

Biodiesel Fuels

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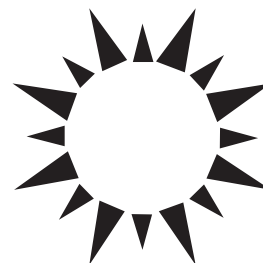
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Glossary

aromatics Any unsaturated hydrocarbon containing resonance stabilized carbon-to-carbon bonds characterized by benzene-type ring structure.

biodiesel A renewable energy fuel from vegetable or animal derived oil (triglyceride) that has been chemically modified to reduce its viscosity. It can be used in any concentration with petroleum-based diesel fuel in existing diesel engines with little or no modification. Biodiesel is not the same thing as raw vegetable oil. It is produced by a chemical process, which removes the glycerol from the oil.

distillation curve A measure of volatility of a fluid. More specifically, it is the temperature of the fluid (fuel) when a specific volume of the fluid has evaporated.

feedstock Raw or processed material that is chemically reacted to produce biodiesel. Note that the raw material must first be processed before the oil can be used to produce biodiesel.

gas chromatograph A chemical is heated to a gaseous state, and then the gas is passed through a cylinder and the different chemicals that make up the gas “stick” to the wall of the cylinder at different intervals. This information is then used to determine the chemical makeup of the gas.

olefin Any unsaturated hydrocarbon containing one or more pairs of carbon atoms linked by a double bond.

triglyceride A naturally occurring ester formed from glycerol and one to three fatty acids. Triglycerides are the main constituent of vegetable and animal derived fats and oils.

The United States depends heavily on imported oil to fuel its transportation infrastructure. The use of alternative fuel derived from plant oils was examined by researchers in the mid-1970s to determine if internal combustion engines could be fueled from sources other than petroleum. The initial research on pure vegetable oils as a replacement for petroleum diesel fuel was met with mostly negative results. Researchers determined that transesterification of these plant- and animal-derived oils reduced the viscosity of the oil without any other significant changes to the oil. Since the new fuel was bio-derived and was used to fuel a diesel engine, the name “biodiesel” was selected to refer to the new fuel. This article focuses more specifically on how biodiesel fuel was developed, its chemical and physical properties, advantages, disadvantages, and how biodiesel is used and stored. The article concludes by reviewing the economic issues associated with its use.

1. BIODIESEL FUELS AND THEIR ORIGINS

1.1 What Is Biodiesel?

Biodiesel is made from a number of feedstocks including vegetable oil, tallow, lard, and waste

cooking oils (yellow grease). "Biodiesel is defined as mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats which conform to American Society of Testing Materials (ASTM D5453) International specifications for use in diesel engines." Biodiesel contains no petroleum, but it can be blended at any level with petroleum diesel to create a biodiesel blend. Feedstocks can be transesterified to make biodiesel using an alcohol that has been mixed with a catalyst such as potassium hydroxide or sodium hydroxide. The most commonly used alcohol for transesterification is methanol. Methanol reacts easily and is less expensive to use than most other alcohols.

Soybean derived biodiesel is the most commonly used biodiesel in the United States. The most commonly used feedstock for biodiesel production in Europe is rapeseed. Biodiesel is biodegradable, nontoxic, and essentially free of sulfur and aromatics. Biodiesel is considered a renewable resource due to the fact that it is derived from products that can be grown and produced domestically.

1.2 What Biodiesel Is Not

In 1898 when Rudolph Diesel's compression ignition engine was demonstrated at the World's Exhibition in Paris, it ran on virgin peanut oil. Some document this event as the first use of biodiesel. However, biodiesel is not vegetable oil or animal fats. Biodiesel refers to the alkyl esters produced from a transesterification reaction between the oil or fat and an alcohol. Others refer to mixtures of biodiesel and petroleum diesel fuel as "biodiesel." This mixture is referred to as a biodiesel blend and is commonly designated in much the same way as a blend of gasoline and alcohol (E85). For example, B100 is 100% biodiesel; B20 is a blend of 20% biodiesel and 80% diesel fuel.

1.3 Beginnings

Vegetable oils were transesterified prior to the mid-1800s. Transesterification is the process of reacting a triglyceride molecule with an excess of alcohol in the presence of a catalyst (KOH, NaOH, NaOCH₃, etc.) to produce glycerol and fatty esters as shown in the chemical reaction in Fig. 1.

Companies such as Proctor & Gamble have used this process to make soap for years. According to Knothe, the earliest known use of alkyl esters for fuel appears in a Belgian patent granted in 1937 to G. Chavanne.

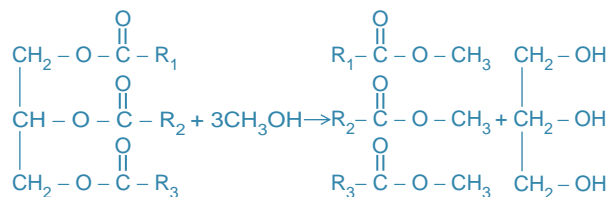


FIGURE 1 Chemical structure of biodiesel.

Methyl and ethyl esters are essentially by-products of this process. Ethyl esters are made using ethanol and methyl esters are made using methanol. Ethanol is made from grain such as corn. The methanol is either wood based or derived from natural gas (methane).

Peanut oil, hemp oil, corn oil, and tallow are typically transesterified in the soap-making process. Soybeans, industrial or edible rapeseed (or its cousin, canola oil), corn, recycled fryer oil, lard, and tallow are common resources for the complex fatty acids and their by-products.

