fuel composition sensor was tested for its suitability as a biodiesel blend sensor. The sensor was originally designed for detection of the methanol concentration in methanol-gasoline blends. The sensor is shown in Figure 29. The sensor gives a square wave output with a frequency that is proportional to the blend composition and the duration of the high portion of the wave is proportional to the temperature of the blend.

Figure 29. Flexible Fuel Composition Sensor (Ford Part No. 9C044).

Figure 30, reproduced from the paper by Tat and Van Gerpen, presents the measured results for the square wave frequency for 12 biodiesel fuel samples. Even though many types of biodiesel fuels were tested, the range of frequencies produced by the sensor was quite narrow. The biodiesel frequencies varied from 58.75 Hz to 60.23 Hz. There does not appear to be a consistent trend for the sensor response corresponding to the different esters. While both of the highly unsaturated esters (methyl linoleate and ethyl linoleate) gave frequencies that were on the high end of the range, the highest frequency came from the brown grease methyl ester, which was highly saturated. There also appears to be no consistent trend with methyl and ethyl esters. The ethyl soy ester frequency was higher than the methyl soy ester, but the oxidized methyl and ethyl soy esters were about the same. The methyl linoleate and ethyl linoleate also gave about the same sensor response. The slight variations in frequency between the biodiesel samples are apparently due to differences that were not controlled for this experiment but they are not large enough to interfere with the sensor's ability to distinguish between biodiesel and diesel fuel.
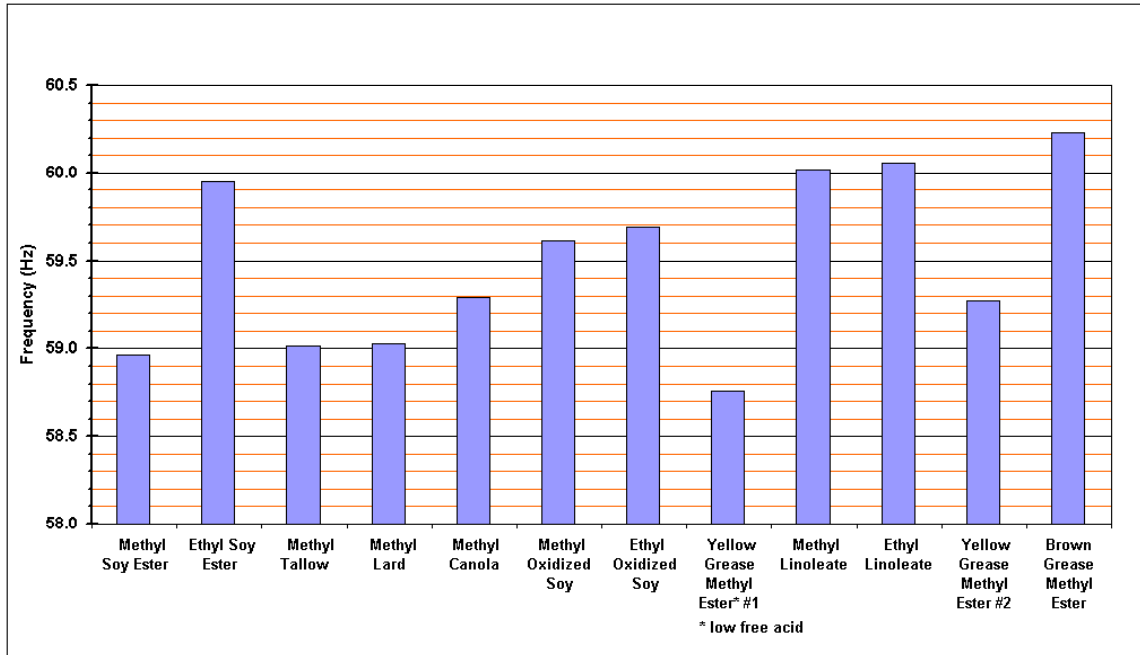
Figure 30. Biodiesel Fuel Samples [Tat and Van Gerpen, 2001]

In Figure 31, it can be seen that for the six diesel fuels there was even less variation than for the biodiesel samples. The minimum frequency was found for the No. 1 diesel fuel at 51.84 Hz and the highest was 52.63 Hz from the commercial No. 2 diesel fuel. The average values of the biodiesel and diesel fuel samples were 59.49 Hz and 52.35 Hz, respectively. The difference between the averages was 7.15 Hz and this corresponds to a 0.07 Hz increase in frequency per percent of the blend.

