

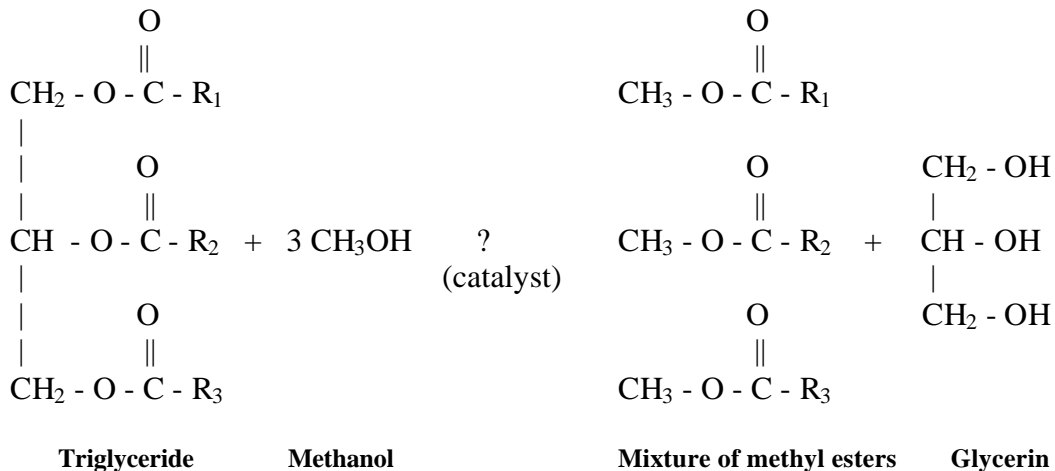
Biodiesel Production and Fuel Quality

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Biodiesel processing and quality are closely related. The processes used to refine the feedstock and convert it to biodiesel determine whether the fuel will meet the applicable specifications. This paper will describe the processing and production of biodiesel and how this determines fuel quality. The emphasis will be on processing as it is conducted in the United States, where most biodiesel is produced by reacting soybean oil or used cooking oils with methanol and the standard for fuel quality will be ASTM D 6751-02.

Background

Biodiesel is produced by chemically reacting a fat or oil with an alcohol, in the presence of a catalyst. The product of the reaction is a mixture of methyl esters, which are known as *biodiesel*, and glycerol, which is a high value co-product. The process is known as *transesterification*, as shown in the equation below, where R₁, R₂, and R₃ are long hydrocarbon



chains, sometimes called fatty acid chains. There are only five chains that are common in most vegetable oils and animal fats (others are present in small amounts). The relative amounts of the five methyl esters determines the physical properties of the fuel, including the cetane number, cold flow, and oxidative stability.

Biodiesel can be used neat and when used as a pure fuel it is known as B100. However, it is often blended with petroleum-based diesel fuel and when this is done the blend is designated "BXX" where XX is the percentage of biodiesel in the blend. For example, B20 is a blend of 20% biodiesel and 80% petroleum diesel fuel.

While virtually all commercial biodiesel producers use an alkali-catalyzed process for the transesterification process, other approaches have been proposed including acid catalysis [1] and enzymes [2-5]. The use of acid catalysts has been found to be useful for pretreating high free fatty acid feedstocks but the reaction rates for converting triglycerides to methyl esters are very slow. Enzymes have shown good tolerance for the free fatty acid level of the feedstock but the enzymes are expensive and unable to provide the degree of reaction completion required to meet the ASTM fuel specification [6]. Immobilization of the enzyme and use of multiple enzymes in sequence may provide future opportunities in this area [3-5].

Alkali-catalyzed Transesterification

Figure 1 shows a schematic diagram of the processes involved in biodiesel production from feedstocks containing low levels of free fatty acids (FFA). This includes soybean oil, canola (rapeseed) oil, and the higher grades of waste restaurant oils. Alcohol, catalyst, and oil are combined in a reactor and agitated for approximately one hour at 60°C. Smaller plants often use batch reactors [7] but most larger plants (> 4 million liters/yr) use continuous flow processes involving continuous stirred-tank reactors (CSTR) or plug flow reactors [8]. The reaction is sometimes done in two steps where approximately 80% of the alcohol and catalyst is added to the oil in a first stage CSTR. Then, the product stream from this reactor goes through a glycerol removal step before entering a second CSTR. The remaining 20% of the alcohol and catalyst are added in this second reactor. This system provides a very complete reaction with the potential of

