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## Biodiesel Production and Quality

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### 1. Introduction

Fossil fuels are, nowadays, the most used worldwide but that are some problems involving their utilization. First of all, the price, which is growing often and makes petroleum no longer economically sustainable. Second, during the burning of petrochemical sources there is emission of very dangerous pollutants for human health, like carbon dioxide that is the main reason of the global warming. In addition, fossil fuels are non-renewable resources, so they will last for a limited period of time. For all these reasons, vegetable oils are emerging as a great alternative fuel, because of their renewable nature and environmental benefits (Ferella et al., 2010).

Despite all the advantages, the use of vegetable oils as fuel has some disadvantages. The direct use in internal combustion engines is problematic because vegetables oils have high viscosity than diesel fuel and low volatility, so they do not burn completely and form deposits in the fuel injectors of diesel engine.

According to specialized literature there are five ways to reduce the problems mentioned above: blending of vegetable oil and diesel, thermal cracking (pyrolysis), microemulsions, esterification and transesterification (Ma & Hanna, 1999). Esterification and transesterification reactions are currently the most favored reaction pathways to produce biodiesel (Janaun & Ellis, 2010).

Biodiesel, defined as the simple alkyl monoesters of long chain fatty acids derived from renewable feedstocks, is the most suitable substitute to diesel. For this reason the research on this biofuel are steadily growing all over the planet. In Brazil, the focus of research is the production of biodiesel using ethanol, since this alcohol is produced on a large scale in the country. Ethanolysis produces a biodiesel less damage to the environment than that produced by methyl alcohol, since ethanol is derived from sugar cane or corn. In the rest of the world, the production takes place mostly in the methyl route and with use of heterogeneous catalysts (Pighinelli, 2010).

Biodiesel is highly biodegradable in fresh water as well as in soil and great part of it is mineralized in until 28 days under aerobic or anaerobic conditions (Makareviciene & Janulis, 2003; Pasqualino et al., 2006; Zhang et al., 1998). It is also a carbon-free fuel, as the plants that serve as raw material for its production absorb more carbon than that which is released during the burning of this biofuel (Antolin et al., 2002; Lang et al., 2001; Sharma et al., 2008; Vicente & Martinez, 2004).

Moreover, when biodiesel is burned in diesel engines the emissions of hydrocarbons, carbon monoxide, particulate matter and sulphur dioxide are reduced with the exception of

nitrogen oxides, that emission increases due to the oxygen content of biodiesel (Canakci et al., 2006; Labeckas & Slavinskas, 2006; Turrio-Baldassarri, 2004).

Biodiesel sold today is still considered expensive, since the production costs involved are influenced by the main raw material, which are vegetable or animal fat and oils. It is estimated that approximately 80% of the total cost of biodiesel production is related to the acquisition of triglycerols source (Pighinelli, 2010). Another problem that has been discussed frequently is the competition between "food production" and "energy production". Some researchers argue that there will be food shortages if the available land is used for oilseed cultivation.

In order to reduce the production costs and to make it competitive with petroleum diesel, biodiesel producers should choose a raw material longer available in their territory, as soybean in Brazil, but also, search for alternatives crops, such as non-edible oils, as *Crambe Abyssinica*, *Jatropha Curcas* and others, and also waste frying oils (Marchetti et al., 2007).

The production of biodiesel is considered a current topic of great relevance worldwide. Thus, this chapter will be discussed: how biodiesel is produced, which are the main parameters affecting the chemical reactions and the most important issues for assuring biodiesel quality related to its production as well as some post-production parameters.

## 2. Biodiesel production

Transesterification is the technological route more used for biodiesel production, and can be applied on a small scale, as in laboratories, or in industry, producing millions of gallons of biofuel. Although the esterification also results in biodiesel and is recommended when the raw material is composed of oils rich in free fatty acids, this technique is applied commercially in few industries. That's why we decide to mention in this chapter only the transesterification process. In this section, mechanisms of the transesterification reaction are going to be explained, identifying all process variables affecting the biodiesel yield and finally some important optimization studies will be presented.

### 2.1 Transesterification

Transesterification, also known as alcoholysis is the reaction of oil or fat with an alcohol to form esters and glycerol. To complete a transesterification reaction, stoichiometrically, a 3:1 molar ratio of alcohol to triglyceride is needed. In practice, to have a maximum ester yield, this ratio needs to be higher than the stoichiometric ratio. A catalyst is usually used to improve the reaction rate and yield. Because the reaction is reversible, excess alcohol is used to shift the equilibrium to the products side (Ma & Hanna, 1999). The reaction is shown in Fig. 1.

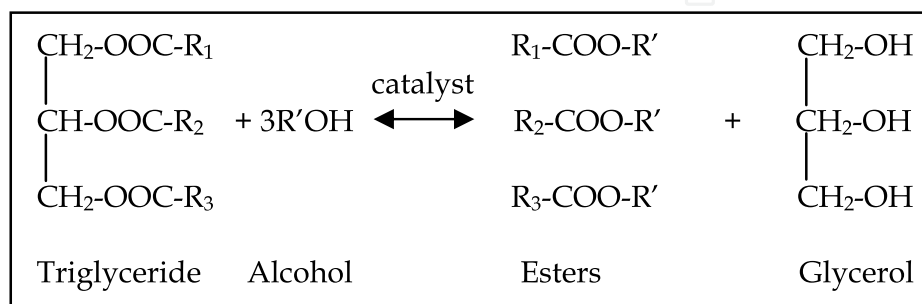


Fig. 1. Transesterification of triglycerides with alcohols.