Figure 32 shows the variations in the sensor frequency output as the blend level of biodiesel and diesel fuel was varied. It is clear that the change in sensor output from diesel fuel to biodiesel is linear.

The biodiesel and diesel fuel variations from their maximum value to their minimum value were about 20% and 11% of the 7.15 Hz difference between the averages for the two types of fuel. The greatest deviation occurred for the methyl ester of yellow grease #1 with the lowest frequency output of 58.75 Hz. The difference between the lowest frequency output and the average value for biodiesel was 0.7141 Hz. If we divide this number with frequency change for per percentage (0.0714) the error was about 10.5 percent. This result showed that the total variation is large enough and maximum error small enough to use this sensor for biodiesel blend detection. Because the maximum timing change due to biodiesel use in diesel engine is likely to be only 2 - 3 crank angle degrees (Tat et al. 2000b) an error of 10% in blend concentration should only produce an error of 0.2° - 0.3° in injection timing, which is close to current manufacturing tolerances.
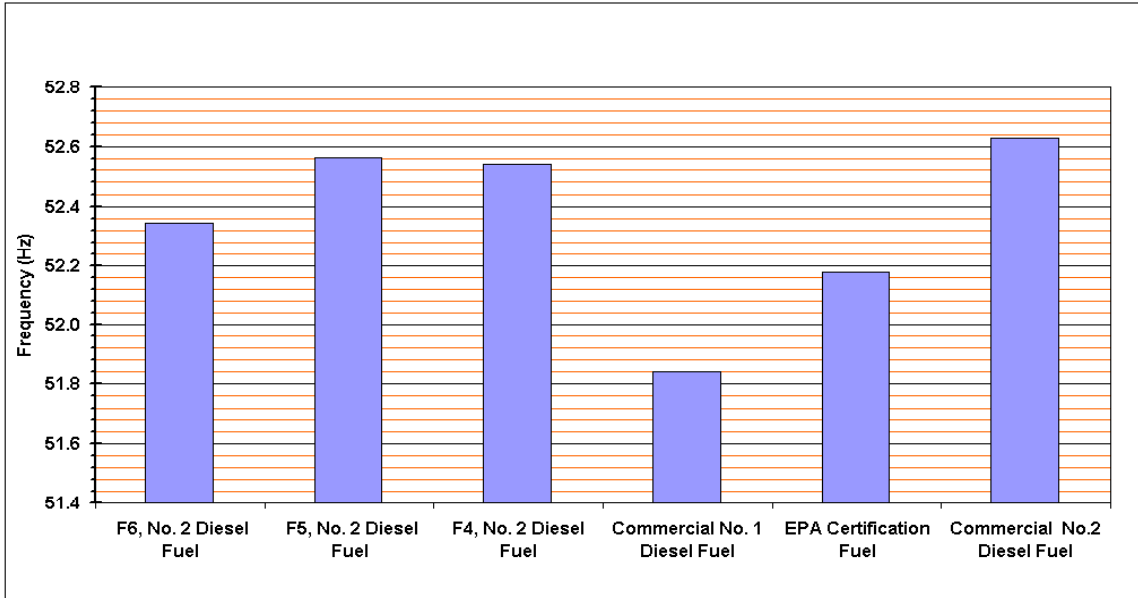
Figure 31. Diesel Fuel's Frequency Distribution [Tat and Van Gerpen, 2001]
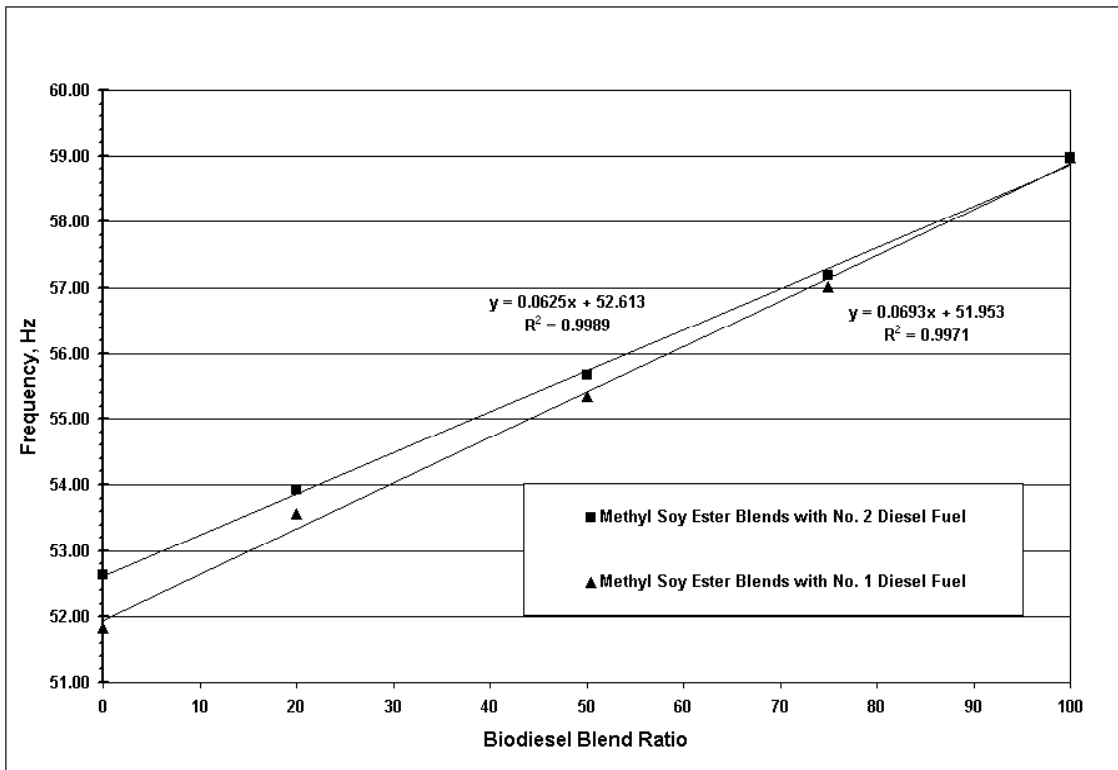

