Chapter 2
Introduction to Biodiesel Production

2.1 Introduction

Biodiesel [1–5] 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.

ASTM International (originally known as the American Society for Testing and Materials) defines biodiesel as a mixture of long-chain monoalkylic esters from fatty acids obtained from renewable resources, to be used in diesel engines.

Blends with diesel fuel are indicated as “Bx”, where “x” is the percentage of biodiesel in the blend. For instance, “B5” indicates a blend with 5% biodiesel and 95% diesel fuel; in consequence, B100 indicates pure biodiesel.

2.1.1 *Advantages of the Use of Biodiesel*

Some of the advantages of using biodiesel as a replacement for diesel fuel are [1–4]:

- 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 (100°C minimum).

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- May be blended with diesel fuel at any proportion; both fuels may be mixed during the fuel supply to vehicles.
- Excellent properties as a lubricant.
- It is the only alternative fuel that can be used in a conventional diesel engine, without modifications.
- Used cooking oils and fat residues from meat processing may be used as raw materials.

2.1.2 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.

2.2 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 (mainly in the European Union countries), soybean (Argentina and the United States of America), palm (Asian and Central American countries) 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.

2.2.1 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].

2.2.1.1 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. However, there were technological limitations for sowing and harvesting in some Central and South American countries, mainly due to the lack of adequate information about fertilization, seed handling, and storage (the seeds are very small and require specialized agricultural machinery). 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.

2.2.1.2 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 form 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%.

2.2.1.3 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.

2.2.1.4 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%.

2.2.1.5 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, which has a steady demand in the international market. 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.

2.2.1.6 Flax

Flax [12] is a plant of temperate climates, with blue flowers. Linen is made with the threads from the stem of the plant and the oil from the seeds is called linseed oil, used in paint manufacture. Flax seeds have nutritional value for human consumption since they are a source of polyunsaturated fatty acids necessary for human health. Moreover, the cake left over, following oil extraction, is used as a livestock feed.

The plant adapts well to a wide range of temperature and humidity; however, high temperatures and plentiful rain do not favor high yields of seed and fiber.

Flax seeds contain between 30 and 48% of oil, and protein content is between 20 and 30%. It is important to remark that linseed oil is rich in polyunsaturated fatty acids, linolenic acid being from 40 to 68% of the total.

2.2.1.7 Safflower

Safflower adapts well to dry environments. Although the grain yield per hectare is low, the oil content of the seed is high, from 30 to 40%. Therefore, it has economic potential for arid regions. Currently, safflower is used in oil and flour production and as bird feed.

There are two varieties, one rich in mono-unsaturated fatty acids (oleic acid) and the other with a high percentage of polyunsaturated fatty acids (linoleic acid). Both varieties have a low content of saturated fatty acids.

The oil from safflower is of high quality and low in cholesterol content. Other than being used for human consumption, it is used in the manufacture of paints and other coating compounds, lacquers and soaps.

It is important to note that safflower oil is extracted by means of hydraulic presses, without the use of solvents, and refined by conventional methods, without anti-oxidant additives.

The flour from safflower is rich in fiber and contains about 24% proteins. It is used as a protein supplement for livestock feed.

2.2.1.8 Castor Seed

The castor oil plant grows in tropical climates, with temperatures in the range 20–30°C; it cannot endure frost. It is important to note that once the seeds start germinating, the temperature must not fall below 12°C. The plant needs a warm and humid period in its vegetative phase and a dry season for ripening and harvesting. It requires plenty of sunlight and adapts well to several varieties of soils. The total rainfall during the growth cycle must be in the range 700–1,400 mm; although it is resistant to drought, the castor oil plant needs at least 5 months of rain during the year.

Castor oil is a triglyceride, ricinolenic acid being the main constituent (about 90%). The oil is non-edible and toxic owing to the presence of 1–5% of ricin, a toxic protein that can be removed by cold pressing and filtering. The presence of hydroxyl groups in its molecules makes it unusually polar as compared to other vegetable oils.

2.2.1.9 Tung

Tung [12] is a tree that adapts well to tropical and sub-tropical climates. The optimum temperature for tung is between 18 and 26°C, with low yearly rainfall.

During the harvest season, the dry nuts fall off from the tung tree and are collected from the ground. Nut production starts 3 years after the planting.

The oil from tung nuts is non-edible and used in the manufacture of paints and varnishes, especially for marine use.