The conventional technology of biodiesel production employs a basic homogeneous catalyst such as sodium or potassium hydroxides but when oil rich in free fatty acids (FFA) is used the basic catalyst and the FFA will interact to produce soap. This makes the amount of available catalyst for the transesterification reaction to be reduced and also complicates the down streaming separation and the biodiesel purification. Alternative processes for fatty acid ethyl ester (FAEE) production have been under development in order to employ different catalysts as heterogeneous ones (Marchetti & Errazu, 2011) such as metal oxides, metal complexes, active metals loaded on supports, zeolite, resins, membranes, and lipases (Kansedo et al., 2009).

Transesterification consists of a sequence of three consecutive reversible reactions, as can be seen on Figure 2. The first step is the conversion of triglycerides to diglycerides, followed by the conversion of diglycerides to monoglycerides, and finally monoglycerides to glycerol, yielding one ester molecule for each glyceride at each step.

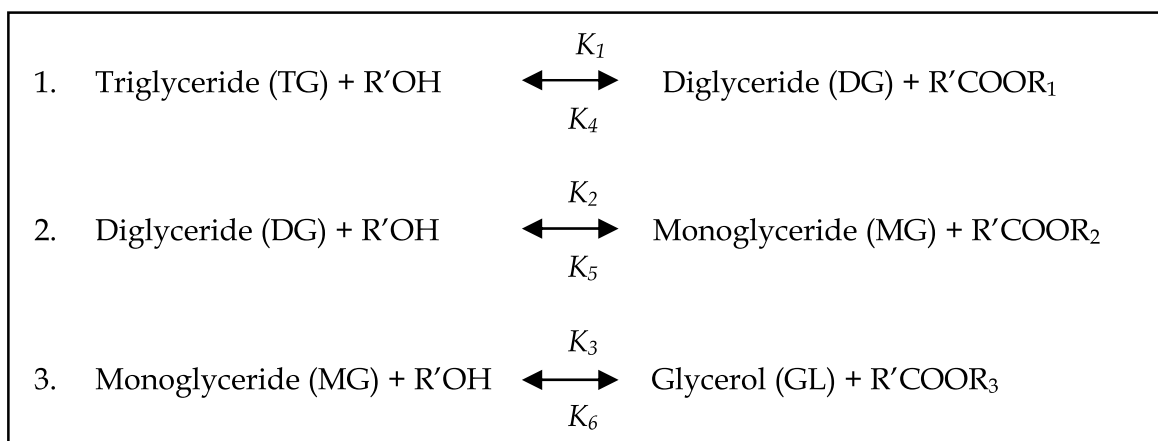


Fig. 2. The transesterification reactions of vegetable oil with alcohol to esters and glycerol (Freedman et al., 1986).

The main parameters affecting the transesterification reaction are molar ratio of vegetable oil to alcohol, catalyst type and amount, reaction time and temperature, the contents of free fatty acids (FFAs) and water in substrate oil (Freedman et al., 1984) and also the intensity of mixing during the chemical reaction.

### 2.1.1 The effects of moisture and free fatty acids

The starting materials used for alkali-catalyzed transesterification of glycerides must meet certain specifications. The presence of water during alkali catalyzed transesterification causes a partial reaction change to saponification, which produces soap. For that reason, the glycerides and alcohol must be substantially anhydrous (Wright et al., 1944). A small amount of soap favors the consumption of catalyst and reduces the catalytic efficiency, as well as causing an increase in viscosity, the formation of gels, and difficulty in achieving separation of glycerol. Ma et al. (1998) suggested that the free fatty acid content of the refined oil should be as low as possible, below 0.5%, and Feuge & Grose (1949) also stressed the importance of oils being dry and free of free fatty acids.

The use of alkali catalysts in the transesterification of used cooking oil is somewhat limited because the FFA in used cooking oil reacts with the most common alkaline catalysts (NaOH, KOH, and CH<sub>3</sub>ONa) and forms soap. Because water makes the reaction partially change to

saponification, the alkali catalyst is consumed in producing soap and reduces catalyst efficiency. The soap causes an increase in viscosity, formation of gels which reduces ester yield and makes the separation of glycerol difficult. These two problems notwithstanding, literature is replete with studies on the transesterification of waste cooking oil using alkaline catalyst (Marchetti & Errazu, 2010).

### 2.1.2 The effect of molar ratio

One of the most important variables affecting the yield of ester is the molar ratio of alcohol to triglyceride. The stoichiometric ratio for transesterification requires three moles of alcohol and one mole of glyceride to yield three moles of fatty acid ester and one mole of glycerol. The molar ratio is associated with the type of catalyst used. For example, a reaction conducted with an acid catalyzed needed a 30:1 ratio of BuOH to soybean oil, while a alkali-catalyzed reaction required only a 6:1 ratio to achieve the same ester yield for a given reaction time (Freedman et al., 1986). Higher molar ratios result in greater ester conversion in a shorter time. During the ethanolysis of peanut oil with a molar ratio alcohol:oil of 6:1 the amount of glycerin liberated was more than did a 3:1 molar ratio (Feuge and Grose, 1949). In this point is important to consider the type of alcohol that is been used. This is because during ethanolysis, as this alcohol has chemical affinity for both glycerine and ester, the higher the molar ratio is more difficult to separate the both phases.