Figure 32. Methyl Soy Ester Blends with No. 2 and No. 1 Diesel Fuel
[Tat and Van Gerpen, 2001]

13. Chemical Plant Instrumentation

A biodiesel manufacturing plant is a chemical plant and as such will need to have the capability to measure properties of the biodiesel product. Many of the properties of the biodiesel product will be amenable to analysis at the production facility in an associated wet chemistry laboratory. Most chemical manufacturing facilities include a wet chemistry laboratory on the premises. This module will discuss the chemical plant instrumentation used to analyze product quality in biodiesel production. The process control instrumentation used in the manufacture of biodiesel will not be discussed here.

The role of the wet chemistry laboratory in a chemical production facility is to monitor product specifications as well as to provide quality control. The equipment required in the wet chemistry laboratory to measure the biodiesel fuel properties is dictated by the specifications delineated in ASTM D6751 and the underlying ASTM standards discussed within it. While the product properties are important, there may also be a need to have capabilities to measure oil feedstock properties if the production philosophy is to accommodate variable feedstocks. For example, if the plant will be run only on soybean oil as the feedstock, the feedstock variability will not be significant. However, if yellow greases such as from animal rendering or spent cooking oil are to be used, then feedstock quality can vary significantly.

While all of the specifications in ASTM D6751 must be met, the specifications can be grouped into several categories. First are processing specifications that include free and total glycerol, kinematic viscosity, and flash point. Although these specifications are influenced by the choice of feedstock, they are significantly influenced by the processing of the feedstock, i.e., how the manufacturing plant is operated. Other quality specifications that can be influenced by processing conditions are water and sediment, copper strip corrosion, and acid number. For these specifications, the performance of the manufacturing process and the properties of the feedstocks are both important. A third specification category can be called property specifications. The specification set includes cloud point, cetane number, distillation temperature and sulfated ash. The intrinsic chemical characteristics of the feedstocks are extremely important for these specifications. For example, higher saturation in the oil feed typically leads to biodiesel fuels with higher cloud points since saturated methyl esters will "freeze" at higher temperatures than unsaturated methyl esters. The final specification category, which is completely linked to the feedstock properties, is natural contaminants. Included in this category would be the specifications on sulfur and phosphorus.