2.2.1.10 Cotton

Among non-foodstuffs, cotton is the most widely traded commodity. It is produced in more than 80 countries and distributed worldwide. After the harvest, it may be traded as raw cotton, fiber or seeds. In cotton mills, fiber and seeds are separated from raw cotton.

Cotton fiber is processed to produce fabric and thread, for use in the textile industry. In addition, cotton oil and flour are obtained from the seed; the latter is rich in protein and is used in livestock feed and after further processing, for human consumption.

2.2.1.11 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.

2.2.1.12 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 non-edible. The toxicity is due to the presence of curcasin (a globulin) and jatrophic acid (as toxic as ricin).

2.2.1.13 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%.

2.2.1.14 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 CO_2, water, light, nutrients and mineral salts are necessary for the growth of microalgae. Production processes take place in raceway ponds and photobiological reactors [13].

Leading oil crops used in biodiesel production are indicated in Box 2.1.

Box 2.1 Leading Oil Crops for Biodiesel Production

Rapeseed
Palm
Soybean

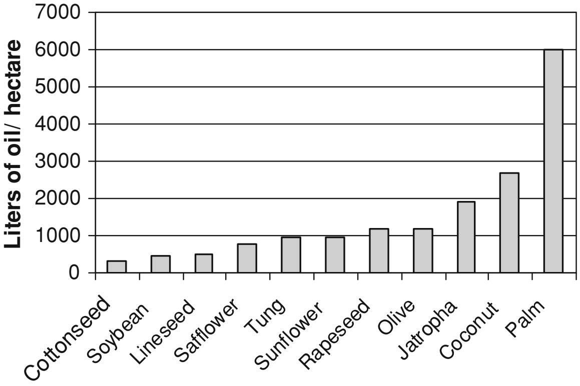


Fig. 2.1 Approximate oil yields for different crops

Figure 2.1 presents approximate oil-yield values (in liters per hectare) for some of the crops [13] discussed in this chapter.

It is important to note that the data in Fig. 2.1 only show the oil yields of different crops. However, for the comparison of economical suitability it must be borne in mind that in addition to oil, some crops are grown for fiber or protein production. For instance, soybean has an oil content of 18% (maximum), whereas the remainder is mostly protein (usually used as livestock feed).

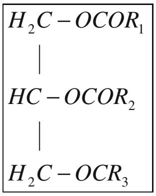
2.2.2 Characteristics of Oils and Fats Used in Biodiesel Production

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. 2.2.

In Fig. 2.2, R_1, R_2 y R_3 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. The

Fig. 2.2 General chemical formula of triglycerides



$$\begin{array}{l} H_2C-OCOR_1 \\ \quad | \\ HC-OCOR_2 \\ \quad | \\ H_2C-OCR_3 \end{array}$$

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)	$CH_3\ (CH_2)_{14}\ COOH$
Estearic (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)	$CH_3\ CH_2\ (CH = CH\ CH2)_3\ (CH2)_6\ COOH$
Erucic (22:1)	$CH_3\ (CH_2)_7\ CH = CH\ (CH2)_{11}\ COOH$
Ricinoleic (18:1)	$CH_3\ (CH_2)_5\ CHOH\ CH_2\ CH = CH\ (CH_2)_7\ COOH$

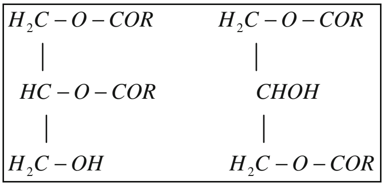
Table 2.2 Approximate content (in weight) of saturated and non-saturated fatty acids in some vegetable oils and animal fats

Oil/fat	SFA (≈ % w/w)	NSFA (≈ % 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.

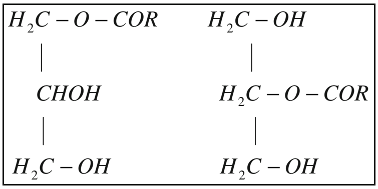
The most frequent fatty acids in oils are lauric, palmitic, estearic, linoleic and linolenic, although others may also be present. It is important to note that vegetable oils differ in their content of fatty acids. For instance, ricinoleic acid is the main component of castor oil, whereas in olive oil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



$$\begin{array}{ll} H_2C-O-COR & H_2C-O-COR \\ | & | \\ HC-O-COR & CHOH \\ | & | \\ H_2C-OH & H_2C-O-COR \end{array}$$

Fig. 2.3 Chemical formula of diglycerides



$$\begin{array}{ll} H_2C-O-COR & H_2C-OH \\ | & | \\ CHOH & H_2C-O-COR \\ | & | \\ H_2C-OH & H_2C-OH \end{array}$$

Fig. 2.4 Chemical formula of monoglycerides

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.

