



Biodiesel processing and production

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Abstract

Biodiesel is an alternative diesel fuel that is produced from vegetable oils and animal fats. It consists of the monoalkyl esters formed by a catalyzed reaction of the triglycerides in the oil or fat with a simple monohydric alcohol. The reaction conditions generally involve a trade-off between reaction time and temperature as reaction completeness is the most critical fuel quality parameter. Much of the process complexity originates from contaminants in the feedstock, such as water and free fatty acids, or impurities in the final product, such as methanol, free glycerol, and soap. Processes have been developed to produce biodiesel from high free fatty acid feedstocks, such as recycled restaurant grease, animal fats, and soapstock.

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1. Introduction

Biodiesel is an alternative fuel for diesel engines that is produced by chemically reacting a vegetable oil or animal fat with an alcohol such as methanol. The reaction requires a catalyst, usually a strong base, such as sodium or potassium hydroxide, and produces new chemical compounds called methyl esters. It is these esters that have come to be known as *biodiesel*.

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Because its primary feedstock is a vegetable oil or animal fat, biodiesel is generally considered to be renewable. Since the carbon in the oil or fat originated mostly from carbon dioxide in the air, biodiesel is considered to contribute much less to global warming than fossil fuels. Diesel engines operated on biodiesel have lower emissions of carbon monoxide, unburned hydrocarbons, particulate matter, and air toxics than when operated on petroleum-based diesel fuel.

The objective of this paper is to describe the processing and production of biodiesel. 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.

2. Background

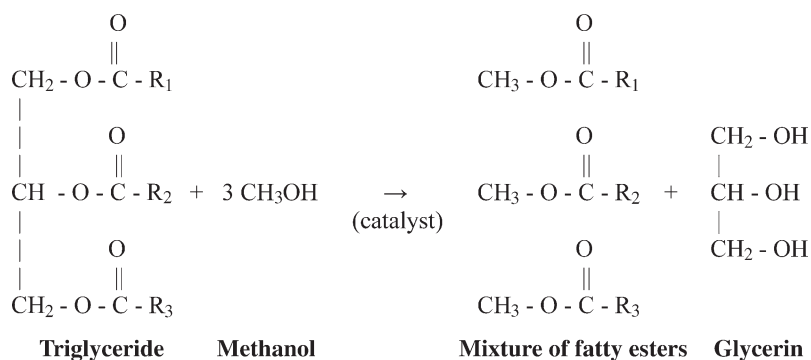
At current production levels, biodiesel requires a subsidy to compete directly with petroleum-based fuels. However, federal and state governments are providing incentives that encourage the rapid growth of the biodiesel industry. Current production levels are 20–25 million gallons/year, but achieving current European levels of 500 million to 1 billion gallons/year should be feasible.

The combined vegetable oil and animal fat production in the United States totals about 35.3 billion pounds per year [1]. This production could provide 4.6 billion gallons of biodiesel. However, the annual consumption of on-highway diesel fuel in the United States is about 33 billion gallons. If all of the vegetable oil and animal fat produced in the U.S. were available to produce biodiesel, it would only displace about 14% of the current demand for on-highway diesel fuel.

Although biodiesel cannot entirely replace petroleum-based diesel fuel, there are at least five reasons that justify its development.

1. It provides a market for excess production of vegetable oils and animal fats.
2. It decreases, although will not eliminate, the country's dependence on imported petroleum.
3. Biodiesel is renewable and does not contribute to global warming due to its closed carbon cycle. A life cycle analysis of biodiesel showed that overall CO₂ emissions were reduced by 78% compared with petroleum-based diesel fuel [2].
4. The exhaust emissions of carbon monoxide, unburned hydrocarbons, and particulate emissions from biodiesel are lower than with regular diesel fuel. Unfortunately, most emissions tests have shown a slight increase in oxides of nitrogen (NO_x).
5. When added to regular diesel fuel in an amount equal to 1–2%, it can convert fuel with poor lubricating properties, such as modern ultra-low-sulfur diesel fuel, into an acceptable fuel.

Biodiesel is produced through a process known as *transesterification*, as shown in the equation below,



where R_1 , R_2 , and R_3 are long hydrocarbon chains, sometimes called fatty acid chains. There are only five chains that are most common in soybean oil and animal fats (others are present in small amounts).