It is important to find other sources of oil to enhance our ability to produce biodiesel. Research has been conducted concerning oil production from algae according to sources at the National Renewable Energy Laboratory (NREL). This oil source could have yields greater than any feedstock now known. Most biodiesel researchers worldwide agree that it would be difficult to replace more than 10% of the diesel fuel that is used for transportation purposes with biodiesel.

2. CHEMICAL PROPERTIES

Researchers have determined that the following properties characterize the chemical properties of biodiesel: fatty acid content, aromatics, olefins, paraffins, carbon, hydrogen, oxygen, and sulfur content, acid neutralization number, iodine number, and Conradson carbon residue number.

Note the chemical structure of a triglyceride (Fig. 2). R₁, R₂, and R₃ represent the hydrocarbon chain of the fatty acid elements of the triglyceride. There is a three-carbon chain called the glycerol backbone that runs along the left side of the molecule. Extending away from this backbone are the three long fatty acid chains. The properties of the triglyceride and the biodiesel fuel will be determined by the amounts of each fatty acid that are present in the molecules.

Fatty acids are designated by two numbers: the first number denotes the total number of carbon

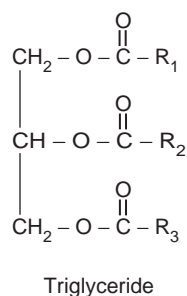


FIGURE 2 Chemical structure of a triglyceride.

atoms in the fatty acid, and the second is the number of double bonds. For example, 18:1 designates oleic acid, which has 18 carbon atoms and one double bond. A typical sample of soybean oil based biodiesel would have the fatty acid profile shown in Fig. 3.

Biodiesel is essentially free of sulfur and aromatics. This is an advantage for biodiesel because sulfur poisons catalytic converter technology that is used to reduce engine exhaust emissions. The sulfur levels in biodiesel by ASTM D5453 are found to be as low as 0.00011% by mass (1 ppm), where petroleum diesel is often no lower than 0.02% (200 ppm). The lack of aromatic hydrocarbons is also an advantage for biodiesel, as many of these compounds are believed to be carcinogenic. The test procedure normally used to measure aromatics in petroleum fuel (ASTM D1319) should not be used to determine the aromatics of biodiesel. This analytical procedure mistakenly identifies the double bonds commonly found in biodiesel as the resonance stabilized bonds normally associated with aromatics.

Paraffins are hydrocarbon compounds that are normally associated with petroleum diesel fuel. These compounds help increase the cetane value of the diesel fuel. However, they also typically increase cold flow problems of petroleum diesel fuel. Olefins are hydrocarbons that contain carbon-carbon double bonds. Molecules having these types of bonds are called unsaturated. Biodiesel from common feedstocks is usually 60 to 85% unsaturated. Some olefins are present in petroleum-based diesel fuel. However, the amount of olefins is usually small as they contribute to fuel oxidation.

The carbon content of biodiesel is nearly 15% lower than petroleum diesel fuel on a weight basis. Conversely, biodiesel has approximately 11% oxygen, on a weight basis, while petroleum diesel has almost no oxygen. Very little differences exist between biodiesel and petroleum diesel fuel concerning the weight percentage of hydrogen.

Chain	Percentage by weight
C14:0	0.278
C16:0	10.779
C18:0	4.225
C18:1	20.253
C18:2	54.096
C18:3	9.436
C20:0	0.395

FIGURE 3 Fatty acid profile for soybean derived biodiesel.

The neutralization number is used to reflect the acidity or alkalinity of an oil. This number is the weight in milligrams of the amount of acid (hydrochloric acid [HCL]) or base (potassium hydroxide [KOH]) required to neutralize one gram of the oil, in accordance with ASTM test methods. If the neutralization number indicates increased acidity (i.e., high acid number) of an oil, this may indicate that the oil or biodiesel has oxidized or become rancid. Biodiesel is allowed to have a neutralization number up to 0.8mg KOH/g.

The iodine value is a measure of the unsaturated fatty acid content of biodiesel, and reflects the ease with which biodiesel will oxidize when exposed to air. The iodine value for petroleum diesel fuel is very low, but the iodine value of biodiesel will vary from 80 to 135.

A weighed quantity of fuel is placed in a crucible and heated to a high temperature for a fixed period to determine the Conradson carbon residue of a fuel. The crucible and the carbonaceous residue is cooled in a desiccator and weighed. The residue that remains is weighed and compared to the weight of the original sample. This percentage is reported as the Conradson carbon residue value. This procedure provides an indication of relative coke forming properties of petroleum oils. No real differences are to be expected when comparing biodiesel with petroleum diesel fuel (0.02 versus 0.01).

3. PHYSICAL PROPERTIES

The following properties reflect the physical properties of biodiesel: distillation curve, density/specific gravity, API gravity, cloud point, pour point, cold filter plug point, flash point, corrosion, viscosity, heat of combustion, and cetane number.

Each fuel has its own unique distillation curve. Some compare this to a fingerprint. This curve tells a chemist which components are in the fuel, their

molecular weights by identifying their boiling points and their relative amounts. The temperature at which a specific volume boils off is used to establish this curve (0, 10, 50, 90, and 100%). The range of boiling points for biodiesel is much narrower than petroleum diesel fuel. For example, the initial boiling point of petroleum diesel fuel is 159°C, and the end boiling point is 336°C. The initial boiling point of biodiesel is 293°C, and the end boiling point is 356°C. Thus, the distillation range for diesel fuel is 177° versus 63°C for biodiesel fuel.

