

Review: Oils, Fats and Alcohols Used in Biodiesel Production

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ABSTRACT

Today, as oil prices climb and pollution levels soar, there is significant worldwide interest in alternative fuels. Biodiesel is one of the most popular alternative fuels available today. It may be used in engines, either pure or blended with diesel fuel, to reduce exhaust pollutants. Defines biodiesel as a mixture of long-chain monoalkylic esters from fatty acids obtained from renewable resources, to be used in diesel engines. Our objective is to use different types of oils, fats and alcohols in biodiesel production. Alcohols that can be used in biodiesel production are those with short chains, including methanol, ethanol, butanol, and amylic alcohol. The most widely used alcohols are methanol (CH_3OH) and ethanol ($\text{C}_2\text{H}_5\text{OH}$) because of their low cost and properties.

Introduction and use of biodiesel

Biodiesel is a liquid biofuel obtained by chemical processes from vegetable oils or animal fats and an alcohol that can be used in diesel engines, alone or blended with diesel oil. Some of the advantages of using biodiesel as a replacement for diesel fuel are

- Renewable fuel, obtained from vegetable oils or animal fats.
- Low toxicity, in comparison with diesel fuel.
- Degrades more rapidly than diesel fuel, minimizing the environmental consequences of biofuel spills.
- Lower emissions of contaminants: carbon monoxide, particulate matter, polycyclic aromatic hydrocarbons, aldehydes.
- Lower health risk, due to reduced emissions of carcinogenic substances.
- No sulfur dioxide (SO_2) emissions. • Higher flash point (100C minimum).

Disadvantages of the Use of Biodiesel

There are certain disadvantages of using biodiesel as a replacement for diesel fuel that must be taken into consideration:

- Slightly higher fuel consumption due to the lower calorific value of biodiesel.
- Slightly higher nitrous oxide (NO_x) emissions than diesel fuel.
- Higher freezing point than diesel fuel. This may be inconvenient in cold climates.
- It is less stable than diesel fuel, and therefore long-term storage (more than six months) of biodiesel is not recommended.
- May degrade plastic and natural rubber gaskets and hoses when used in pure form, in which case replacement with Teflon

components is recommended.

- It dissolves the deposits of sediments and other contaminants from diesel fuel in storage tanks and fuel lines, which then are flushed away by the biofuel into the engine, where they can cause problems in the valves and injection systems. In consequence, the cleaning of tanks prior to filling with biodiesel is recommended.

It must be noted that these disadvantages are significantly reduced when biodiesel is used in blends with diesel fuel.

Raw Materials for Biodiesel Production

The raw materials for biodiesel production are vegetable oils, animal fats and short chain alcohols. The oils most used for worldwide biodiesel production are rapeseed, soybean, palm and sunflower, although other oils are also used, including peanut, linseed, safflower, used vegetable oils, and also animal fats. Methanol is the most frequently used alcohol although ethanol can also be used. Since cost is the main concern in biodiesel production and trading (mainly due to oil prices), the use of non-edible vegetable oils has been studied for several years with good results.

Besides its lower cost, another undeniable advantage of non-edible oils for biodiesel production lies in the fact that no foodstuffs are spent to produce fuel [4].

These and other reasons have led to medium- and large-scale biodiesel production trials in several countries, using non-edible oils such as castor oil, tung, cotton, jojoba and jatropha. Animal fats are also an interesting option, especially in countries with plenty of livestock resources, although it is necessary to carry out preliminary treatment since they are solid; furthermore, highly acidic grease from cattle, pork, poultry, and fish can be used. Microalgae appear to be a very important alternative for future biodiesel production due to their very high oil yield; however, it must be taken into account that only some species are useful for biofuel production. Although the properties of oils and fats used as raw materials may differ, the properties of biodiesel must be the same, complying with the requirements set by international standards.

Typical Oil Crops Useful for Biodiesel Production

The main characteristics of typical oil crops that have been found useful for biodiesel production are summarized in the following paragraphs [6–10].

Rapeseed and Canola

Rapeseed adapts well to low fertility soils, but with high sulfur content. With a high oil yield (40–50%), it may be grown as a winter-cover crop, allows double cultivation and crop rotation. It is the most important raw material for biodiesel production in the European Community. Moreover, low prices in comparison to wheat (its main competitor for crop rotation) and low production per unit area have limited its use. Rapeseed flour has high nutritional value, in comparison to soybean; it is used as a protein supplement in cattle rations. Sometimes canola and rapeseed are considered to be synonymous; canola (Canadian oil low acid) is the result of the genetic modification of rapeseed in the past 40 years, in Canada, to reduce the content of erucic acid and glucosinolates in rapeseed oil, which causes inconvenience when used in animal and human consumption. Canola oil is highly appreciated due to its high quality, and with olive oil, it is considered as one of the best for cooking as it helps to reduce blood cholesterol levels.