Although the research did not anticipate the production of alkyl esters for fuel, most of the processes for biodiesel production were developed in the early 1940s and are described in a series of patents by researchers from E.I. duPont and Colgate–Palmolive–Peet [3–12]. The original objective of this work was to develop a simplified method for extracting glycerol during soap production. The glycerol was needed for war-time explosives production. By chemically converting oils and fats to methyl esters, the glycerol could be separated because it is insoluble in the esters. The glycerol has a much higher density so it is easily removed by settling or centrifuge. The glycerol-free methyl esters were then reacted with alkali to form soap. Bradshaw [3–5] received a patent for a process that added about 1.6 times the theoretical amount of an alcohol, such as methanol, which contained 0.1 to 0.5% sodium or potassium hydroxide, to an oil or fat. When performed at 80 °C, this process provided 98% conversion to alkyl esters and high-quality glycerol. These patents contain the following observations about the transesterification process:

- Excess alcohol of more than 1.6 times the stoichiometric amount is required for complete reaction.
- The amount of alcohol used can be reduced by conducting the reaction in steps, where part of the alcohol and catalyst are added at the start of each step, and the glycerol is removed at the end of each step.
- Besides methanol, other alcohols can be used including ethanol, propanol, isopropanol, butanol, and pentanol.
- Water and free fatty acids inhibit the reaction. Higher alcohols are particularly sensitive to water contamination.

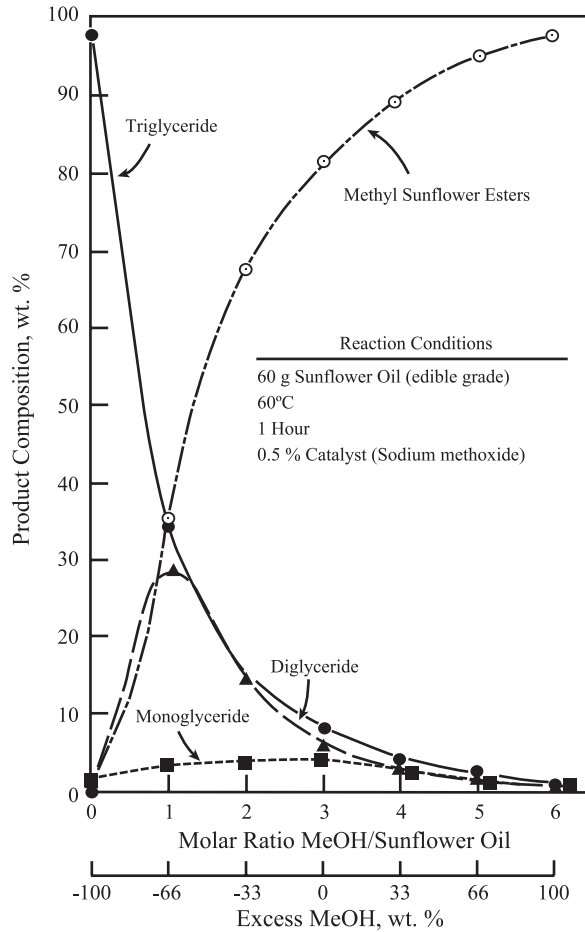


Fig. 1. Effect of alcohol to oil ratio on product composition for transesterification [19].

- Free fatty acids in the oils or fats can be converted to alkyl esters with an acid catalyst. This can be followed by a standard alkali-catalyzed transesterification to convert the triglycerides.
- Acid catalysts can be used for the transesterification of oils to alkyl esters, but they are much slower than alkali catalysts.

Knothe [13] has described how ethyl esters were proposed as diesel fuel substitutes as early as 1937 in the Belgian Congo. Widespread investigation of these esters did not occur until the late 1970s and early 1980s when high petroleum prices inspired extensive research into alternative fuels. Vegetable oils were proposed as diesel fuels but were found to be problematic due mostly to their greater viscosity [14–18]. Problems were found with piston and injector deposits and crankcase oil dilution and resultant oil thickening. Conversion of the oils to their alkyl esters reduced the viscosity to near

diesel fuel levels and produced a fuel with properties that were similar to petroleum-based diesel fuel and which could be used in existing engines without modifications.