The specific gravity of a product is the weight of the product compared to an equal volume of water. The specific gravity of biodiesel is slightly higher than petroleum diesel fuel. For example, the specific gravity of No. 2 petroleum diesel fuel is approximately 0.84 (7.01 pounds per gallon). The specific gravity of biodiesel is approximately 0.88 (7.3 pounds per gallon).

ASTM test procedures are used to determine cloud and pour point of biodiesel. Cloud point is the temperature at which the first wax crystals appear. Pour point is the temperature when the fuel can no longer be poured. According to ASTM specifications for diesel fuel, the cloud points of petroleum diesel fuel are determined by the season (temperature) that the fuel is used. For example, ASTM standards essentially require that the fuel distributor treat number 2 petroleum diesel fuel with cold flow improvers (CFI) for winter operation. Cold weather operation with 100% biodiesel also forces the distributor to use a CFI. However, the CFI of choice for petroleum diesel fuel is usually not as effective when used with biodiesel. The cloud point for biodiesel is higher than petroleum diesel fuel (1.6°C for biodiesel compared with -9.4° to -17.7°C for diesel fuel). Chemical companies (Lubrizol, Octell Starreon) are experimenting with CFI chemicals that work effectively with biodiesel.

An alternative method used to determine how the fuel will perform during cold weather operation is the cold filter plugging point. The cold filter plugging point is the lowest temperature at which the fuel, when cooled under specific conditions, will flow through a filter during a given period of time. The filter is a defined wire mesh. This procedure indicates the low temperature operability of a fuel with/without cold flow improver additives when cooled below the cloud point temperature. The cold filter plugging point for fuels has become an important issue due to the reduction in the size of the openings in the fuel filters (2–5 microns versus 45 microns).

The flash point of a fuel is defined as the temperature at which the air/fuel vapor mixture above the product will ignite when exposed to a spark or flame. A sample is heated and a flame is passed over the surface of the liquid. If the temperature is at or above the flash point, the vapor will ignite and a detectable flash (unsustained or sustained flame) will be observed. The flash point of biodiesel is substantially higher (159°C versus 58°C) than for petroleum diesel fuel. Biodiesel is categorized as a combustible fuel, not a flammable fuel, as is the standard classification for petroleum diesel fuel. Biodiesel is a safer fuel to transport due to its higher flash point.

As fuel deteriorates it becomes acidic. Copper is particularly susceptible to corrosion by the acids in the fuel. As a result, test procedures have been developed to detect the fuel's corrosiveness to copper. A polished copper strip is immersed in a heated sample of fuel. After a prescribed period of time, the strip is removed and examined for evidence of corrosion. A standardized system is used to assign a value between 1 and 4. This number is assigned based on a comparison with the ASTM Copper Strip Corrosion Standards. No differences have been detected using this methodology between petroleum diesel fuel and biodiesel.

The viscosity of a fluid is a measure of its resistance to flow. The greater the viscosity, the less readily a liquid will flow. Test procedures are used to measure the amount of time necessary for a specific volume of fuel to flow through a glass capillary tube. The kinematic viscosity is equal to the calibration constant for the tube multiplied by the time needed for the fuel to move through the tube. The viscosity of biodiesel is approximately 1.5 times greater than petroleum diesel fuel (4.01 versus 2.6 cSt@40°C).

The heat of combustion is the amount of energy released when a substance is burned in the presence of oxygen. The heat of combustion, also known as the heating value, is reported in two forms. The higher, or gross, heating value assumes that all of the water produced by combustion is in the liquid phase. The lower, or net, heating value assumes the water is vapor. The lower heating value for biodiesel is less than for number 2 diesel fuel (37,215 kJ/kg versus 42,565 kJ/kg).

The cetane number reflects the ability of fuel to self-ignite at the conditions in the engine cylinder. In general, the higher the value, the better the performance. The cetane number of biodiesel varies depending on the feedstock. It will be 48 to 52 for soybean oil based biodiesel and more than 60 for recycled greases. This is much higher than the typical

TABLE I
ASTM Biodiesel Specification—D6751 versus ASTM LS #2 Diesel Fuel—D975

Property	ASTM Method	Limits D6751	Units D6751	Limits D975	Units D975
Flash point	D3	130.0 min.	°C	52.0 min.	°C
Water and Sediment	D2709	0.050 max.	% vol.	0.050 max.	% vol.
Carbon residue, 100% sample	D4530	0.050 max.	% mass	N/A	N/A
Ramsbottom carbon residue	D524	N/A	N/A	0.35	% mass
Sulfated ash	D874	0.020 max.	% mass	N/A	N/A
Ash	D482	N/A	N/A	0.01	% mass
Kinematic viscosity, 40°C	D445	1.9–6.0	mm ² /s	1.9–4.1	mm ² /s
Sulfur	D5453	0.05 max.	% mass	N/A	N/A
Sulfur	D2622	N/A	N/A	0.05 max.	% mass
Cetane	D613	47 min.		40 min.	
Cloud point	D2500	By customer	°C	By customer	°C
Copper strip corrosion	D130	No. 3 max.		No. 3 max.	
Acid number	D664	0.80 max.	mg KOH/gm	N/A	N/A
Free glycerol	D6584	0.020 max.	% mass	N/A	N/A
Total glycerol	D6584	0.240 max.	% mass	N/A	N/A
Phosphorus content	D4951	0.001	% mass	N/A	N/A
Distillation temperature, 90% recovered	D1160	360 max.	°C	N/A	N/A
Distillation temperature, 90% recovered	D86	N/A	N/A	338 max.	°C

43 to 47 observed for petroleum diesel fuel. The cetane number is typically estimated for petroleum diesel fuel using the cetane index. However, due to the fact that this index was developed for diesel fuel and not biodiesel, this ASTM test procedure provides faulty information for biodiesel. A cetane engine must be used to determine the cetane number for biodiesel. See Table I.