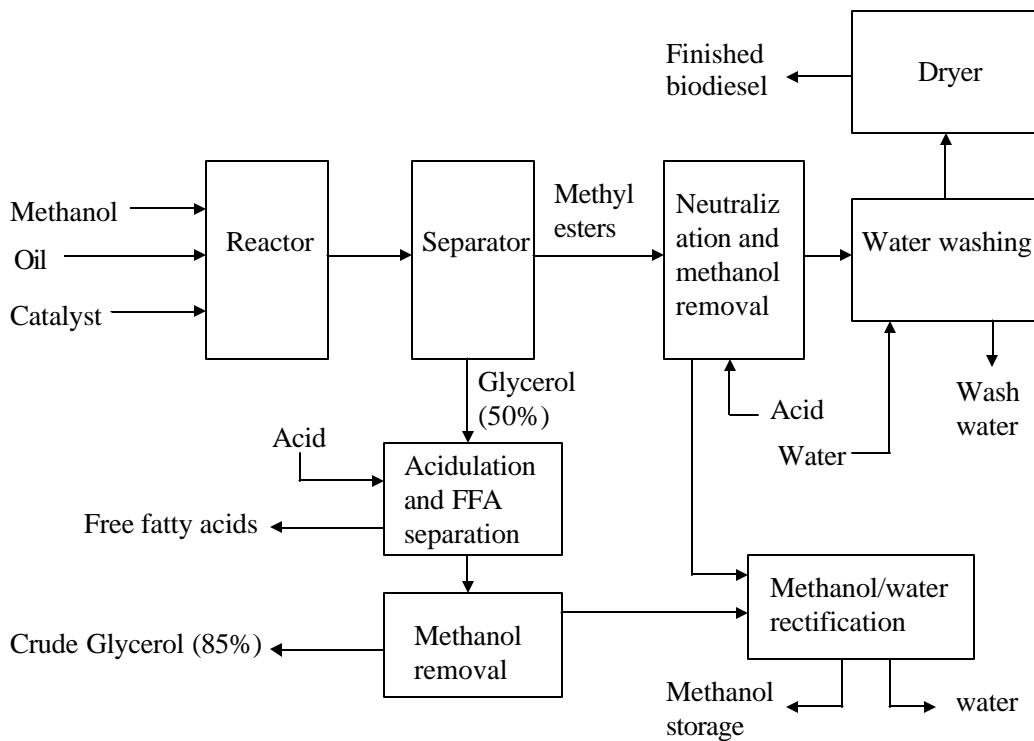


Figure 1. Process Flow Schematic for Biodiesel Production

using less alcohol than single step systems.

Following the reaction, the glycerol is removed from the methyl esters. Due to the low solubility of glycerol in the esters, this separation generally occurs quickly and may be accomplished with either a settling tank or a centrifuge. The excess methanol tends to act as a solubilizer and can slow the separation. However, this excess methanol is usually not removed from the reaction stream until after the glycerol and methyl esters are separated due to concern about reversing the transesterification reaction. Water may be added to the reaction mixture after the transesterification is complete to improve the separation of glycerol [7, 9].

Saka and Kusiana [10-12, 14], Dasari et al. [13], and Diasakou et al. [15] claim that it is possible to react the oil and methanol without a catalyst, which eliminates the need for the water washing step. However, high temperatures and large excesses of methanol are required. Dasari et al. [13] noted the difficulty of reproducing the reaction kinetics results of other researchers and attributed it to catalytic effects at the surfaces of the reaction vessels and noted these effects would be exacerbated at higher temperatures. Not including the effect of surface reactions could cause difficulties when scaling up reactors due to the decrease in the ratio of reactor surface area to volume. Kreutzer [16] has described how higher pressures and temperatures (90 bar, 240°C) can transesterify the fats without prior removal or conversion of the free fatty acids. However, most biodiesel plants use lower temperatures, near atmospheric pressure, and longer reaction times to reduce equipment costs.

Boocock et al. [17-19] have developed a novel technique for accelerating the transesterification reaction rate. During its early stages, the transesterification reaction is limited by the low solubility of the alcohol, especially methanol, in the oil. Boocock proposes the addition of a cosolvent to create a single phase and this greatly accelerates the reaction so that it reaches substantial completion in a few minutes. The technique is applicable for use with other alcohols and for acid-catalyzed pretreatment of high free fatty acid feed stocks. The primary concerns with this method are the additional complexity of recovering and recycling the cosolvent although this can be simplified by choosing a cosolvent with a boiling point near that of the alcohol being used. Additional concerns have been raised about the hazard level associated with the cosolvents most commonly proposed, tetrahydrofuran and methyl tertiary butyl ether.