### 2.1.3 The effect of catalyst

The catalysts for biodiesel can be separated into two major groups: homogeneous e heterogeneous. Homogeneous type forms a single phase mixture when added to oil and alcohol while the heterogeneous do not mix in the reaction medium. The group of homogeneous catalysts is divided into acid and basic and heterogeneous into metal oxides, metal complexes, active metals loaded on supports, zeolite, resins, membranes, and lipases. The criterion for choosing which type of catalyst use should take into account firstly, the quality of raw material, but also the type of alcohol, the costs of the catalysts and technological route to be used for biodiesel production.

### 2.1.4 The effect of reaction time

The conversion rate of vegetable oils into biodiesel increases with reaction time. Freedman et al. (1984) transesterified peanut, cottonseed, sunflower and soybean oils under the condition of methanol to oil ratio of 6:1, 0.5% sodium methoxide catalyst and 60°C. After 1 minute, a yield of 80% of biodiesel was observed for soybean and sunflower oils, and after 60 minutes, the conversions were almost the same for all four oils.

During the transesterification of beef tallow with methanol the reaction was very slow during the first minute due to the mixing and dispersion of methanol into beef tallow. In the next five minutes, the reaction proceeded very fast (Ma et al., 1998). The production of beef tallow slowed down and reached the maximum value at about 15 min. The di- and monoglycerides increased at the beginning and then decreased. At the end, the amount of monoglycerides was higher than that of diglycerides.

### 2.1.5 The effect of reaction temperature

Transesterification can occur at different temperatures depending on the vegetable oil used, taking care not to exceed the boiling point of the alcohols used. In methanolysis of castor oil to methyl ricinoleate, with a molar ratio of 6:1-12:1 and 0.005-0.35% (by weight of oil) of

NaOH catalyst, the reaction proceeded most satisfactorily at 20-35°C (Smith, 1949). For the transesterification of refined soybean oil with methanol, molar ratio alcohol:oil of 6:1 and 1% NaOH of catalyst, three different temperatures were used (Freedman et al., 1984). After 0.1 h, ester yields were 94, 87 and 64% for 60, 45 and 32°C, respectively. After 1 h, ester formation was identical for the 60 and 45°C runs and only slightly lower for the 32°C run.

## 2.2 Optimization of biodiesel production

In the world economic context, the optimization of industrial processes is a tool that has been applied frequently in order to reduce the consumption of raw materials, with the main objective of reducing production costs. Response surface methodology (RSM) is a powerful tool for the optimization of chemical reactions and/or industrial processes. The main advantages of this method include: (1) an understanding of how the test variables (process variables) affect the selected process response; (2) the determination of any possible interrelationship among the test variables; and (3) the characterization of the combined effect that all test variables may have on the process response (Myers & Montgomery, 1995). There are only few examples in the literature involving optimization of transesterification of vegetable oils to produce biodiesel, even knowing that the costs of biofuel production are high (Domingos et al., 2008).

Pinzi et al. (2011) evaluated together with the process variables, how raw material fatty acid composition affects the biodiesel production. The authors applied a factorial design to determine how the operation conditions affected the transesterification process (reaction temperature, initial catalyst concentration by oil mass and methanol concentration), while the reaction yield was considered as the response variable. The vegetable oils studied were maize (MME), sunflower (SFME), olive (OOME), coconut (CME), linseed (LME) and palm (PME). A different range of temperature (from 40 °C to 60 °C) was selected for coconut oil and palm oil, since these oils are rich in unsaturated fatty acids. Molar ratio methanol:oil ranged from 4.2:1 to 5.4:1 and catalyst concentration from 0.8 to 2.1%. Optimized conditions for each of the raw materials are shown in Table 1.

A complementary study aimed to define the optimum time of reaction based on a study of reaction kinetics. During the transesterification reaction carried out at the optimized condition, samples were taken at 30s, 1, 2, 5, 10, 35, 60, 90 and 120 min. Kinetic curves showed that every transesterification reaction presents similar performance curve, with the exception of coconut that exhibits the lowest yield of fatty acid methyl esters (FAME). After 20-min reaction oils with longer fatty-acid chains (olive, corn, linseed and sunflower) achieve the optimal yield of FAME, but on the other hand palm oil and coconut oil show the best performance after 40-min reaction. The authors observed that the effect of catalyst concentration was influenced by fatty-acid composition. Vegetable oils composed by unsaturated fatty acids show a directly proportional dependence between the concentration of catalyst and yield, up to a maximum. Whereas, considering vegetable oils with (mono) saturated fatty acids, amounts of catalyst greater than the optimal value lead to soap production. Fatty acids chain length also seems to influence biodiesel conversion. Oils with longer fatty-acid chains need half of the reaction time requested by oils comprising shorter fatty-acid chains to achieve maximum yield.