4. BIODIESEL PRODUCTION

4.1 Introduction

Biodiesel consists of the monoalkyl esters of fatty acids derived from vegetable oils or animal fats. It is most commonly produced through a process known as transesterification, which is a chemical reaction where an alkoxy group of an ester is exchanged with that of another alcohol to form the new ester product. The chemical reaction with methanol is shown schematically in Fig. 1.

This reaction is reversible so to force the equilibrium in the direction of the products, from 60% to 200% excess methanol is added. The reaction requires a catalyst and strong bases such as potassium hydroxide and sodium hydroxide. The actual reaction using 100% excess methanol is shown in Fig. 4.

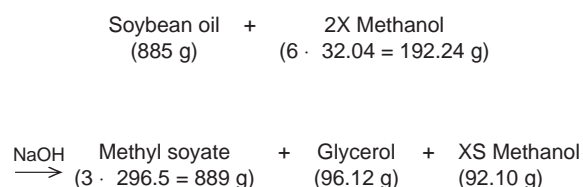


FIGURE 4 Basic transesterification reaction for soybean oil.

The alkali catalysts usually result in the reaction proceeding to completion in 4 to 8 hours at ambient conditions and in 1 hour at 60°C. In general, the catalyst is dissolved in the methanol before addition to the oil to prevent direct contact between the concentrated catalyst and the oil. Since the methanol is only slightly soluble in the soybean oil, agitation is required during the early part of the reaction. The reaction proceeds through a sequence of steps involving the removal of fatty acid chains from the triglyceride to produce diglycerides, monoglycerides, and, ultimately, free glycerol. When the reaction has proceeded to the point where substantial amounts of di- and monoglycerides have been produced, agitation is less important. To further drive the equilibrium to products, the reaction is often conducted in steps. During the first step, only a portion, say 80%, of the methanol and catalyst are added. The reaction proceeds substantially to equilibrium and then the

reactants are allowed to settle so the resulting glycerol can be removed. Then, the remaining methanol and catalyst are added and the reaction continued. Removal of the glycerol forces the reaction to the product side and since the alkali catalyst is selectively attracted to the glycerol, the presence of the glycerol can limit the speed of the reaction.

The most important characteristics of the triglyceride feedstocks are low water content (preferably less than 0.2%) and low free fatty acids (less than 0.5%). High free fatty acid (FFA) feedstocks can be processed but pretreatment to remove the FFAs or to convert them to biodiesel is required. This pretreatment will be described later. Water should be excluded from the reaction because it contributes to soap formation as the fatty acid chains are stripped from the triglycerides. The soap sequesters the alkali catalyst and inhibits the separation of the glycerol from the biodiesel. Excessive soap also contributes to the formation of emulsions when water washing is used at a later stage of the production process.

Another important characteristic of the feedstock is the presence of saturated and polyunsaturated triglycerides. Excessive levels of saturated fatty acid chains can produce biodiesel with a high pour point making it difficult to use at low temperatures. High levels of polyunsaturates can provide poor oxidative stability requiring the resulting fuel to be treated with an antioxidant.

While most biodiesel is made using methanol, because of its low price (and quick conversion), other alcohols, such as ethanol and isopropanol, can also be used. Higher alcohols provide superior cold flow properties but are generally more difficult to produce, requiring higher temperatures, lower levels of water contamination, and more complex alcohol recycling due to the formation of azeotropes.

As mentioned earlier, strong alkalis such as sodium hydroxide and potassium hydroxide are common catalysts. These bases form the corresponding methoxides when dissolved in methanol. Water is also formed in this reaction and is probably responsible for some soap formation although not enough to inhibit the transesterification reaction. A more desirable option is to use sodium methoxide formed using a water-free process. This catalyst is available as a concentrated solution in methanol (25% and 30%), which is easier to use because it is a liquid. Research is underway to develop heterogeneous catalysts for biodiesel production that would minimize soap formation and provide cleaner glycerol. Since most of the catalyst ends up as a contaminant in the glycerol, either as soap or free

alkali, a heterogeneous catalyst would simplify glycerol refining. Research is also being conducted to find reaction conditions that do not require a catalyst. However, these conditions are at very high temperature ($>250^{\circ}\text{C}$) and appear to produce undesirable contaminants in the biodiesel.

Figure 5 shows a schematic of a biodiesel production process. Oil enters the reactor where it is mixed with methanol and catalyst. Usually, the catalyst has been mixed with the methanol before contacting the oil to prevent direct contact of the concentrated catalyst and the oil to minimize soap formation. The reactor can be either a batch process or, as is more common with larger plants, a continuously stirred tank reactor (CSTR) or plug flow reactor. When a CSTR is used, it is common to use more than one stage to ensure complete reaction. After the reaction is complete, the glycerol is separated from the biodiesel. This separation can be accomplished with a gravity decanter or using a centrifuge. The unreacted methanol will split between the biodiesel and glycerol giving about 1 to 3% methanol in the biodiesel and 30 to 50% in the glycerol. The methanol in the biodiesel should be recovered for reuse. It may be as much as half of the excess methanol. This is usually accomplished by a vacuum flash process, but other devices such as falling film evaporator have also been used. The methanol-free biodiesel is then washed with water to remove residual methanol, catalyst, soap, and free glycerol. If the biodiesel contains excessive soap, this washing process can be problematic, as the soap will cause an emulsion to form between the water and the biodiesel. To minimize the formation of emulsions, a strong acid is sometimes added to the biodiesel to split the soap into free fatty acids (FFA) and salt. Without the soap, water consumption is greatly reduced and the salt, methanol, catalyst, and glycerol are removed with as little as 3 to 10% water. The water should be heated to 60°C to assist in the removal of free glycerol and should be softened to minimize the transfer of calcium and magnesium salts to the biodiesel. The final step in the process is to heat the biodiesel to remove water that may be dissolved in the biodiesel or entrained as small droplets. This is accomplished with a flash process.