Of the processing specifications, the most important for monitoring the manufacturing process is the free and total glycerol since this value addresses the extent of the transesterification reaction. While free and total glycerol is a very important product quality test it is difficult to test for and will likely require the most costly equipment for the wet chemistry laboratory. Nonetheless, it is a test that needs to be available at the manufacturing plant. As discussed previously, there are several possible methods for measuring free and total glycerol. The wet chemistry method is the least costly in terms of equipment since only standard glassware is required. However, this method is both

very slow and cumbersome. The gas chromatography method requires a gas chromatograph. This method is somewhat faster than the wet chemistry method, but in many ways is just as cumbersome. A new method is near infrared (NIR), which requires appropriate IR equipment. This method is quicker and less cumbersome than the other two methods, but the equipment must be appropriately calibrated, which requires the necessary expertise.

The additional processing specifications are the kinematic viscosity and flash point. In addition to standard wet chemistry glassware and thermometers, measurement of the kinematic viscosity requires a viscometer. The flash point is measured using a specialized apparatus, so a flash point apparatus must be available to measure this property.

The other quality specification category includes water and sediment, copper strip corrosion, and acid number and can reasonably be measured in a standard wet chemistry laboratory. The water and sediment measurement requires standard wet chemistry equipment and a centrifuge. This specification is a product quality specification that relates to both processing and storage conditions, so it must be measured accordingly. The copper strip corrosion can be measured using a test bomb and also requires access to a set of standards. The acid number can be measured using a potentiometric titration cell.

The property specification set, which includes cloud point, cetane number, distillation temperature and sulfated ash, all require specialized equipment that generally do not have to be included in an onsite wet chemistry laboratory. The use of an external laboratory can also be considered for the natural contaminant specifications for sulfur and phosphorus. The values of the property and natural contaminant specifications are strongly related to the characteristics of the feedstock used in the biodiesel facility. If a standard feedstock such as soybean oil is to be used then these two specification sets can readily be handled by external testing. However, if variable feedstocks are to be used it might require some additional test facilities for some of the specification measurements to be available at the plant or to have ready availability to the tests at an external laboratory.

There are a number of external laboratories that will measure the necessary properties to determine whether a biodiesel sample meets specifications. While not an exhaustive list and not meant as an endorsement of any specific laboratories, three laboratories that offer the full range of diesel fuel measurements are:

Phoenix Chemical Laboratory, Inc.
3953 Shakepeare Ave.
Chicago, IL 60647-3497
(773) 772-3577

Southwest Research Institute
Petroleum Products Research Department
6220 Culebra Road
San Antonio, TX 78228-0510

Williams Laboratory Services
1090-A Sunshine Road
Kansas City, KS 66115
(913) 621-3603

These laboratories can measure all the values required in biodiesel, as specified
by ASTM D6751 except for the free and total glycerol. Only Williams Laboratory
Services performs from this test. The fatty acid profiles of oils and biodiesel as
well as the free fatty acid content of an oil can be measured by the following
laboratories:

Williams Laboratory Services
1090-A Sunshine Road
Kansas City, KS 66115
(913) 621-3603

Woodson-Tenent Laboratories
3507 Delaware Ave.
Des Moines, IA 50313
(515) 265-1461

Representative costs for the various tests are given in the following table. These values
represent the minimum values given as of December, 2002. The actual prices are
negotiable based on the number of samples and the number of tests to be run.

Table 11. Representative costs of standard tests

ASTM No.	Test	Cost per Sample
D93	Flash Point	$25
D130	Copper Corrosion	$15
D445	Kinematic Viscosity	$20
D613	Cetane Number	$65
D664	Acid Value	$43
D874	Ash, Sulfated	$83
D1160	Distillation (vacuum)	$145
D2709	Water & Sediment	$19
D4751	Phosphorus	$60
D5453	Sulfur	$30
D5773	Cloud Point	$35
D6584	Free & Total Glycerol	$89

From a quality control perspective, it is important to note that all of the specifications
listed in ASTM D6751 are off-line measurements. In fact, essentially all of the
specifications in ASTM D6751 are too slow for on-line measurement. Therefore, a key

question becomes how is product quality monitored during production when the quality measures are all "after the fact" measurements.

The discrepancy between specifications and real time measurements to determine product quality is a common problem in the chemical/fuel industry. Typical process variables that can be measured on-line include temperature, pressure, fluid level, residence time, and flow rates. These on-line measurements are critical for tracking the progress of the manufacturing process, but they must be correlated to the final specifications, which are the ultimate determination of product quality. Process models are used to provide the correlation between on-line measurements and final product quality. Process models can exist in a number of different forms including statistical models and empirical models. Statistical models are developed by measuring product quality values relative to a range of process variable combinations. The model results from a statistical correlation between product quality values and process variables. Empirical models correlate the process variables to product quality values using chemical models.