Silva et al. (2011) discussed in their paper the production process optimization for biodiesel by transesterification of soybean oil with ethanol, where several parameters, including catalyst, alcohol/vegetal oil molar ratio, and temperature would influence the transesterification. The authors' main objective was to study how the process variables (ethanol-to-oil ratio, catalyst concentration, reaction time and temperature) affecting the

yield of biodiesel and then optimize this process. The levels of process variables studied were: ethanol/oil ratio (i.e., 3:1, 6:1, 9:1, 12:1 and 15:1), catalyst concentration (0.1%, 0.5%, 0.9%, 1.3% and 1.7% w/v of NaOH), reaction time (40, 60, 80, 100, and 120 min) and temperature (40, 50, 60, 70 and, 80 °C). Optimum values of the process parameter for maximum efficiency (95% of ethyl esters) were molar ratio ethanol: soybean oil 9:1, catalyst concentration 1.3% w/v, temperature 40 °C and reaction time 80 minutes. The analysis of the effects of process variables on yield in ethyl esters showed that the molar ratio, catalyst concentration and reaction time had a positive effect while the temperature had a negative effect. A positive effect means that the larger the values of process variables, the greater the yield of biodiesel.

Factor	Optimum value
MME	Yield: 98.67 (wt%)
Reaction temperature (°C)	47.53
Catalyst concentration (wt%)	1.92
Methanol/oil (molar ratio)	5.4
SFME	Yield: 99.70 (wt%)
Reaction temperature (°C)	59.82
Catalyst concentration (wt%)	1.81
Methanol/oil (molar ratio)	5.4
OOME	Yield: 98.02 (wt%)
Reaction temperature (°C)	45
Catalyst concentration (wt%)	1.6
Methanol/oil (molar ratio)	6.03
CME	Yield: 90.01 (wt%)
Reaction temperature (°C)	60
Catalyst concentration (wt%)	1.7
Methanol/oil (molar ratio)	6.6
LME	Yield: 97.71 (wt%)
Reaction temperature (°C)	53
Catalyst concentration (wt%)	1.8
Methanol/oil (molar ratio)	6.02
PME	Yield: 98.91 (wt%)
Reaction temperature (°C)	65
Catalyst concentration (wt%)	1.81
Methanol/oil (molar ratio)	6.15

Table 1. Optimization results according to Pinzi et al. (2011)

Another optimization study used *Raphanus sativus* (L. Var) crude oil in ethanolysis with sodium hydroxide as catalyst. Three process variables were used to develop the experimental design: the ethanol:oil molar ratio (MR of 6:1 and 12:1), the catalyst concentration in relation to oil mass (C of 0.4 and 0.8 wt% NaOH) and the alcoholysis temperature (T of 45 and 65 °C). This yield was expressed in relation to the oil mass used for ethanolysis, reason why some values were greater than 100%. Reaction temperature had no statistical significance over biodiesel yield. The highest biodiesel yield was 101.7% obtained at 65 °C with a MR of 12:1 and 0.4 wt% of C. Nevertheless, when the alcoholysis temperature

was decreased to 45 °C, phase separation improved and lower levels of soap accumulation were obtained in the ethyl ester phase. The authors recommend the following procedure for the ethanolysis of *Raphanus sativus* crude oil: MR of 11.7:1, NaOH concentration of 0.4 wt%, 45 °C and vigorous agitation for 60 min as the first reaction stage, followed by a second stage in which MR and NaOH concentration can be reduced to 6:1 and 0.03 wt%, respectively (Domingos et al., 2008).

Heterogeneous catalysis optimization was studied by Marchetti & Errazu (2011). The reaction temperature's effects (30, 45 and 55 °C), the initial amount of free fatty acid (2.8%, 9.9% and 19.5% w/w), the molar ratio of alcohol/oil (4.2:1, 5.01:1 and 6.1:1) and the type of catalyst (homogeneous - sulfuric acid or heterogeneous - Dowex monosphere 550A) over the main reaction are analyzed and their effects compared. Temperature and molar ratio had a positive effect over biodiesel production: when the temperature and molar ratio increase the final conversion increases as well. When the initial amount of free fatty acid was varied, experimental results show that the final conversion increases as the initial amount of free fatty acid increases. Therefore, this effect could also be seen on the total FAEE production since the final amount of biofuel will be produced from the triglycerides as well as from the fatty acids present in the reaction mixture. The last part of this paper, a comparative study was made between the production of esters using sulfuric acid and a base solid resin with ethanol anhydrous under similar operational conditions, such as T=55 °C, initial amount of FFA=9.9% w/w, 2.2% w/w of each catalyst, and a molar ratio of alcohol/mixture of 6.1:1. Sulfuric acid reaches its final conversion in about 3 days time, while base solid resin reaches almost 100% in 70 hours.

As can be seen by the results showed earlier, biodiesel production is influenced by several process variables. The ideal combination of these variables will result in a higher yield in esters as well as a final product of higher quality. In addition, production costs could be reduced, including the industrial level. It was observed that depending on the feedstock, the type of alcohol and catalyst, the optimum conditions change. Another relevant point is related to the diversification of oil sources, which also help to reduce costs and to produce a quantity of fuel that meets global demand. In this scenario come acid oils, such as waste frying, and the heterogeneous catalysts, which are being actively researched.

### 3. Biodiesel quality

Generally, the biodiesel quality 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.