The US Department of Energy [15] indicates that a perfect biodiesel should only comprise mono-unsaturated fatty acids.

Vegetable oils may also contain small percentages of monoglycerides and diglycerides. Their chemical formulae are shown in Figs. 2.3 and 2.4. In addition, there will also be small amounts of free fatty acids (in most vegetable oils, less than 1%, except for palm oil, where they can reach up to 15%).

The composition of vegetable oils influences their properties [16]. For instance, the pour point and cloud point temperatures, cetane number and the iodine index depend on the number of unsaturations and the length of the fatty acid chains. A higher content of double-covalent bonds gives a lower solidification point and a higher iodine index.

2.2.3 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 (CH_3OH) and ethanol (C_2H_5OH) 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. Several countries are carrying out research towards this objective, such as Spain and Brazil.

Box 2.2 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.

2.3 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, as indicated in Box 2.3.

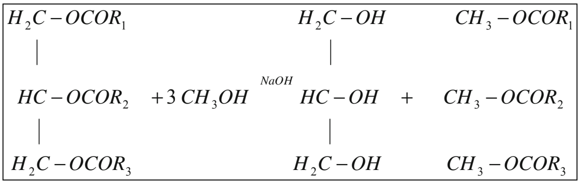
Box 2.3 Transesterification Reactions for Biodiesel Production

Basic. Most frequently used at all production scales.
Acid. Less frequent in industrial production, sometimes used a first stage with highly acidic raw materials.
Enzymatic. Less used; the enzymes are usually lipases.

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:

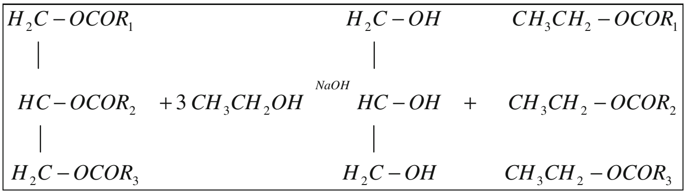
$$\mathrm{RCOOR'} + \mathrm{R''OH} \overset{\text{cat}}{\Leftrightarrow} \mathrm{R'OH} + \mathrm{RCOOR''} \tag{2.1}$$

When methanol is the alcohol used in the transesterification process, the product of the reaction is a mixture of methyl esters; similarly, if ethanol were



$$\begin{array}{lcccl} H_2C-OCOR_1 & & H_2C-OH & & CH_3-OCOR_1 \\ | & & | & & \\ HC-OCOR_2 & +3\,CH_3OH \overset{NaOH}{} & HC-OH & + & CH_3-OCOR_2 \\ | & & | & & \\ H_2C-OCOR_3 & & H_2C-OH & & CH_3-OCOR_3 \end{array}$$

Fig. 2.5 Basic transesterification reaction with methanol



$$\begin{matrix} H_2C-OCOR_1 & & H_2C-OH & & CH_3CH_2-OCOR_1 \\ | & & | & & \\ HC-OCOR_2 & +3\,CH_3CH_2OH \xrightarrow{NaOH} & HC-OH & + & CH_3CH_2-OCOR_2 \\ | & & | & & \\ H_2C-OCOR_3 & & H_2C-OH & & CH_3CH_2-OCOR_3 \end{matrix}$$

Fig. 2.6 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 (since it originates the mixture of esters), additional steps are necessary to obtain a product that complies with international standards [4, 17], as shown in Box 2.4. In consequence, once the chemical reaction is completed and the two phases (mix of esters and glycerin) are separated, the mix of methyl esters must be purified to reduce the concentration of contaminants to acceptable levels. These include remnants of catalyst, water and methanol; the latter is usually mixed in excess proportion with the raw materials in order to achieve higher conversion efficiency in the transesterification reaction. In the following sections the steps of the purification process will be described in detail.

2.3.1 Treatment of Raw Materials

The content of free fatty acids, water and non-saponificable substances are key parameters to achieve high conversion efficiency in the transesterification reaction.