Effective quality control monitoring combines the on-line monitoring of key process control variables and off-line monitoring of product quality. As discussed above, process models are used to track the on-line variables relative to product quality. Process models will typically be supplied by the process licensor although the models will commonly be refined by the operations at an individual plant. Since the process models will almost always be empirical, the models will likely be feedstock dependent. These models will be used as part of process control strategy for the manufacturing process. Process control will be discussed in more detail in the Biodiesel Production Technology course.

In summary, a biodiesel manufacturing facility will need to have a wet chemistry laboratory associated with it. Testing equipment will be needed for some of the product specifications while other product property values can be measured using external laboratories. A potential set of equipment to consider for the wet chemistry laboratory includes, standard glassware, viscometer, flash point apparatus, centrifuge, copper strip corrosion test bomb, potentiometric titration cell, and equipment for free and total glycerol testing (gas chromatograph or wet chemistry method).

14. Fuel Sampling Procedures

Most fuels have the potential to develop stratification during storage. This is true of both petroleum-based fuels and biodiesel. The stratification may be associated with different levels of contaminates between the top and bottom of a tank, or due to certain fuel components separating, or possibly due to fuel deterioration occurring at different rates within the fuel depending on location. When testing the fuel, it is important to sample the fuel in a manner that is appropriate for the information that is desired. For example, if a 20,000 gallon tank of fuel has 2 or 3 gallons of water that has collected on the bottom of the tank near an outlet, a sample from the outlet may indicate a very high water level while a sample from the top of the tank would indicate no water. If the entire tank of fuel is being offered for sale, the small amount of water may not be important. However, if fuel is being withdrawn from the bottom of the tank and supplied to a vehicle, the water will contribute to a high level of contamination. It is important to have consistent sampling procedures that provide the information needed from the follow-on analysis procedure.

ASTM standard D 4057-95, Standard Practice for Manual Sampling of Petroleum and Petroleum products provides procedures for collecting samples from fuels that are in the liquid, semi-liquid, and solid state. ASTM D 4177 describes procedures for automatic sampling of liquids flowing through pipelines, but since biodiesel is not currently transported through pipelines, this standard will not be discussed here.

D 4057 defines the following sample types:

All-levels sample – a sample obtained by submerging a stoppered bottle to a point near the draw-off level, then opening the sampler and raising it at a rate such that it is approximately three-fourths full as it emerges from the liquid.

Spot sample – a sample taken at a specific location in a tank.

Bottom sample – A spot sample collected from the material at the bottom of the tank at its lowest point.

Outlet sample – A spot sample taken from the level of the bottom of the tank outlet.

Lower sample – a spot sample from the lower one-third of the tank's contents (a distance of five-sixths of the depth of liquid below the surface).

Middle sample – a spot sample taken from the middle tank's contents (a distance of one-half of the depth of liquid below the surface).

Upper sample – A spot sample taken from the middle of the upper one-third of the tank's contents (a distance of one-sixth of the liquid depth below the surface).

Top sample – A spot sample obtained 6 inches below the top surface of the liquid.