#### 3.1 Production process factors

##### 3.1.1 Reaction

The most important issue during biodiesel production is the completeness of the transesterification reaction. 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 or ethyl 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.

### 3.1.2 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. Alcohol can act as co-solvent to increase the solubility of glycerol in the biodiesel. Most of this glycerol should be removed during the purification 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.

### 3.1.3 Residual alcohol and catalyst

Since methanol or 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 phase. 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.

## 3.2 Post-production factors

### 3.2.1 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 (Van Gerpen et al.,

1997). 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.

### 3.2.2 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 (butylated hydroxytoluene) 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.

### 3.3 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 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 are available that can analyze the samples but there are costs and the time required may be several days. Smaller producers will need to use a more robust production process involving extra methanol or ethanol 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 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.

## 4. Biodiesel standards

The primary criterion for biodiesel quality is adherence to the appropriate standard. The technical specifications for biodiesel depend on the country or the region where the fuel was produced. Biodiesel has a number of standards for its quality including European standard EN 14214 (Table 2), ASTM D6751 (Table 3), and others.

The European standard for Fatty Acid Methyl Esters (FAME) used as automotive fuel was set in 2003 by the Comité Européen de Normalisation (CEN) and is known under the standard number EN 14214. This standard sets limits and measurement methods for FAME, known as biodiesel that may be used either as a stand alone fuel or as a blending component in diesel fuel. The CEN standard for diesel fuel, EN 590, requires that all biodiesel blended in the fuel must conform to the standard EN 14214. At present, the European diesel fuel allows biodiesel to be blended at up to and including 5% by volume. Some national standards in EU countries allow biodiesel to be distributed as a stand-alone fuel, notably in Germany, for specially adapted vehicles. The CEN is presently studying a revised EN 590 specification for diesel fuel that will permit up to and including 7% of biodiesel blend. Simultaneously CEN is studying a revision of the biodiesel standard EN 14214 with a view to widening the range of feedstock oils that may be used, without compromising the security of vehicles using this product either in blends or as a stand-alone fuel. At the same time the European Commission has mandated CEN to revise the EN 590 specification for diesel fuel up to 10% of biodiesel blend.

The United States of America has chosen to use the specifications developed by ASTM International for both conventional diesel fuel and biodiesel. Specification efforts for biodiesel in the United States of America began in 1993 in Committee D02 on 24 Petroleum

Products and Lubricants. While the initial proposal for the biodiesel specifications at ASTM was for B100 (pure biodiesel) as a stand alone fuel, experience of the fuel in-use with blends above B20 (20% biodiesel with 80% conventional diesel) was insufficient to provide the technical data needed to secure approval from the ASTM members. Based on this, after 1994 biodiesel efforts within ASTM were focused on defining the properties for pure biodiesel which would provide a 'fit for purpose' fuel for use in existing diesel engines at the B20 level or lower. A provisional specification for B100 as a blend stock was approved by ASTM in 1999, and the first full specification was approved in 2001 and released for use in 2002 as "ASTM D6751 Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels".

Property	Test method	Limits		Unit
		min	max	
Ester content	EN 14103	96.5		% (m/m)
Density, 15°C	EN ISO 3675	860	900	kg/m <sup>3</sup>
Viscosity, 40°C	EN ISO 12185			
	EN ISO 3104	3.5	5.0	mm <sup>2</sup> /s
Flash point	EN ISO 3105			
	EN ISO 3679	120		°C
Sulfur content	EN ISO 20846		10.0	mg/kg
	EN ISO 20884			
Carbon residue (10% dist. residue)	EN ISO 10370		0.30	% (m/m)
Cetane number	EN ISO 5165	51		
Sulfated ash	ISO 3987		0.02	% (m/m)
Water content	EN ISO 12937		500	mg/kg
Total contamination	EN 12662		24	mg/kg
Copper strip corrosion (3hr, 50°C)	EN ISO 2160		1	
Oxidative stability, 110°C	EN 14112	6.0		hr
Acid value	EN 14111		0.50	mg KOH/g
Iodine value	EN 14111		120	g iodine/100g
Linolenic acid content	EN 14103		12	% (m/m)
Content of FAME with ≥4 double bonds			1	% (m/m)
Methanol content	EN 14110		0.20	% (m/m)
Monoglyceride content	EN 14105		0.80	% (m/m)
Diglyceride content	EN 14105		0.20	% (m/m)
Triglyceride content	EN 14105		0.20	% (m/m)
Free glycerol	EN 14105, EN			
	14106		0.02	% (m/m)
Total glycerol	EN 14105		0.25	% (m/m)
Alkali metals (Na + K)	EN 14108, EN			
	14109		5.0	mg/kg
Earth alkali metal (Ca + Mg)	prEN 14538		5.0	mg/kg
Phosphorus content	EN 14107		10.0	mg/kg

Table 2. Biodiesel Standard EN 14214 (Europe)

The philosophy used to approve D6751 was the same as that used for the No. 1 and No. 2 grades of fuels within the conventional specification, ASTM D975: If the parent fuels meet their respective specifications then the two can be blended in any percentage and used in conventional diesel engines. No separate set of properties was needed for the finished blends of No. 1 and No. 2, if the parent fuels met their respective specifications. These same conditions hold true for biodiesel; if biodiesel meets D6751 and conventional diesel meets D975 the two can be blended and used in conventional engines with the restriction of the upper limit of 20% biodiesel content in the finished fuel.