Returning to Figure 1, after separation from the glycerol, the methyl esters enter a neutralization step and then pass through a methanol stripper, usually a vacuum flash process or a falling film evaporator, before water washing. Acid is added to the biodiesel to neutralize any residual catalyst and to split any soap that may have formed during the reaction. Soaps will react with the acid to form water soluble salts and free fatty acids, as shown in the following reaction.



The salts will be removed during the water washing step and the free fatty acids will stay in the biodiesel. The water washing step is intended to remove any remaining catalyst, soap, salts, methanol, or free glycerol from the biodiesel. Neutralization before washing reduces the water required and minimizes the potential for emulsions to form when the wash water is added to the

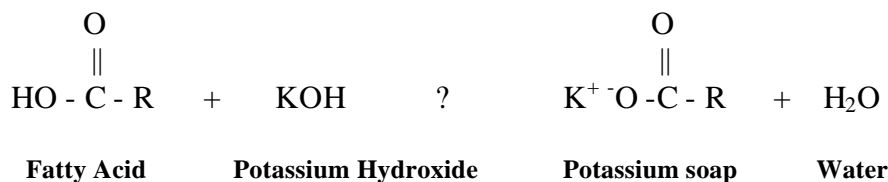
biodiesel. Following the wash process, any remaining water is removed from the biodiesel by a vacuum flash process.

The glycerol stream leaving the separator is only about 50% glycerol. It contains some of the excess methanol and most of the catalyst and soap. In this form, the glycerol has little value and disposal may be difficult. The methanol content requires the glycerol to be treated as hazardous waste. The first step in refining the glycerol is usually to add acid to split the soaps into free fatty acids and salts. The free fatty acids are not soluble in the glycerol and will rise to the top where they can be removed and recycled. The salts remain with the glycerol although depending on the chemical compounds present, some may precipitate out. Mittelbach and Koncar describe a process for esterifying these free fatty acids and then returning them to the transesterification reaction stream [20]. One frequently touted option is to use potassium hydroxide as the reaction catalyst and phosphoric acid for neutralization so that the salt formed is potassium phosphate, which can be used for fertilizer. After acidulation and separation of the free fatty acids, the methanol in the glycerol is removed by a vacuum flash process, or another type of evaporator. At this point, the glycerol should have a purity of approximately 85% and is typically sold to a glycerol refiner. The glycerol refining process takes the purity up to 99.5 to 99.7% using vacuum distillation or ion exchange processes.

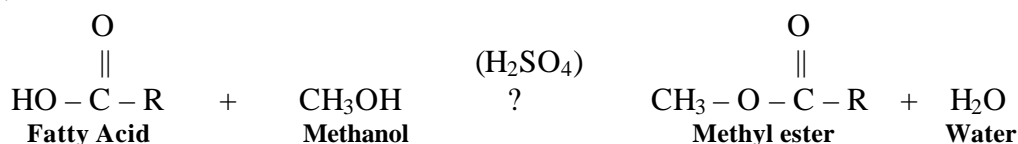
The methanol that is removed from the methyl ester and glycerol streams will tend to collect any water that may have entered the process. This water should be removed in a distillation column before the methanol is returned to the process. This step is more difficult if an alcohol such as ethanol or isopropanol is used that forms an azeotrope with water. Then, a molecular sieve is used to remove the water.

Acid Catalyzed Pretreatment

Special processes are required if the oil or fat contains significant amounts of FFAs. Used cooking oils typically contain 2-7% FFAs and animal fats contain from 5-30% FFAs. Some very low quality feedstocks, such as trap grease, can approach 100% FFAs. When an alkali catalyst is added to these feedstocks, the free fatty acids react with the catalyst to form soap and water as shown in the reaction below:



Up to about 5% FFAs, the reaction can still be catalyzed with an alkali catalyst but additional catalyst must be added to compensate for that lost to soap. The soap created during the reaction is either removed with the glycerol or is washed out during the water wash. When the FFA level is above 5%, the soap inhibits separation of the glycerol from the methyl esters and contributes to emulsion formation during the water wash. For these cases, an acid catalyst such as sulfuric acid can be used to esterify the FFAs to methyl esters as shown in the following reaction:



As shown in Figure 2, this process can be used as a pretreatment to convert the FFAs to methyl esters and thereby reduce the FFA level. Then, the low FFA pretreated oil can be transesterified with an alkali catalyst to convert the triglycerides to methyl esters [21]. As shown in the reaction, water is formed and, if it accumulates, it can stop the reaction well before completion. Kawahara and Ono [22] propose allowing the alcohol to separate from the pretreated oil or fat following the reaction. Removal of this alcohol also removes the water formed by the esterification reaction and allows for a second step of esterification or proceeding directly to alkali-catalyzed transesterification. Note that the methanol-water mixture will also contain some dissolved oil and FFAs that should be recovered and reprocessed. Jeromin et al. [23] has described using acidic ion exchange resins in a packed bed for the pretreatment. Haas et al. [24-25] have shown that acid-catalyzed esterification can be used to produce biodiesel from low-grade by-products of the oil refining industry such as soapstock. Soapstock, a mixture of water, soaps, and oil, is dried, saponified, and then esterified with methanol or some other simple alcohol using an inorganic acid as a catalyst. The procedure relies on a large excess of alcohol and the cost of recovering this alcohol determines the feasibility of the process.

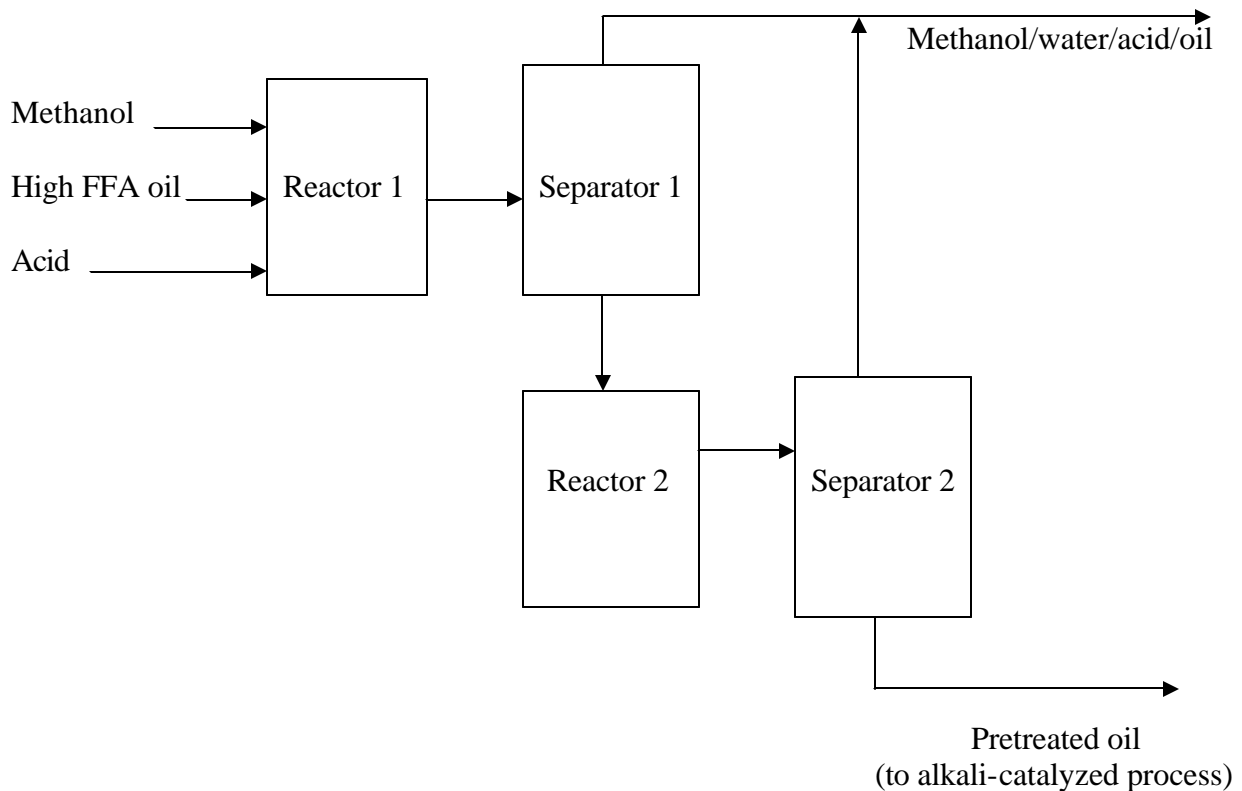


Figure 2. Pretreatment process for high free fatty acids feedstocks

Fuel Quality

The primary criterion for biodiesel quality is adherence to the appropriate standard. In the United States, this standard is ASTM D 6751-02 “Standard Specification for Biodiesel Fuel (B100) Blend Stock for Distillate Fuels”. Generally, the fuel quality of biodiesel can be influenced by several factors:

- The quality of the feedstock.
- The fatty acid composition of the parent vegetable oil or animal fat.
- The production process and the other materials used in this process.
- Post-production parameters.