Also shown in the diagram is the preliminary processing of the co-product glycerol. This glycerol contains virtually all of the catalyst and a considerable amount of soap and unreacted methanol. Usually the glycerol will be acidulated to split the soaps into FFA and salt. The FFAs are not soluble in the glycerol and rise to the top where they can be

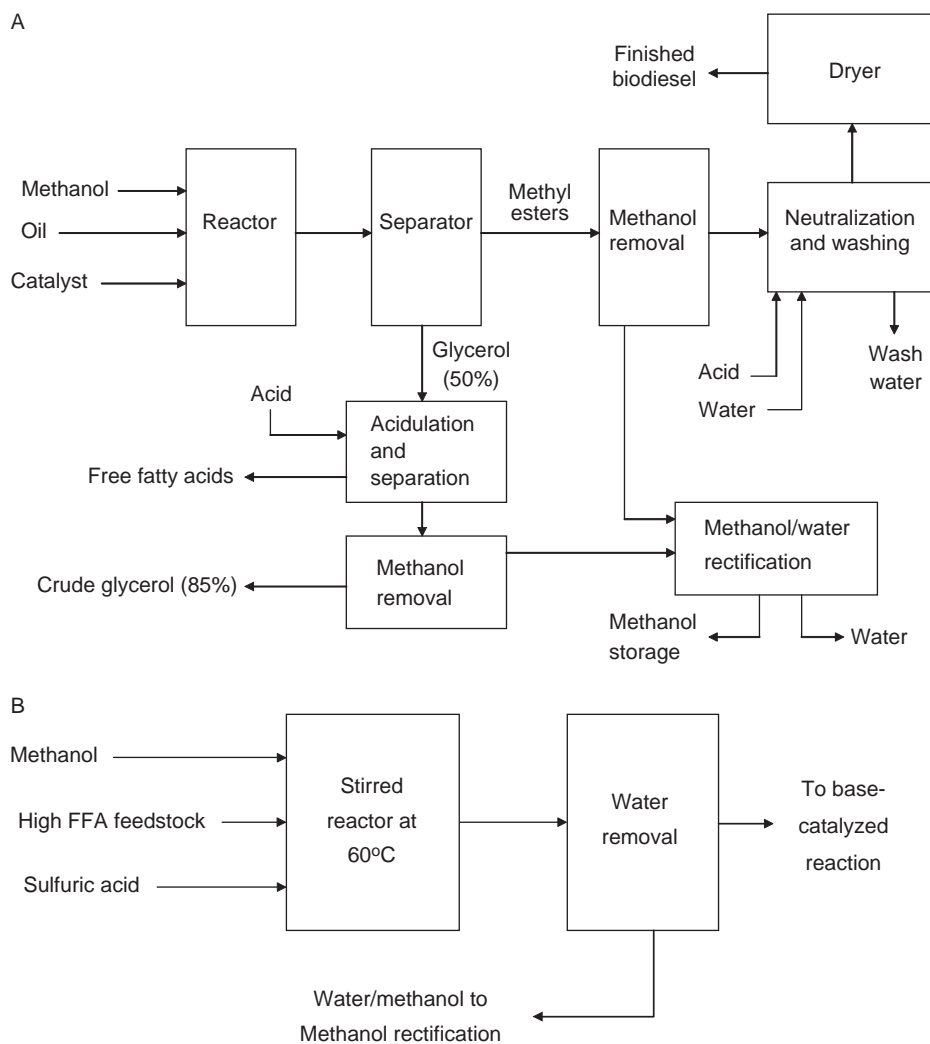


FIGURE 5 (A) Process flow schematic for biodiesel production. (B) Acid-catalyzed pretreatment process.

decanted and returned to the biodiesel process after pretreatment. After FFA removal, the methanol is removed by a flash process or by a thin-film evaporator leaving a crude glycerol product that is 80 to 90% pure. The balance will be salts, residual FFAs, water, and phosphotides, color-bodies, and other contaminants from the oil.

Although water is not deliberately added to the process until after the methanol has been removed, small amounts of water will enter the system as a contaminant in the oil, alcohol, and catalyst. This water will tend to accumulate in the methanol, so before it can be returned to the process, the methanol should undergo fractional distillation.

Biodiesel plants can use either batch or continuous flow processing. Batch processing is most common in small plants of less than 4 million liters/year. Batch

processing provides the ability to modify the process for variations in feedstock quality. Continuous flow requires greater uniformity in the feedstock quality, generally requires 24 hour operation, 7 days per week, increases labor costs, and is most suitable for larger operations of greater than 40 million liters/year.

4.2 Pretreatment

Small amounts of FFAs can be tolerated by adding enough alkali catalyst to neutralize the FFAs while still leaving enough to catalyze the reaction. When an oil or fat has more than 3 to 5% FFA, the amount of soap formed with the use of an alkali catalyst will be large enough that separation of the glycerol from the oil may not be possible. In addition, when excess

alkali is added, the FFAs are lost and not available for conversion to biodiesel.