Property	Test method	Limits	Unit
Flash point (closed cup)	D 93	130.0 min.	°C
Water and sediment	D 2709	0.050 max.	% vol.
Kinematic viscosity, 40°C	D 445	1.9-6.0	mm <sup>2</sup> /s
Sulfated ash	D 874	0.020 max.	% mass
Sulfur	D 5453	0.0015 max or 0.05 max <sup>a</sup>	% mass
Copper strip corrosion	D 130	No. 3 max	
Cetane number	D 613	47 min	
Cloud point	D 2500	Report	°C
Carbon residue (100% sample)	D 4530	0.050 max	% mass
Acid number	D 664	0.80 max	mg KOH/g
Free glycerin	D 6584	0.020 max	% mass
Total glycerin	D 6584	0.240 max	% mass
Phosphorus content	D 4951	0.001 max	% mass
Distillation temperature, atmospheric equivalent temperature, 90% recovered	D 1160	360 max	°C

<sup>a</sup>The limits are for Grade S15 and Grade S500 biodiesel, respectively. S15 and S500 refer to maximum sulfur specifications (ppm).

Table 3. Biodiesel Standard ASTM D6751 (United States)

While this mode of operation has served the US market well, there has been substantial effort since 2003 to develop and formally approve specifications for the finished blend of biodiesel and conventional diesel fuel. In addition, several improvements and changes to D6751 were also undertaken, some as a result of changes needed to secure approval of the finished blended biodiesel specifications. At the time of this report ballots to allow the formal acceptance of up to 5% biodiesel (B5) into the conventional diesel specifications for on/off road diesel fuel (ASTM D975) and fuel oil burning equipment (ASTM D396) and a new stand alone specification covering biodiesel blends between 6% and 20% have been approved through the Subcommittee level of Committee D02. In addition, a ballot to implement a new parameter in D6751 to control the potential for filter clogging above the cloud point in B20 blends and lower has also passed the subcommittee and is on track for a June 2008 vote. Efforts to approve B100 and B99 as stand alone fuels have been discussed at ASTM, but have been put on hold in order to focus on the B5 and B6 to B20 blended fuel specification efforts.

This section describes the parameters of the specifications normally used in the biodiesel standards:

#### 4.1 Ester content

This parameter is an important tool, like distillation temperature, for determining the presence of other substances and in some cases meeting the legal definition of biodiesel (i.e. mono-alkyl esters). Low values of pure biodiesel samples may originate from inappropriate reaction conditions or from various minor components within the original fat or oil source. A high concentration of unsaponifiable matter such as sterols, residual alcohols, partial glycerides and unseparated glycerol can lead to values below the limit.

As most of these compounds are removed during distillation of the final product, distilled methyl esters generally display higher ester content than undistilled ones (Mittelbach and Enzelsberger, 1999).

#### 4.2 Density

The densities of biodiesels are generally higher than those of fossil diesel fuel. The values depend on their fatty acid composition as well as on their purity. Density increases with decreasing chain length and increasing number of double bonds, or can be decreased by the presence of low density contaminants such as methanol.

#### 4.3 Viscosity

The kinematic viscosity of biodiesel is higher than that of fossil diesel, and in some cases at low temperatures becomes very viscous or even solid. High viscosity affects the volume flow and injection spray characteristics in the engine, and at low temperatures may compromise the mechanical integrity of injection pump drive systems (when used as stand alone B100 diesel fuel).

#### 4.4 Flash point

Flash point is a measure of flammability of fuels and thus an important safety criterion in transport and storage. The flash point of petrol diesel fuel is only about half the value of those for biodiesels, which therefore represents an important safety asset for biodiesel.

The flash point of pure biodiesels is considerably higher than the prescribed limits, but can decrease rapidly with increasing amount of residual alcohol. As these two aspects are strictly correlated, the flash point can be used as an indicator of the presence of methanol in the biodiesel. Flash point is used as a regulation for categorizing the transport and storage of fuels, with different thresholds from region to region, so aligning the standards would possibly require a corresponding alignment of regulations.

#### 4.5 Sulfur

Fuels with high sulfur contents have been associated with negative impacts on human health and on the environment, which is the reason for current tightening of national limits. Low sulfur fuels are an important enabler for the introduction of advanced emissions control systems. Engines operated on high sulfur fuels produce more sulfur dioxide and particulate matter, and their emissions are ascribed a higher mutagenic potential. Moreover, fuels rich in sulfur cause engine wear and reduce the efficiency and life-span of catalytic systems. Biodiesel fuels have traditionally been praised as virtually sulfur-free. The national standards for biodiesel reflect the regulatory requirements for maximum sulfur content in fossil diesel for the region in question.