Soybean

It is a legume originating in East Asia. Depending on environmental conditions and genetic varieties, the plants show wide variations in height. Leading soybean producing countries are the United States, Brazil, Argentina, China, and India. Biodiesel production from soybean yields other valuable sub-products in addition to glycerin: soybean meal and pellets (used as food for livestock) and flour (which have a high content of lecithin, a protein). Grain yield varies between 2,000 and 4,000 kg/hectare. Since the seeds are very rich in protein, oil content is around 18%.

Oil Palm

Oil palm [11] is a tropical plant that reaches a height of 20–25 m with a life cycle of about 25 years. Full production is reached 8 years after planting. Two kinds of oil are obtained from the fruit: palm oil proper, from the pulp, and palm kernel oil, from the nut of the fruit (after oil extraction, palm kernel cake is used as livestock food). Several high oil-yield varieties have been developed. Indonesia and Malaysia are the leading producers. International demand for palm oil has increased steadily during the past years, the oil being used for cooking, and as a raw material for margarine production and as an additive for butter and bakery products. It is important to remark that pure palm oil is semisolid at room temperature (20–22°C), and in many applications is mixed with other vegetable oils, sometimes partially hydrogenated.

Sunflower

Sunflower “seeds” are really a fruit, the inedible wall (husk) surrounding the seed that is in the kernel. The great importance of sunflower lies in the excellent quality of the edible oil extracted from its seeds. It is highly regarded from the point of view of nutritional quality, taste and flavor. Moreover, after oil extraction, the remaining cake is used as a livestock feed. It must be noted that sunflower oil has a very low content of linoleic acid, and therefore it may be stored for long periods. Sunflower adapts well to adverse environmental conditions and does not require specialized agricultural equipment and can be used for crop rotation with soybean and corn. Oil yield of current hybrids is in the range 48–52%.

Peanut

The quality of peanut is strongly affected by weather conditions during the harvest. Peanuts are mainly used for human consumption, in the manufacture of peanut butter, and as an ingredient for confectionery and other processed foods. Peanuts of lower quality (including the rejects from the confectionery industry) are used for oil production, Peanut oil is used in blends for cooking and as a flavoring agent in the confectionery industry. The flour left over, following oil extraction, is of high quality with high protein content; in pellet form, it is used as a livestock feed.

Jojoba

Although jojoba can survive extreme drought, it requires irrigation to achieve an economically viable yield. Jojoba needs a warm climate, but a cold spell is necessary for the flowers to mature. Rainfall must be very low during the harvest season (summer). The plant reaches its full productivity 10 years after planting. The oil from jojoba is mainly used in the cosmetics industry; therefore, its market is quickly saturated.

Jatropha

Jatropha is a shrub that adapts well to arid environments. Jatropha curcas is the most known variety; it requires little water or additional care; therefore, it is adequate for warm regions with little fertility. Productivity may be reduced by irregular rainfall or strong winds during the flowering season. Yield depends on climate, soil, rainfall and treatment during sowing and harvesting. Jatropha plants become productive after 3 or 4 years, and their lifespan is about 50 years. Oil yield depends on the method of extraction; it is 28–32% using presses and up to 52% by solvent extraction. Since the seeds are toxic, jatropha oil is nonedible. The toxicity is due to the presence of curcasin (a globulin) and jatrophaic acid (as toxic as ricin).

Avocado

Avocado is a tree between 5 and 15 m in height. The weight of the fruit is between 120 and 2.5 kg and the harvesting period varies from 5 to 15 months. The avocado fruit matures after picking and not on the tree. Oil may be obtained from the fruit pulp and pit. It has a high nutritional value, since it contains essential fatty acids, minerals, protein and vitamins A, B6, C, D, and E. The content of saturated fatty acids in the pulp of the fruit

and in the oil is low; on the contrary, it is very high in mono-unsaturated fatty acids (about 96% being oleic acid). The oil content of the fruit is in the range 12–30%.

Microalgae

Microalgae have great potential for biodiesel production, since the oil yield (in liters per hectare) could be one to two orders of magnitude higher than that of other raw materials. Oil content is usually from 20 to 50%, although in some species it can be higher than 70% [13]. However, it is important to note that not all microalgae are adequate for biodiesel production. High levels of CO₂, water, light, nutrients and mineral salts are necessary for the growth of microalgae. Production processes take place in raceway ponds and photo biological reactors [13].