Table 1 shows the property values required for a mixture of methyl esters to be considered biodiesel. When these limits are met, the biodiesel can be used in most modern engines without modifications while maintaining the engine’s durability and reliability. Even in low level blends with conventional diesel fuel, the biodiesel blending stock is expected to meet the standard before being blended. While some properties in the standard, such as cetane

Table 1. ASTM D 6751–02 Biodiesel Specifications [6]

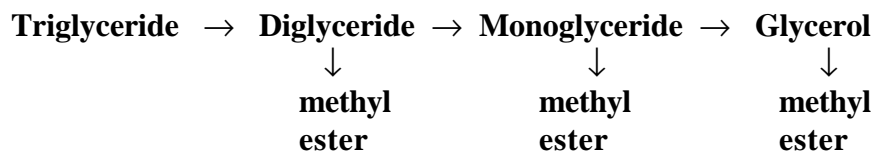
<i>Property</i>	<i>Method</i>	<i>Limits</i>	<i>Units</i>
<i>Flash point, closed cup</i>	<i>D 93</i>	<i>130 min</i>	<i>° C</i>
<i>Water and sediment</i>	<i>D 2709</i>	<i>0.050 max</i>	<i>% volume</i>
<i>Kinematic viscosity, 40 ° C</i>	<i>D 445</i>	<i>1.9 – 6.0</i>	<i>mm²/s</i>
<i>Sulfated ash</i>	<i>D 874</i>	<i>0.020 max</i>	<i>wt. %</i>
<i>Total Sulfur</i>	<i>D 5453</i>	<i>0.05 max</i>	<i>wt. %</i>
<i>Copper strip corrosion</i>	<i>D 130</i>	<i>No. 3 max</i>	
<i>Cetane number</i>	<i>D 613</i>	<i>47 min</i>	
<i>Cloud point</i>	<i>D 2500</i>	<i>Report to customer</i>	<i>° C</i>
<i>Carbon residue</i>	<i>D 4530</i>	<i>0.05 max</i>	<i>wt. %</i>
<i>Acid number</i>	<i>D 664</i>	<i>0.8 max</i>	<i>mg KOH/g</i>
<i>Free glycerin</i>	<i>D 6584</i>	<i>0.02</i>	<i>wt. %</i>
<i>Total glycerin</i>	<i>D 6584</i>	<i>0.24</i>	<i>wt. %</i>
<i>Phosphorus</i>	<i>D 4951</i>	<i>10</i>	<i>ppm</i>
<i>Vacuum distillation end point</i>	<i>D 1160</i>	<i>360 °C max, at T-90</i>	
<i>Storage stability</i>	<i>To be determined</i>	<i>To be determined</i>	<i>To be determined</i>

number and density, reflect the properties of the chemical compounds that make up biodiesel, other properties provide indications of the quality of the production process. Generally, the parameters given in ASTM D6751 are defined by other ASTM standards. However, other test methods, such as those developed for the American Oil Chemists' Society, (AOCS) may also be suitable (or even more appropriate as they were developed for fats and oils and not for petroleum-derived materials addressed in the ASTM standards). This discussion will focus on the most important issues for assuring product quality for biodiesel as it is related to production as well as some post-production parameters.