#### 4.6 Carbon residue

Carbon residue is defined as the amount of carbonaceous matter left after evaporation and pyrolysis of a fuel sample under specific conditions. Although this residue is not solely composed of carbon, the term carbon residue is found in all three standards because it has long been commonly used. The parameter serves as a measure for the tendency of a fuel sample to produce deposits on injector tips and inside the combustion chamber when used as automotive fuel. It is considered as one of the most important biodiesel quality criteria, as it is linked with many other parameters. So for biodiesel, carbon residue correlates with the respective amounts of glycerides, free fatty acids, soaps and remaining catalyst or contaminants (Mittelbach 1996). Moreover, the parameter is influenced by high concentrations of polyunsaturated FAME and polymers (Mittelbach and Enzelsberger 1999). For these reasons, carbon residue is limited in the biodiesel specifications.

#### 4.7 Cetane number

The cetane number of a fuel describes its propensity to combust under certain conditions of pressure and temperature. High cetane number is associated with rapid engine starting and smooth combustion. Low cetane causes deterioration in this behaviour and causes higher exhaust gas emissions of hydrocarbons and particulate. In general, biodiesel has slightly higher cetane numbers than fossil diesel. Cetane number increases with increasing length of both fatty acid chain and ester groups, while it is inversely related to the number of double bonds. The cetane number of diesel fuel in the EU is regulated at  $\geq 51$ . The cetane number of diesel fuel in the USA is specified at  $\geq 40$ . The cetane number of diesel fuel in Brazil is regulated and specified at  $\geq 42$ .

#### 4.8 Sulfated ash

Ash content describes the amount of inorganic contaminants such as abrasive solids and catalyst residues, and the concentration of soluble metal soaps contained in the fuel. These compounds are oxidized during the combustion process to form ash, which is connected with engine deposits and filter plugging (Mittelbach, 1996). For these reasons sulfated ash is limited in the fuel specifications.

#### 4.9 Water content and sediment

The Brazilian and American standards combine water content and sediment in a single parameter, whereas the European standard treats water as a separate parameter with the sediment being treated by the Total Contamination property. Water is introduced into biodiesel during the final washing step of the production process and has to be reduced by drying. However, even very low water contents achieved directly after production do not guarantee that biodiesel fuels will still meet the specifications during combustion. As biodiesel is hygroscopic, it can absorb water in a concentration of up to 1000 ppm during storage. Once the solubility limit is exceeded (at about 1500 ppm of water in fuels containing 0.2% of methanol), water separates inside the storage tank and collects at the bottom (Mittelbach 1996). Free water promotes biological growth, so that sludge and slime formation thus induced may cause blockage of fuel filters and fuel lines. Moreover, high water contents are also associated with hydrolysis reactions, partly converting biodiesel to free fatty acids, also linked to fuel filter blocking. Finally, corrosion of chromium and zinc parts within the engine and injection systems have been reported (Kosmehl and Heinrich,

1997). Lower water concentrations, which pose no difficulties in pure biodiesel fuels, may become problematic in blends with fossil diesel, as here phase separation is likely to occur. For these reasons, maximum water content is contained in the standard specifications.

#### **4.10 Total contamination**

Total contamination is defined as the quota of insoluble material retained after filtration of a fuel sample under standardized conditions. It is limited to  $\leq 24$  mg/kg in the European specification for both biodiesel and fossil diesel fuels. The Brazilian and American biodiesel standards do not contain this parameter, as it is argued that fuels meeting the specifications regarding ash content will show sufficiently low values of total contamination as well. The total contamination has turned out to be an important quality criterion, as biodiesel with high concentration of insoluble impurities tend to cause blockage of fuel filters and injection pumps. High concentrations of soaps and sediments are mainly associated with these phenomena (Mittelbach, 2000).

#### **4.11 Copper corrosion**

This parameter characterizes the tendency of a fuel to cause corrosion to copper, zinc and bronze parts of the engine and the storage tank. A copper strip is heated to 50°C in a fuel bath for three hours, and then compared to standard strips to determine the degree of corrosion. This corrosion resulting from biodiesel might be induced by some sulfur compounds and by acids, so this parameter is correlated with acid number. Some experts consider that this parameter does not provide a useful description of the quality of the fuel, as the results are unlikely to give ratings higher than class 1.

#### **4.12 Oxidation stability**

Due to their chemical composition, biodiesel fuels are more sensitive to oxidative degradation than fossil diesel fuel. This is especially true for fuels with a high content of di- and higher unsaturated esters, as the methylene groups adjacent to double bonds have turned out to be particularly susceptible to radical attack as the first step of fuel oxidation (Dijkstra et al. 1995). The hydroperoxides so formed may polymerize with other free radicals to form insoluble sediments and gums, which are associated with fuel filter plugging and deposits within the injection system and the combustion chamber (Mittelbach & Gangl, 2001). Where the oxidative stability of biodiesel is considered insufficient, antioxidant additives might have to be added to ensure the fuel will still meet the specification.