Freedman et al. [19] presented the results of a parametric study of the transesterification reaction variables that included temperature, molar ratio of alcohol to oil, type of catalyst, and the degree of refinement of the oil. They observed that the reaction proceeded to completion in 1 h at 60 °C but took 4 h at 32 °C. Fig. 1, from that work, shows how the degree of reaction depends on the alcohol-to-oil ratio. Significant amounts of partially reacted mono- and diglycerides will be present when the alcohol-to-oil ratio is too low. The figure shows that an alcohol-to-oil ratio of 6:1 is necessary for a complete single-step reaction. Mono- and diglycerides of saturated fatty acids crystallize easily from the biodiesel fuel and can cause fuel filter plugging and other performance problems.

Freedman compared both crude and refined vegetable oils as feedstocks and found that the yield of methyl esters was reduced from 93% to 98% for the refined oil to 67% to 86% for the crude oil. This was attributed mostly to the presence of up to 6.66% free fatty acids in the crude oil, although phospholipids were also suggested as a source of catalyst destruction. In a study of the effects of phospholipids on biodiesel production, Van Gerpen and Dvorak [20] found that phosphorus compounds in the oil did not carry over into the methyl esters, and while yield was reduced by 3–5% for phosphorus levels above 50 ppm, this was due mostly to added difficulty separating the glycerol from the esters.

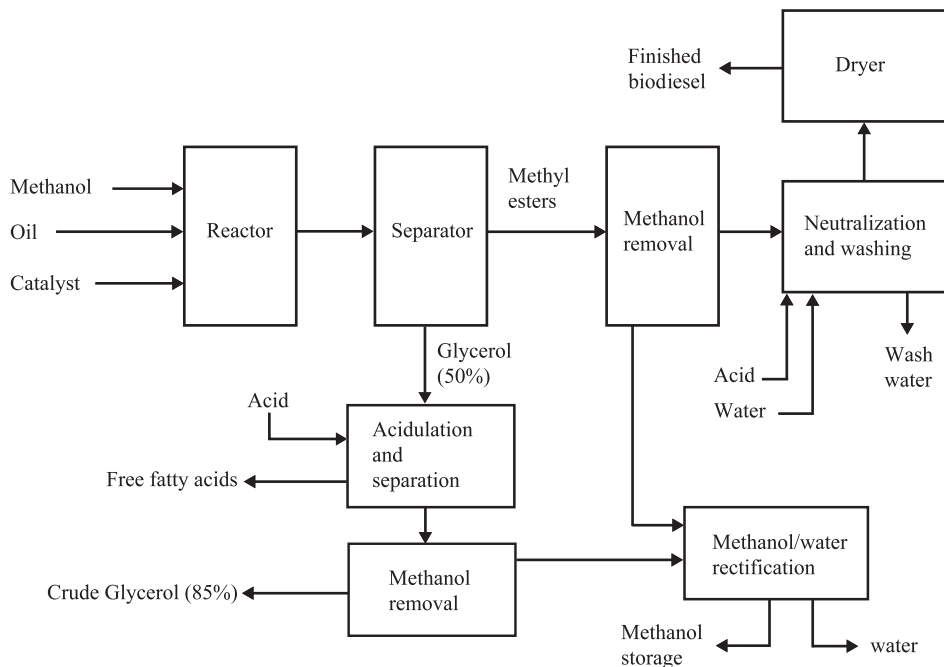


Fig. 2. Process flow schematic for biodiesel production.

While virtually all commercial biodiesel producers use an alkali-catalyzed process for the transesterification process, other approaches have been proposed, including acid catalysis [21] and enzymes [22–25]. The use of acid catalysts has been found to be useful for pretreating high free fatty acid feedstocks to convert the FFAs to esters but the reaction rates for converting triglycerides to methyl esters are too 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 [26]. Immobilization of the enzyme and use of multiple enzymes in sequence may provide future opportunities in this area [23–25].

Fig. 2 shows a schematic diagram of the processes involved in biodiesel production. Alcohol, catalyst, and oil are combined in a reactor and agitated for approximately 1 h at 60 °C. Smaller plants often use batch reactors [27], but most larger plants (>4 million liters/year) use continuous flow processes involving continuous stirred-tank reactors (CSTR) or plug flow reactors [28]. The reaction is sometimes done in two steps (as suggested by the patent literature discussed earlier). In this system, approximately 80% of the alcohol and catalyst is added to the oil in a first stage CSTR. Then the reacted 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 reactor. This system provides a very complete reaction with the potential of 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 [27,29].