These sample locations are shown on Figure 33. The sample locations only apply to tanks with side outlets. Samples should not be taken from solid stand pipes as they will not necessarily be representative of the material in the tank at that time.
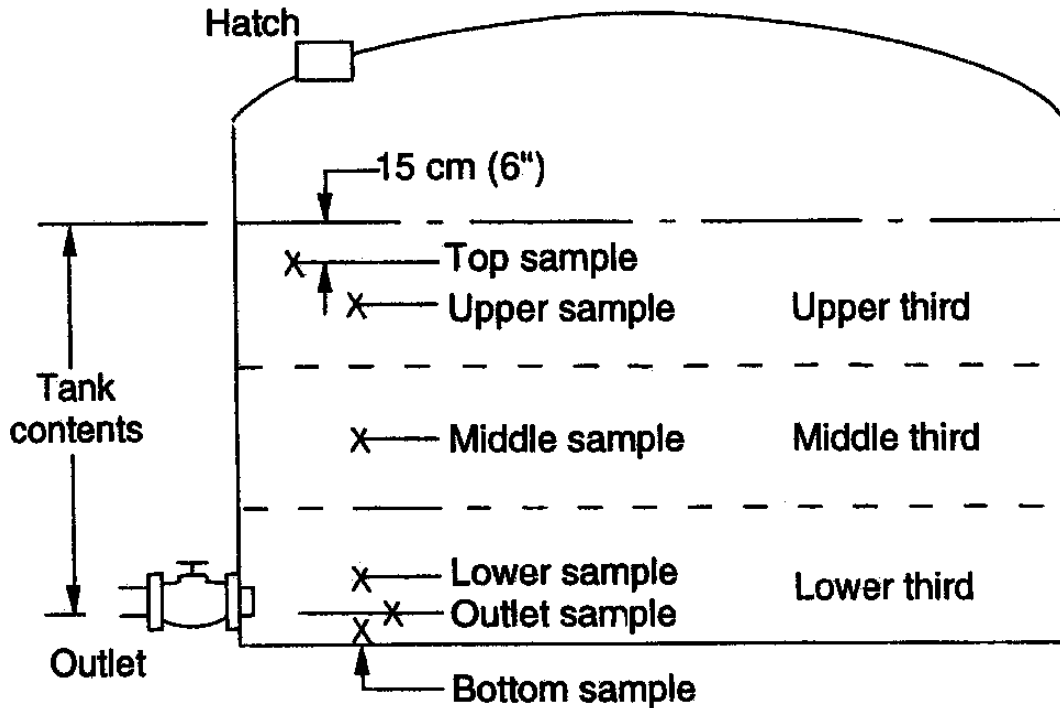

Figure 33. Sampling Points in a Fuel Storage Tank [ASTM D 4057-95]

The sampling locations given in Figure 33 apply only to vertical cylindrical tanks. Horizontal tanks have different locations given in Table 12.

Other considerations for sampling include:

1. When stratification is possible, allow sufficient time for the heavy component to separate and settle.
2. To avoid mixing of the layers in the tank, sampling should start with the upper-most sample and work downward.
3. Sampling equipment should be clean at the start of sampling. It is good practice to rinse the sample container with the product to be sampled prior to drawing samples.
4. If samples are to be stored for an extended period, use brown glass bottles or wrapped clear bottles to limit exposure of the sample to light.

Table 12. Sampling Locations for Horizontal Cylindrical Tanks.

Liquid Depth (% of Diameter)	Sampling Level (% of Diameter Above Bottom)			Composite Sample (Proportionate Parts of)		
	Upper	Middle	Lower	Upper	Middle	Lower
100	80	50	20	3	4	3
90	75	50	20	3	4	3
80	70	50	20	2	5	3
70		50	20		6	4
60		50	20		5	5
50		40	20		4	6
40			20			10
30			15			10
20			10			10
10			5			10

5. All samples should be labeled immediately after the sample is collected. The label should include date, time, name of sampler, name and number of the supplier, grade of material, and any other reference or identification numbers.

Equipment for Spot Sampling

Figures 34 and 35 show typical equipment used for collecting spot samples from fuel storage tanks. A device that is intended to be dropped into a fuel tank to collect a sample is often called a *thief*. Figure 34 shows two types of sampling thieves that allow bottom sampling. Both of these devices can be lowered to the bottom of a tank. When they strike bottom, the protruding stem opens the bottom valve to allow fuel to enter and the top valve to allow air to escape. The extended tube sampler shown in Figure 35 can provide a sample at any location in the tank.

BQ-9000, Quality Management System Requirements

The National Biodiesel Accreditation Commission, an autonomous committee of the National Biodiesel Board has developed a voluntary program for the accreditation of biodiesel producers and marketers. The procedure proposed by this group for sampling biodiesel to ensure quality control includes the following:

- After every addition to a fuel storage tank, an all-level or composite sample shall be taken and retained for 60 days in case of a dispute about product quality.
- Prior to use in blending, an outlet sample of the diesel fuel must be taken.
- Blended fuel must be sampled to assure the fuel is well-mixed. Upper, middle, lower, and outlet samples shall be collected and tested. After testing, the upper, middle, and

lower samples will be mixed and retained for 60 days, or the estimated life of the product, whichever is longer.