An alternative is to convert the FFAs to methyl esters using an acid catalyst such as sulfuric acid with a large excess of methanol (>20:1 molar ratio based on the FFA content) (Fig. 5B). The acid-catalyzed reaction is relatively fast (1 hour at 60°C), converting the FFAs to methyl esters with water produced as a by-product. The water eventually stops the reaction before all of the FFAs have been converted and must be removed from the system, either by decanting with the methanol or by vaporization. After the FFAs have been converted to methyl esters, an alkali catalyst can be used to convert the triglycerides. Acid catalysis can be used to complete the transesterification reaction, but the time required is prohibitive.

4.3 Product Quality

Modern diesel engines require high-quality fuels. The fuel injection system, which is often the most expensive element of the engine, can be damaged by fuel contaminants. Water and solid particles are the largest problem.

The contaminants most frequently found in biodiesel are the products of incomplete reaction and residual alcohol, catalyst, and free glycerol. Incompletely reacted biodiesel will contain monoglycerides, diglycerides, and triglycerides. These compounds are usually detected using a gas chromatograph and then the glycerol portion is summed to yield a total glycerol quantity for the fuel. ASTM standards require that the total glycerol be less than 0.24%. This means that more than 98% of the original glycerol portion of the triglycerides feedstock must be removed. Excessive amounts of monoglycerides, especially for saturated compounds, may precipitate from the fuel and plug fuel filters.

If the biodiesel is not washed with water, it may contain some unreacted alcohol. The amount will usually be small enough that it does not adversely affect the operation of the engine, but it can lower the flash point of the fuel to where it must be considered flammable and accorded the same safety requirements as gasoline. The residual catalyst can cause excessive ash formation in the engine. Free glycerol can separate from the fuel and collect in the bottom of storage tanks. This glycerol layer can extract mono- and diglycerides from the biodiesel and produce a sludge layer that may plug filters and small passages in the fuel system.

5. ADVANTAGES OF BIODIESEL

Table II shows the changes that were observed in the regulated exhaust emissions of three diesel engines that were tested to produce emissions characterization data for the U.S. Environmental Protection Agency's Fuels and Fuel Additives registration program. The reductions in unburned hydrocarbons (HC) and carbon monoxide (CO) are dramatic although these specific pollutants are not generally a concern with diesel engines. The particulate matter (PM) reductions are also quite striking. Oxides of nitrogen (NO_x) were found to increase with the use of biodiesel. The increase varied depending on the engine tested, but it is clear that biodiesel may produce a NO_x increase of 5 to 13%. The reasons for this increase are still under investigation but appear to be a combination of several effects, including biodiesel's higher speed of sound and isentropic bulk modulus and the tendency of many engine fuel injection systems to advance the injection timing when greater volumes of fuel are injected. Due to biodiesel's lower energy content, a typical test protocol may demand a higher fuel flow rate when biodiesel is used, causing an inadvertent timing advance and resulting NO_x increase.

A comprehensive Life-Cycle Inventory of biodiesel conducted by the National Renewable Energy Laboratory showed that biodiesel provided 3.2 units of fuel energy for every unit of fossil energy consumed in its life cycle. Further, although some fossil-based CO₂ is released during biodiesel production, mainly from the methanol consumed, the net production of CO₂ is reduced by 78%.

6. DISADVANTAGES

6.1 Economics

One of the largest factors preventing the adoption of biodiesel is cost. The feedstock costs for biodiesel

TABLE II
Changes in Regulated Emissions with Biodiesel

Engine	HC	CO	PM	NO _x
Cummins N-14	-95.6	-45.3	-28.3	+13.1
DDC S-50	-83.3	-38.3	-49.0	+11.3
Cummins B5.9	-74.2	-38.0	-36.7	+4.3

Derived from Sharp *et al.*

tend to be high in comparison to the cost of petroleum diesel fuel. The end result is that the cost of biodiesel is higher than that of petroleum diesel fuel. In addition, transportation costs are significantly greater for biodiesel due to the fact that the transportation infrastructure for biodiesel is in its infancy. The costs associated with the production and transportation of biodiesel fuels are discussed in more detail in the economics section of this article.

6.2 NO_x and Other Exhaust Emissions

Biodiesel produces more NO_x emissions than diesel fuel. If B100 is used, NO_x production may be increased by 13%. If a B20 blend is used, NO_x production is only increased by 2%, and the engine will typically satisfy the EPA engine exhaust emissions requirements under the Clean Air Act. To meet the EPA emissions requirements in 2006, engine manufacturers will likely use exhaust after-treatment technology that will reduce NO_x emissions. The low sulfur levels in biodiesel fuels make them a good candidate for use with the exhaust after-treatment technologies that are available. Even though biodiesel fuels produce more NO_x emissions, they have been shown to reduce carbon monoxide, particulate matter, unburned hydrocarbons, and other pollutants.

6.3 Fuel Quality

Many problems associated with biodiesel stem from poor fuel quality from the supplier. Most often this is related to the completeness of the production reaction. The ASTM has developed a quality standard for biodiesel. At this point in time, fuel manufacturer compliance with the standard is voluntary. Generally, it is a good idea to ensure that the biodiesel manufacturer sells biodiesel that meets or exceeds the ASTM specifications.

6.4 Energy Content

Biodiesel fuels contain about 12.5% less energy per unit of weight than petroleum diesel fuel (37,215 kJ/kg vs. 42,565 kJ/kg). However, since biodiesel has a higher density, the energy content per unit of volume is only 8% less. As a result, the fuel economy of the diesel engine that is powered with biodiesel tends to be slightly less than when powered with petroleum diesel fuel.