Production Process Factors

Completion of reaction

The most important issue during biodiesel production is the completeness of the transesterification reaction. The basic chemical process that occurs during the reaction is indicated by the following sequence of events:



The triglycerides are converted to diglycerides, which in turn are converted to monoglycerides, and then to glycerol. Each step produces a molecule of a methyl ester of a fatty acid. If the reaction is incomplete, then there will be triglycerides, diglycerides, and monoglycerides left in the reaction mixture. Each of these compounds still contains a glycerol molecule that has not been released. The glycerol portion of these compounds is referred to as *bound glycerol*. When the bound glycerol is added to the free glycerol, the sum is known as the *total glycerol*. The ASTM specification requires that the total glycerol be less than 0.24% of the final biodiesel product as measured using a gas chromatographic method described in ASTM D 6584. Since the glycerol portion of the original oil is usually about 10.5%, this level of total glycerol corresponds to 97.7% reaction completion. Other methods can be used to measure total glycerol such as a high performance liquid chromatograph (HPLC; for example AOCS Recommended Practice Ca 14b-96: Quantification of Free Glycerine in Selected Glycerides and Fatty Acid Methyl Esters by HPLC with Laser Light-Scattering Detection) or a chemical procedure such as that described in AOCS Official Method Ca 14-56 (Total, Free and Combined Glycerol Iodometric Method). All of these techniques require a fairly high level of training and some laboratory equipment. Only the gas chromatographic procedure is acceptable for demonstrating compliance with ASTM D 6751.

Free Glycerol

Free glycerol refers to the amount of glycerol that is left in the finished biodiesel. Glycerol is essentially insoluble in biodiesel so almost all of the glycerol is easily removed by settling or centrifugation. Free glycerol may remain either as suspended droplets or as the very

small amount that is dissolved in the biodiesel. Alcohols can act as cosolvents to increase the solubility of glycerol in the biodiesel. Most of this glycerol should be removed during the water washing process. Water-washed fuel is generally very low in free glycerol, especially if hot water is used for washing. Distilled biodiesel tends to have a greater problem with free glycerol due to glycerol carry-over during distillation. Fuel with excessive free glycerol will usually have a problem with glycerol settling out in storage tanks, creating a very viscous mixture that can plug fuel filters and cause combustion problems in the engine.

Residual Alcohol and Residual Catalyst

Since methanol (and ethanol) and the alkaline catalysts are more soluble in the polar glycerol phase, most will be removed when the glycerol is separated from the biodiesel. However, the biodiesel typically contains 2-4% methanol after the separation, which may constitute as much as 40% of the excess methanol from the reaction. Most processors will recover this methanol using a vacuum stripping process. Any methanol remaining after this stripping process should be removed by the water washing process. Therefore, the residual alcohol level in the biodiesel should be very low. A specific value for the allowable alcohol level is specified in European biodiesel standards (0.2% in EN 14214), but is not included in the ASTM standard. Tests have shown that as little as 1% methanol in the biodiesel can lower the flashpoint of the biodiesel from 170°C to less than 40°C. Therefore, by including a flashpoint specification of 130°C, the ASTM standard limits the amount of alcohol to a very low level (<0.1%). Residual alcohol left in the biodiesel will generally be too small to negatively impact the fuel's performance. However, lowering the flashpoint presents a potential safety hazard as the fuel may need to be treated more like gasoline, which also has a low flashpoint, than diesel fuel.

Most of the residual catalyst is removed with the glycerol. Like the alcohol, remaining catalyst should be removed during the water washing. Although a value for residual catalyst is not included in the ASTM standard, it will be limited by the specification on sulfated ash. Excessive ash in the fuel can lead to engine deposits and high abrasive wear levels. The European standard EN 14214 places limits on calcium and magnesium as well as the alkali metals sodium and potassium.

Post-production Factors

Water and Sediment

Water and sediment contamination are basically housekeeping issues for biodiesel. Water can be present in two forms, either as dissolved water or as suspended water droplets. While biodiesel is generally considered to be insoluble in water, it actually takes up considerably more water than diesel fuel. Biodiesel can contain as much as 1500 ppm of dissolved water while diesel fuel usually only takes up about 50 ppm [26]. The standards for diesel fuel (ASTM D 975) and biodiesel (ASTM D 6751) both limit the amount of water to 500 ppm. For petroleum-based diesel fuel, this actually allows a small amount of suspended water. However, biodiesel must be kept dry. This is a challenge because many diesel storage tanks have water on the bottom due to condensation. Suspended water is a problem in fuel injection equipment because it contributes to the corrosion of the closely fitting parts in the fuel injection system.

Water can also contribute to microbial growth in the fuel. This problem can occur in both biodiesel and conventional diesel fuel and can result in acidic fuel and sludges that will plug fuel filters.