- If no activity has occurred with a tank, a outlet sample should be collected once per month to assure that water and sediment have not collected.
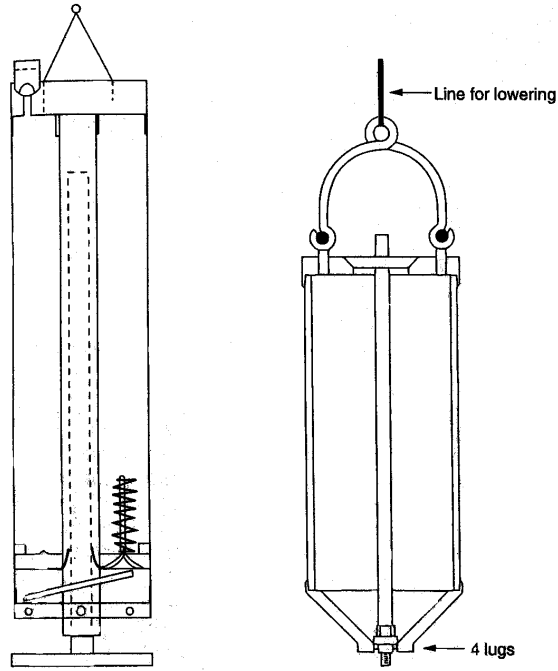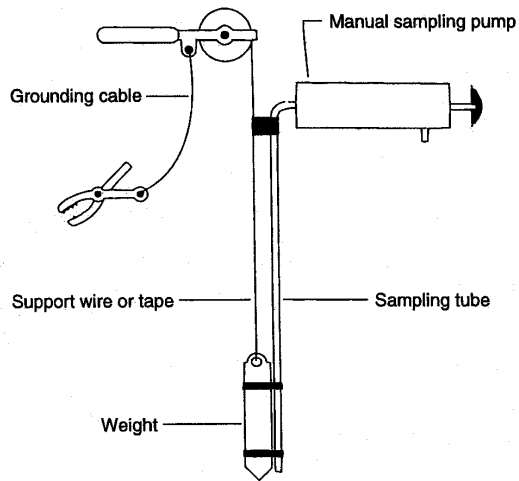

Figure 34. Two Styles of Bottom Sampling Thieves

Figure 35. Extended-Tube Sampler

Laboratory Exercises

<u>Measurement of Total and Free Glycerol Using Gas Chromatography</u>

Biodiesel is usually made with methanol and therefore consists of the methyl esters of fatty acids from fats and oils. There will also be small amounts of other compounds in the fuel due to incomplete reaction or incomplete washing. These contaminants will consist of unreacted triglycerides, and mono- and diglycerides, which are the products of incomplete reaction. There may also be some free glycerol present if the water washing was not complete.

The triglycerides, diglycerides, and monoglycerides are considered to be partially composed of bound glycerol. This is added to the free glycerol to get the total glycerol.

We will be using a Varian Model CP-3800 Gas Chromatograph to measure the amounts of various contaminants in samples of biodiesel.

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)* July 2004	2. REPORT TYPE Subcontract Report	3. DATES COVERED *(From - To)* August 2002 - January 2004

4. TITLE AND SUBTITLE Biodiesel Analytical Methods: August 2002–January 2004	5a. CONTRACT NUMBER DE-AC36-99-GO10337
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S) J. Van Gerpen, B. Shanks, R. Pruszko (ISU) D. Clements (RPDL) G. Knothe (USDA/NNCAUR)	5d. PROJECT NUMBER NREL/SR-510-36240
	5e. TASK NUMBER BB044630
	5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Iowa State University, 2207 Pearsen Hall, Ames IA Renewable Products Development Laboratory USDA/NCAUR	8. PERFORMING ORGANIZATION REPORT NUMBER AC0-2-31056-01
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) National Renewable Energy Laboratory 1617 Cole Blvd. Golden, CO 80401-3393	10. SPONSOR/MONITOR'S ACRONYM(S) NREL
	11. SPONSORING/MONITORING AGENCY REPORT NUMBER NREL/SR-510-36240`

12. DISTRIBUTION AVAILABILITY STATEMENT
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161

13. SUPPLEMENTARY NOTES
NREL Technical Monitor: K. Shaine Tyson

14. ABSTRACT *(Maximum 200 Words)*
Biodiesel is an alternative fuel for diesel engines that is receiving great attention worldwide. The material contained in this book is intended to provide the reader with information about biodiesel engines and fuels, analytical methods used to measure fuel properties, and specifications for biodiesel quality control.

15. SUBJECT TERMS
biodiesel; analysis, specifications

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified	UL		19b. TELEPONE NUMBER *(Include area code)*

Standard Form 298 (Rev. 8/98)
Prescribed by ANSI Std. Z39.18

F1146-E(05/2004)