6.5 Cold Weather

The cloud point and cold filter plugging point are much higher for biodiesel than diesel fuel. This means that the fuel will not work in the engine as well as diesel fuel at lower temperatures. Additives can be used to reduce the cloud point and CFPP of biodiesel fuel. The cold-weather properties of biodiesel can also be improved by using a lower level blend of biodiesel fuel (i.e., B5 instead of B20). Additionally, the fuel may be blended with number 1 diesel instead of number 2 diesel to improve the cold-weather properties.

6.6 Material Compatibility

Biodiesel fuel will react with some plastics and some metals in a negative manner. The plastics that seem to be compatible with biodiesel include nylon, teflon, and viton. When in contact with nonferrous metals, such as copper and zinc, biodiesel fuel can cause precipitates to form. Some of these materials can be found in fuel tank liners, fuel lines, transfer pump diaphragms, injector seals, and injection pump seals (among others).

6.7 Solvency

Biodiesel can also act as a solvent. This creates some problems when used in existing systems. The biodiesel can dissolve existing residues in fuel tanks and lines and carry them to the fuel system. Generally, after a few tanks of fuel have been used, these problems tend to be reduced.

6.8 Stability

The oxidative stability of biodiesel fuel is a major factor in determining the allowable storage time for biodiesel fuel. The iodine number can be used to estimate the oxidative stability of the fuel before any stabilizers are added. Typically biodiesel fuels can be stored for up to 6 months without problems. If biodiesel fuel needs to be stored longer, antioxidants can be added to the fuel to improve the stability. If the fuel is not stabilized, biodiesel can form gums and sediments that clog filters or form deposits on fuel system components, including fuel pumps and injectors.

Additionally, as with diesel fuel, some climatic conditions promote biological growth (such as algae), in the fuel. If this occurs, the problem can be treated with a biocide. Reduction in water

contamination also reduces the amount of biological growth in the fuel since the algae grows on the water.

6.9 Warranties

Most engine manufacturers do not warranty their engines for use with a specific fuel. Consumers with engine problems that can be traced to the fuel are directed to their fuel supplier. Many engine manufacturers have developed policy statements for biodiesel that allow the use of up to 5% biodiesel but indicate that more experience is needed before fueling with higher level blends. Most require that biodiesel meet the ASTM standard. The best practice is to check with the engine and vehicle manufacturer before using biodiesel.

7. BIODIESEL STORAGE AND USE

7.1 Blending

Blending of biodiesel is not recommended if the temperature of either fuel is below 4.4°C. Low temperatures impact how easily the biodiesel mixes with petroleum diesel fuel. In most situations, splash blending works effectively (i.e., splashing or pouring the biodiesel into the diesel fuel), as biodiesel mixes readily with petroleum diesel fuel. Once mixed, the biodiesel tends to remain blended.

If splash blending biodiesel in a large tank, the biodiesel should be introduced after the diesel fuel has been placed in the tank or the blend should be prepared before placing the blended fuel into storage. This is due to the fact that the biodiesel is heavier than diesel fuel and will essentially rest at the bottom of the tank until some type of agitation is provided. Bulk plants or terminals may also use pumps but will most likely rely on electronic injection or in-line blending to prepare the required blend.

7.2 Transportation

Biodiesel, due to its high flash point, is *not* considered flammable. The fuel is considered combustible, just as is vegetable oil (feedstock). As such, the transportation of “neat” biodiesel may be handled in the same manner as vegetable oil (Code of Federal Regulations 49 CFR 171-173). This is not the case for a low-level blend or a B20 blend. These blends exhibit flash point tendencies that essentially mirror diesel fuel. Blends of biodiesel should be handled in the same manner as petroleum diesel fuel.

7.3 Storage Tanks

Storage tanks for biodiesel can be constructed from mild steel, stainless steel, fluorinated polyethylene, fluorinated polypropylene and teflon. Biodiesel, like petroleum diesel fuel, should be stored in a clean, dry, dark environment. In the event that the container selected is made from polyethylene or polypropylene, the container should be protected from sunlight.

Some authors suggest that aluminum is suitable for use as a storage tank. However, nonferrous metals, such as aluminum, tend to react unfavorably with biodiesel by shortening the shelf life of the fuel. Much is the same for tin and zinc. Concrete lined tanks, varnish lined tanks, or tanks lined with PVC cannot be used to store biodiesel. Biodiesel reacts with each of these products, breaking down the chemical structure of each.

As with any fuel, steps must be taken to prevent water from entering the tank. Algae can grow in biodiesel just as it does with petroleum diesel fuel.

Measures should be taken to ensure that the biodiesel will flow in cold weather. This is often accomplished by mixing the fuel with either number 1 or number 2 diesel fuel. Cold flow improvers (CFI) can also be added to enhance the cold flow characteristics of biodiesel.

7.4 Material Compatibility

Essentially the same materials that are used to construct a biodiesel storage tank can be used with biodiesel (stainless steel, mild steel, viton, some forms of teflon, and fluorinated polyethylene/polypropylene). Rubber elastomers cannot be used, as pure biodiesel will dissolve the rubber. The effect is lessened with lower percentage blends, but little research has been conducted to determine the long-term material compatibility of biodiesel blends.

7.5 Safety

Biodiesel is nontoxic, biodegradable, and much less irritating to the skin than petroleum diesel. However, the same safety rules that pertain to petroleum diesel fuel also apply to the use of biodiesel. The following list summarizes several of these issues:

- Store in closed, vented containers between 10°C and 50°C.
- Keep away from oxidizing agents, excessive heat, and ignition sources.
- Store, fill, and use in well-ventilated areas.