Sediment may consist of suspended rust and dirt particles or it may originate from the fuel as insoluble compounds formed during fuel oxidation. Some biodiesel users have noted that switching from petroleum-based diesel fuel to biodiesel causes an increase in sediment that comes from deposits on the walls of fuel tanks that had previously contained diesel fuel. Because its solvent properties are different from diesel fuel, biodiesel may loosen these sediments and cause fuel filter plugging during the transition period.

Storage Stability

Storage stability refers to the ability of the fuel to resist chemical changes during long term storage. These changes usually consist of oxidation due to contact with oxygen from the air. The fatty acid composition of the biodiesel fuel is an important factor in determining stability towards air. Generally, the polyunsaturated fatty acids (C18:2, linoleic acid; C18:3 linolenic acid) are most susceptible to oxidation. The changes can be catalyzed by the presence of certain metals (including those making up the storage container) and light. If water is present, hydrolysis can also occur. The chemical changes in the fuel associated with oxidation usually produce hydroperoxides that can, in turn, produce short chain fatty acids, aldehydes, and ketones. Under the right conditions, the hydroperoxides can also polymerize. Therefore, oxidation is usually denoted by an increase in the acid value and viscosity of the fuel. Often these changes are accompanied by a darkening of the biodiesel color from yellow to brown and the development of a “paint” smell. When water is present, the esters can hydrolyze to long chain free fatty acids which also cause the acid value to increase.

There is currently no generally accepted method for measuring the stability of biodiesel. The techniques generally used for petroleum-based fuels, such as ASTM D 2274, have been shown to be incompatible with biodiesel. Other procedures, such as the Oil Stability Index or the Rancimat apparatus, which are widely used in the fats and oils industry, seem to be more appropriate for use with biodiesel. However, the engine industry has no experience with these tests and acceptable values are not known. Also, the validity of accelerated testing methods has not been established or correlated to actual engine problems. If biodiesel’s acid number, viscosity, or sediment content increase to the point where they exceed biodiesel’s ASTM limits, the fuel should not be used as a transportation fuel.

Additives such as BHT and TBHQ (t-butylhydroquinone) are common in the food industry and have been found to enhance the storage stability of biodiesel. Biodiesel produced from soybean oil naturally contain some antioxidants (tocopherols, i.e., vitamin E), providing some protection against oxidation (some tocopherol is lost during refining of the oil prior to biodiesel production). Any fuel that will be stored for more than 6 months, whether it is diesel fuel or biodiesel, should be treated with an antioxidant additive.

Quality Control

All biodiesel production facilities should be equipped with a laboratory so that the quality of the final biodiesel product can be monitored. It is also important to monitor the quality of the feedstocks.

One strategy used by many producers is to draw a sample of the oil (or alcohol) from each delivery and use that sample to produce biodiesel in the laboratory. This test can be fairly rapid (1 or 2 hours) and can indicate whether serious problems are likely in the plant.

Measuring feedstock quality can usually be limited to acid value and water content. These are not too expensive (\$500 for the acid value equipment and \$5,000 for the water measurement equipment) and can be operated by less experienced technicians.

To monitor the completeness of the reaction according to the total glycerol level specified in ASTM D 6751 requires the use of a gas chromatograph and a skilled operator. Large producers will find that having this equipment on-site is necessary. Commercial laboratories (i.e. Magellan Midstream Partners) are available that can analyze the samples but the cost is \$80-\$150/test and the time required may be several days. Smaller producers will need to use a more robust production process involving extra methanol and probably multiple reaction steps. Then the product quality can be monitored through periodic testing by an outside laboratory.

Other possibilities for monitoring the transesterification reaction and assessing fuel quality are methods based on spectroscopy (such as near-infrared spectroscopy) or physical properties (such as viscometry). These methods, although they are not (yet?) ASTM methods, are usually faster and easier to use than gas chromatography. However, some of them require extensive calibration. They also cannot accurately quantify glycerol at the low levels called for in the ASTM standard. To circumvent this, comparison to a reaction and product known to meet ASTM standards is needed.

Conclusions

Biodiesel is an important new alternative transportation fuel. It can be produced from many vegetable oil or animal fat feedstocks. Conventional processing involves an alkali-catalyzed process but this is unsatisfactory for lower cost high free fatty acid feedstocks due to soap formation. Pretreatment processes using strong acid catalysts have been shown to provide good conversion yields and high quality final products. These techniques have even been extended to allow biodiesel production from feedstocks like soapstock that are often considered to be waste. Adherence to a quality standard is essential for proper performance of the fuel in the engine and will be necessary for widespread use of biodiesel.

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