Characteristics of Oils and Fats Used in Biodiesel Production

Oils and fats, known as lipids, are hydrophobic substances insoluble in water and are of animal or vegetal origin. They differ in their physical states at room temperature. From a chemical viewpoint, lipids are fatty glycerol esters known as triglycerides. The general chemical formula is shown in Fig.

In Fig. 2.2, R₁, R₂ y R₃ represent hydrocarbon chains of fatty acids, which in most cases vary in length from 12 to 18 carbon atoms. The three hydrocarbon chains may be of equal or different lengths, depending on the type of oil; they may also differ on the number of double-covalent bonds in each chain.

Fatty acids may be saturated fatty acids (SFA) or non-saturated fatty acids (NSFA). In the former, there are only single covalent bonds in the molecules.

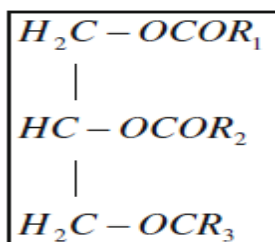


Table 2.1 Chemical formulas of the main fatty acids in vegetable oils

Fatty acid	Chemical formula
Lauric (12:0)	CH ₃ (CH ₂) ₁₀ COOH
Palmitic (16:0)	CH ₃ (CH ₂) ₁₄ COOH
Stearic (18:0)	CH ₃ (CH ₂) ₁₆ COOH
Oleic (18:1)	CH ₃ (CH ₂) ₇ CH = CH (CH ₂) ₇ COOH
Linoleic (18:2)	CH ₃ (CH ₂) ₄ CH = CH CH ₂ CH = CH (CH ₂) ₇ COOH
Linolenic (18:3)	CH ₃ CH ₂ (CH = CH CH ₂) ₃ (CH ₂) ₆ COOH
Erucic (22:1)	CH ₃ (CH ₂) ₇ CH = CH (CH ₂) ₁₁ COOH
Ricinoleic (18:1)	CH ₃ (CH ₂) ₅ CHOH CH ₂ CH = CH (CH ₂) ₇ COOH

Table 2.2 Approximate content (in weight) of saturated and non-saturated fatty acids in some vegetable oils and animal fats

Oil/fat	SFA ($\approx$ % w/w)	NSFA ($\approx$ % w/w)
Coconut	90	10
Corn	13	87
Cottonseed	26	74
Olive	14	86
Palm	49	51
Peanut	17	83
Rapeseed	6	94
Soybean	14	86
Sunflower	11	89
Safflower	9	91
Castor	2	98
Yellow grease	33	67
Lard	41	59
Beef tallow	48	52

names of the most important fatty acids in oils are listed in Table 2.1 along with their chemical formulas [14]. The notation x:y indicates the number of carbon atoms in the oil molecule (x) and the number of unsaturations, i.e. double-covalent bonds (y). For instance, y = 0 for all the SFAs. Table 2.2 indicates the approximate content (in weight) of saturated and non-saturated fatty acids in some vegetable oils and animal fats.

The most frequent fatty acids in oils are lauric, palmitic, stearic, linoleic and linolenic, although others may also be present. It is important to note that vegetable oils differ in their content of fatty acids. For instance, ricinoleic acid is

the main component of castor oil, whereas in olive oil it is oleic acid, in soybean oil it is linoleic acid, and in linseed oil it is linolenic acid. The compositions indicated in Table 2.2 do not discriminate between the different saturated or unsaturated fatty acids. For instance, coconut oil has about 90% of SFAs in its composition (more than half being lauric acid), and palm oil has

about 49% SFAs (more than 80% palmitic acid). Similarly, 60% of NSFAs content in soybean oil is linoleic acid, while in peanut more than 50% is oleic.

Most Important Alcohols Used in Biodiesel Production

Methanol. Most widely used, in spite of its toxicity. It is a substance of petrochemical origin.

Ethanol. Less used, requires more complex production technology and the reaction speeds are lower. It can be produced from biomass.

Characteristics of Alcohols Used in Biodiesel Production

Alcohols that can be used in biodiesel production are those with short chains, including methanol, ethanol, butanol, and amylic alcohol. The most widely used alcohols are methanol (CH₃OH) and ethanol (C₂H₅OH) because of their low cost and properties. Methanol is often preferred to ethanol in spite of its high toxicity because its use in biodiesel production requires simpler technology; excess alcohol may be recovered at a low cost and higher reaction speeds are reached.

The comparison between the two alcohols is summarized in Box 2.2. It must be remembered that in order for biodiesel to be a fully renewable fuel, it should be obtained from vegetable oils and animal fats, together with an alcohol that is produced from biomass, such as bioethanol, instead of being a petrochemical product.