- Do not store or use near heat, sparks, or flames; store out of the sun.
- Do not puncture, drag, or slide the storage tank.
- A drum is not a pressure vessel; never use pressure to empty.
- Wear appropriate eye protection when filling the storage tank.
- Provide crash protection (i.e., large concrete-filled pipe near the storage tank).

8. BIODIESEL ECONOMIC CONSIDERATIONS

The cost of biodiesel consists of five major components: the cost of the feedstock, the cost of the biodiesel, the price of glycerol by-product, and availability of biodiesel. We will examine each of these components.

8.1 Cost of the Feedstock

The cost of the feedstock (oil/tallow/lard, etc.) will vary from one season to the next. The cost will also vary from one crop to the next (soybeans versus rapeseed) as well as from one year to the next, depending on supply and demand. For example, soybean oil has fluctuated from 14.15 cents/pound to 25.8 cents/pound during 1995–2002. Peanut oil has varied from 27 to 49 cents/pound during the same time period. At the same time, lard has sold for 12.5 to 23.02 cents/pound. During 2001–2002, the price of cottonseed oil varied from 14.4 to 22.3 cents per pound and corn oil varied from 11.38 to 23.02 cents/pound. During 2001–2002, the high for corn was in December and the low was in May. The high for cottonseed oil occurred in September and the low occurred in October. Some biodiesel producers have been able to purchase used restaurant grease for as little as 3 to 4 cents/pound (McDonalds, etc.), while some have been paid to haul the waste oil away (transportation was the only feedstock cost).

8.2 Cost of Biodiesel

Economies of scale are a factor when buying biodiesel. Since biodiesel is not yet available on the pipeline network, most deliveries are made by truck or rail. Transportation costs can be a significant portion of the product cost.

The most significant contributor to the cost of the fuel is the cost of the oil itself. As noted in the

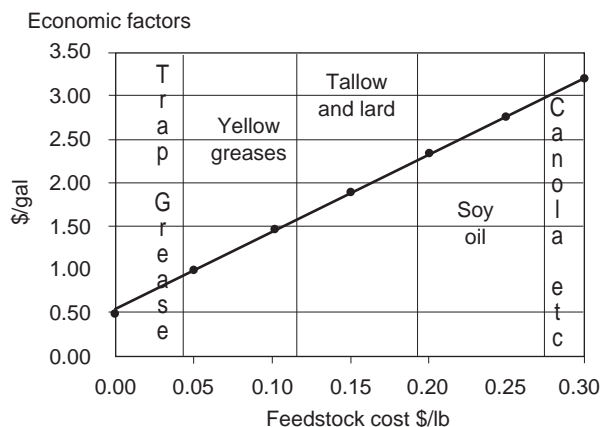


FIGURE 6 Production cost per gallon. Reprinted from National Renewable Energy Laboratory, Kansas Cooperative Development Center/KSU.

feedstock section, the price of the oil has varied from as little as 3 to 4 cents/pound to a high of 25.8 cents/pound. If soybeans were used as the feedstock, the cost could range from \$1.73 to \$3.10/gallon. If a less expensive feedstock were used, the price range would even be greater anywhere from \$0.50 to \$63.10/gallon. (See Fig. 6.)

The next highest cost when producing biodiesel is the cost to convert the feedstock from a pure oil to a transesterified fuel. Some researchers report that this amounts to approximately 30% of the total cost (as nearly 70% of the cost is tied up in the raw materials [soybean oil feedstock, methanol, catalyst]).

The conversion costs for biodiesel can range from \$0.30 to \$0.60/gallon. One study reported that it cost \$0.58/gallon for transesterification and \$0.33/gallon for overhead. A credit of \$0.39/gallon was applied for the resale of the glycerol, bringing the total for transesterification to \$0.52/gallon.

8.3 Price of Glycerol

As noted in the previous paragraph, the glycerol is a valuable by-product that must be disposed of after transesterification (credit = \$0.39/gallon). Glycerol is used in pharmaceuticals, cosmetics, toothpaste, paints, and other products. Most researchers believe that a flood of glycerol on the market (which would result from increased biodiesel production) would reduce the net credit. Alternative uses for the glycerol would develop and these uses should help maintain a solid price for the glycerol. Presently, refined glycerol prices stand in the United States at approximately \$0.65/pound.

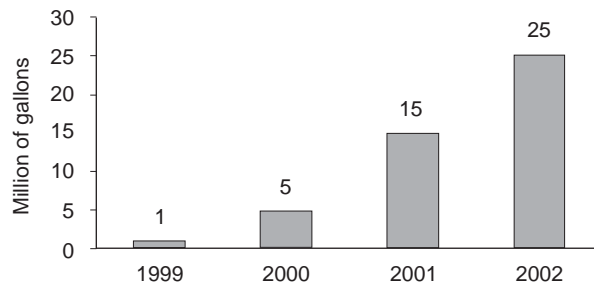


FIGURE 7 U.S. biodiesel production. Reprinted from the National Biodiesel Board, Kansas Cooperative Development Center/KSU.

8.4 Availability

Most economists are of the opinion that biodiesel has the capability to replace about 2 to 5% of the diesel fuel used for transportation in the United States. Although this may seem small in comparison to the volume of diesel fuel used, this would indicate that we would need to produce roughly 6 billion gallons of biodiesel each year. However, Brazil has become a major exporter in the soybean market, and large carryover stocks of soybeans have resulted. The estimated soybean oil carryover for the year 2002 was 1.2 million metric tons. The United States produces 25 million gallons of biodiesel a year. (See Fig. 7.)

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