Saka and Kusiana [30–34] claim that it is possible to react the oil and methanol without a catalyst, which eliminates the need for the water washing step. However, temperatures of 300 °C–350 °C and methanol to oil molar ratios of 42:1 are required. While the reaction only requires 120 s, the purity of the final product needs to be fully characterized, and formation of nonmethyl ester compounds in significant amounts is possible.

Dasari et al. [33] measured reaction rates without catalysts at temperatures of 120 °C to 180 °C. They noted the difficulty of reproducing reaction kinetics results of other researchers [31,35] 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 [33].

Kreutzer [36] 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.

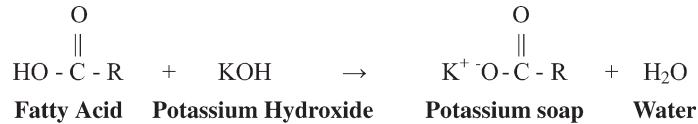
Boocock et al. [37–39] have developed a novel technique for accelerating the transesterification reaction rate. During its early stages, the transesterification reaction is limited by the low solubility of the alcohol, especially methanol, in the oil. Boocock proposed the addition of a cosolvent to create 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 Fig. 2, 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. 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.

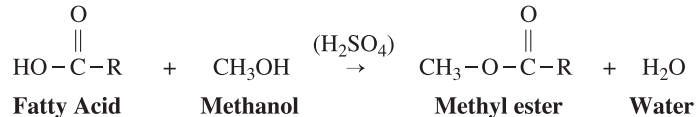
The glycerol stream leaving the separator is only about 50% glycerol. It contains some of the excess methanol and most of the catalyst and soap. In this form, the glycerol has little value and disposal may be difficult. The methanol content requires the glycerol to be treated as hazardous waste. The 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 describes a process for esterifying these free fatty acids and then returning them to the transesterification reaction stream [40]. 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.

Special processes are required if the oil or fat contains significant amounts of free fatty acids (FFAs). Used cooking oils typically contain 2–7% FFAs, and animal fats contain from 5% to 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 the catalyst lost to soap. The soap that is 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 methyl esters and glycerol 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 free fatty acids to methyl esters, as shown in the following reaction:



This process can be used as a pretreatment to convert the FFAs in high FFA feedstocks 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. Keim [9] describes using this approach to convert palm oil containing 50.8% free fatty acids to methyl esters. Methanol (77% of the weight of oil) and sulfuric acid (0.75% of the weight of oil) were added to the oil while stirring at 69 °C for 1 h. After neutralization, 1.25% sodium methoxide was added, and the mixture was stirred for an additional hour at 50 °C. Analysis showed a yield of 97% but a residual acid value equivalent to about 5% palmitic acid. The incomplete reaction was probably due to water in the reactant mixture. As shown in the reaction, water is formed, and if it accumulates, it can stop the reaction well before completion. Kawahara and Ono [42] 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. Jeromin et al. [41] has described using acidic ion exchange resins in a packed bed for the pretreatment.

Haas et al. [43,44] 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.

Zhang et al. [45,46] have reviewed the commonly used procedures for producing biodiesel, including a process simulation using the commercial software package HYSYS. Their economic assessment indicated that use of waste cooking oil feedstocks provided a higher rate of return than refined vegetable oils even after including the additional capital and operating costs of acid-catalyzed pretreatment.

The primary criterion for biodiesel quality is adherence to the appropriate standard. In the United States, this standard is ASTM D 6751-02. This standard gives the required extent of reaction through specifications for the total glycerol remaining in the fuel. The total glycerol is defined as the sum of the free and bound glycerol, and the bound glycerol is equal to the glycerol portion of the residual mono-, di-, and triglycerides. The amount of residual methanol, catalyst, soap, and glycerol is controlled by limits on the fuel's flashpoint, ash level, and free glycerol. When these limits are met, the biodiesel can be used in most modern engines without modifications while maintaining the engine's durability and reliability.

3. 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.

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