Biodiesel Production Process

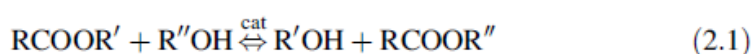
Biodiesel is produced from vegetable oils or animal fats and an alcohol, through a transesterification reaction [1, 2, 4, 5]. This chemical reaction converts an ester (vegetable oil or animal fat) into a mixture of esters of the fatty acids that makes up the oil (or fat). Biodiesel is obtained from the purification of the mixture of fatty acid methyl esters (FAME). A catalyst is used to accelerate the reaction (Fig. 2.5). According to the catalyst used, transesterification can be basic, acidic or enzymatic, the former being the most frequently used.

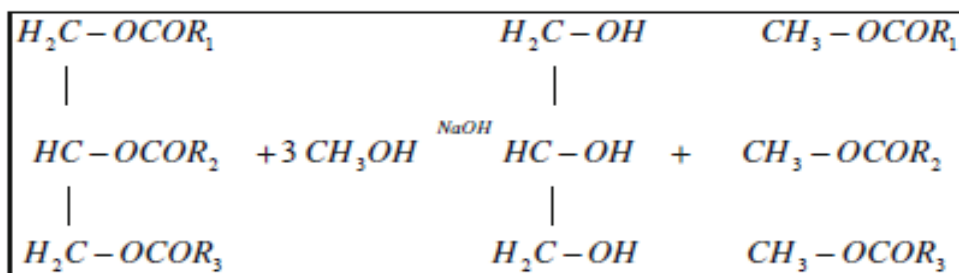
Transesterification Biodiesel Production

Refined corn oil, palm oil, waste cooking cotton seed and rice bran oils were esterified by the transesterification method. Transesterification is otherwise known as alcoholysis. It is the reaction of fat or oil with alcohol to yield esters and glycerin. Transesterification of selected oils was carried out by heating the oil. In this process, alcohol combines with triglyceride molecule from acid to form glycerol and ester. The glycerol is then removed by density separations. Simple alcohols are used for transesterification and this process is usually carried out with a basic catalyst (NaOH, KOH) in the complete absence of water. Transesterification decreases the viscosity of oil, making it similar to diesel fuel in characteristics. A catalyst is used to improve the reaction rate and yield. Transesterification of triglycerides using alcohol .

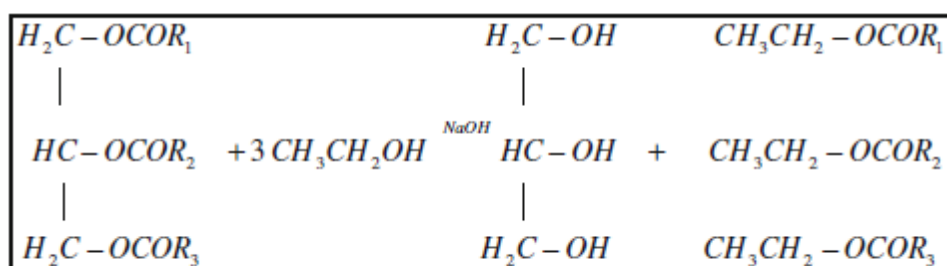
The “catalytic transesterification” process is the reaction of a triglyceride (fat/oil) with an alcohol in the presence of acidic, alkaline or lipase as catalyst to form mono alkyl ester (i.e. Biodiesel) and glycerol.

A generic transesterification reaction is presented in Eq. (2.1); RCOOR' indicates an ester, R''OH an alcohol, R'OH another alcohol (glycerol), RCOOR'' an ester mixture and cat a catalyst:





Figs2.5 Basic transesterifi cation reaction with methanol



Figs2.6 Basic transesterification reaction with ethanol

used, the reaction product would be a mixture of ethyl esters. In both cases, glycerin will be the co-product of the reaction. This is shown schematically in Figs. 2.5 and 2.6. Although transesterification is the most important step in biodiesel production.

Conclusion

The catalytic modification of vegetable oils is a promising method to obtain a substitute fuel for diesel engines. Among various types of modification, the transesterification process is more economical, easier and faster, producing a stable product which can be used directly in current engines. Transesterification yield is often better when employing a basic catalyst, like sodium methoxyde, although acid catalysis might give better results, provided that free fatty acid content is high. Both methanol and ethanol can be used as esterifying agents, being methanol the most often used nowadays. Nevertheless, the use of ethanol would produce a fully renewable and more environmentally friendly fuel. In the transesterification process, reaction variables such as water and free fatty acid content should be carefully controlled to reach high yields, and so should the type of catalyst. Reaction parameters are strongly influenced by the type of oil employed, and a case to case optimization is required.

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