#### **4.13 Acid value**

Acid value or neutralization number is a measure of free fatty acids contained in a fresh fuel sample and of free fatty acids and acids from degradation in aged samples. If mineral acids are used in the production process, their presence as acids in the finished fuels is also measured with the acid number. It is expressed in mg KOH required to neutralize 1g of biodiesel. It is influenced on the one hand by the type of feedstock used for fuel production and its degree of refinement. Acidity can on the other hand be generated during the production process. The parameter characterises the degree of fuel ageing during storage, as it increases gradually due to degradation of biodiesel. High fuel acidity has been discussed in the context of corrosion and the formation of deposits within the engine which is why it is



limited in the biodiesel specifications of the three regions. It has been shown that free fatty acids as weak carboxylic acids pose far lower risks than strong mineral acids (Cvengros, 1998)

#### **4.14 Iodine value, linolenic acid ester content and polyunsaturated**

Iodine number is a measure of the total unsaturation within a mixture of fatty acids, and is expressed in grams of iodine which react with 100 grams of biodiesel. Engine manufacturers have argued that fuels with higher iodine number tend to polymerize and form deposits on injector nozzles, piston rings and piston ring grooves when heated (Kosmehl and Heinrich 1997). Moreover, unsaturated esters introduced into the engine oil are suspected of forming high-molecular compounds which negatively affect the lubricating quality, resulting in engine damage (Schaefer et al 1997). However, the results of various engine tests indicate that polymerization reactions appear to a significant extent only in fatty acid esters containing three or more double bonds (Worgetter et al. 1998, Prankl and Worgetter 1996, Prankl et al 1999). Three or more-fold unsaturated esters only constitute a minor share in the fatty acid pattern of various promising seed oils, which are excluded as feedstock according to some regional standards due to their high iodine value. Some biodiesel experts have suggested limiting the content of linolenic acid methyl esters and polyunsaturated biodiesel rather than the total degree of unsaturation as it is expressed by the iodine value.

#### **4.15 Methanol or ethanol**

Methanol (MeOH) or ethanol (EtOH) can cause fuel system corrosion, low lubricity, adverse affects on injectors due to its high volatility, and is harmful to some materials in fuel distribution and vehicle fuel systems. Both methanol and ethanol affect the flash point of esters. For these reasons, methanol and ethanol are controlled in the specification.

#### **4.16 Mono, di and triglyceride**

The EU standard specifies individual limit values for mono-, di- and triglyceride as well as a maximum value for total glycerol. The standards for Brazil and the USA do not provide explicit limits for the contents of partial acylglycerides. In common with the concentration of free glycerol, the amount of glycerides depends on the production process. Fuels out of specification with respect to these parameters are prone to deposit formation on injection nozzles, pistons and valves (Mittelbach et al. 1983).

#### **4.17 Free glycerol**

The content of free glycerol in biodiesel is dependent on the production process, and high values may stem from insufficient separation or washing of the ester product. The glycerol may separate in storage once its solvent methanol has evaporated. Free glycerol separates from the biodiesel and falls to the bottom of the storage or vehicle fuel tank, attracting other polar components such as water, monoglycerides and soaps. These can lodge in the vehicle fuel filter and can result in damage to the vehicle fuel injection system (Mittelbach 1996). High free glycerol levels can also cause injector coking. For these reasons free glycerol is limited in the specifications.

#### **4.18 Total glycerol**

Total glycerol is the sum of the concentrations of free glycerol and glycerol bound in the form of mono-, di- and triglycerides. The concentration depends on the production process.

Fuels out of specifications with respect to these parameters are prone to coking and may thus cause the formation of deposits on injector nozzles, pistons and valves (Mittelbach et al. 1983). For this reason total glycerol is limited in the specifications of the three regions.

#### **4.19 Metals (Na+K) and (Ca+Mg)**

Metal ions are introduced into the biodiesel fuel during the production process. Whereas alkali metals stem from catalyst residues, alkaline-earth metals may originate from hard washing water. Sodium and potassium are associated with the formation of ash within the engine, calcium soaps are responsible for injection pump sticking (Mittelbach 2000). These compounds are partially limited by the sulphated ash, however tighter controls are needed for vehicles with particulate traps. For this reason these substances are limited in the fuel specifications.

#### **4.20 Phosphorus**

Phosphorus in biodiesel stems from phospholipids (animal and vegetable material) and inorganic salts (used frying oil) contained in the feedstock. Phosphorus has a strongly negative impact on the long term activity of exhaust emission catalytic systems and for this reason its presence in biodiesel is limited by specification.

#### **4.21 Distillation**

This parameter is an important tool, like ester content, for determining the presence of other substances and in some cases meeting the legal definition of biodiesel (i.e. monoalkyl esters).

#### **4.22 Cold climate operability**

The behaviour of automotive diesel fuel at low ambient temperatures is an important quality criterion, as partial or full solidification of the fuel may cause blockage of the fuel lines and filters, leading to fuel starvation and problems of starting, driving and engine damage due to inadequate lubrication. The melting point of biodiesel products depend on chain length and degrees of unsaturation, with long chain saturated fatty acid esters displaying particularly unfavourable cold temperature behaviour.

### **5. Conclusion**

Biodiesel is an important new alternative biofuel. 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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## **Biofuel's Engineering Process Technology**

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This book aspires to be a comprehensive summary of current biofuels issues and thereby contribute to the understanding of this important topic. Readers will find themes including biofuels development efforts, their implications for the food industry, current and future biofuels crops, the successful Brazilian ethanol program, insights of the first, second, third and fourth biofuel generations, advanced biofuel production techniques, related waste treatment, emissions and environmental impacts, water consumption, produced allergens and toxins. Additionally, the biofuel policy discussion is expected to be continuing in the foreseeable future and the reading of the biofuels features dealt with in this book, are recommended for anyone interested in understanding this diverse and developing theme.

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