The use of basic catalysts in triglycerides with high content of free fatty acids is not advisable [18], since part of the latter reacts with the catalyst to form soaps. In consequence, part of the catalyst is spent, and it is no longer available for transesterification. In summary the efficiency of the reaction diminishes with the increase of the acidity of the oil; basic transesterification is viable if the content of free fatty acids (FFAs) is less than 2%. In the case of highly acidic raw materials

Box 2.4 Stages of Biodiesel Production Process

Treatment of raw materials
Alcohol-catalyst mixing
Chemical reaction
Separation of the reaction products
Purification of the reaction products

(animal fats from cattle, poultry, pork; vegetable oils from cotton, coconut, most used oils, etc.) an acid transesterification [19] is necessary as a preliminary stage, to reduce the level of FFAs to the above-mentioned value.

Besides having low humidity and acid content, it is important that the oil presents a low level of non-saponificable substances. If the latter were to be present in significant amounts and soluble in biodiesel, it would reduce the level of esters in the product, making it difficult to comply with the minimum ester content required by the standards.

The AOCS standards [20] list the required properties of oils. Anyway, the properties required by the oils are finally determined by the biodiesel industry in each country. For instance, in Argentina the oils for biodiesel production usually have:

- Acidity level <0.1 mg KOH/g
- Humidity <500 ppm
- Peroxide index <10 meq/kg
- Non-saponificable substances <1%.

2.3.2 Alcohol-Catalyst Mixing

The alcohol used for biodiesel production must be mixed with the catalyst before adding the oil. The mixture is stirred until the catalyst is completely dissolved in the alcohol. It must be noted that the alcohol must be water-free (anhydrous) for the reasons explained in the previous paragraph.

Sodium and potassium hydroxides are among the most widely used basic catalysts. For production on an industrial scale, sodium or potassium methoxides or methylates are commercially available.

Of course, due caution must be exercised, and all applicable safety regulations must be followed, when working with methanol, hydroxides and methoxides, independently of the production scale.

The alcohol-to-oil volume ratio, R, is another key variable of the transesterification process. The stoichiometric ratio (Fig. 2.5) requires 1 mol of oil to react with 3 mol of alcohol, to obtain 3 mol of fatty acids methyl esters (FAME) and 1 mol of glycerin. However, since the reaction is reversible, excess alcohol as a reactant will shift the equilibrium to the right side of the equation, increasing the amount of products (as it may be inferred from Le Chatelier's principle). Although a high alcohol-to-oil ratio does not alter the properties of FAME, it will make the separation of biodiesel from glycerin more difficult, since it will increase the solubility of the former in the latter. Usually, a 100% alcohol excess is used in practice, that is, 6 mol of alcohol per mole of oil. This corresponds to a 1:4 alcohol-to-oil volume ratio ($R = 0.25$). The relation between the dielectric properties of FAME and the alcohol-to-oil ratio, R, will be discussed in Chap. 7.

Finally, it must be noted that the necessary amount of catalyst is determined taking into account the acidity of the oil, by titration.

2.3.3 Chemical Reaction

The chemical reaction takes place when the oil is mixed with the alkoxide (alcohol–catalyst mix) described in the previous paragraph. This requires certain conditions [17, 21] of time, temperature and stirring. Since alcohols and oils do not mix at room temperature, the chemical reaction is usually carried out at a higher temperature and under continuous stirring, to increase the mass transfer between the phases.

Usually, emulsions form during the course of the reaction; these are much easier and quicker to destabilize when methanol is used, in comparison to ethanol [22]. Due to the greater stability of emulsions formed, difficulties arise in the phase separation and purification of biodiesel when ethanol is used in the reaction.

The transesterification process may be carried out at different temperatures. For the same reaction time, the conversion is greater at higher temperatures. Since the boiling point of methanol is approximately 68°C (341 K), the temperature for transesterification at atmospheric pressure is usually in the range between 50 and 60°C.

It is very useful to know the chemical composition of the mixture during the reaction; then, if the reaction mechanism and kinetics are known, the process can be optimized. However, the determination of the mixture composition is not easy, since more than a hundred substances are known to be present [23]. For instance, for biodiesel production from rapeseed oil (whose main SFAs are palmitic, oleic, linoleic and linolenic) and methanol, with potassium hydroxide as a catalyst, it could be theoretically possible to find 64 isomers of triglycerides, 32 diglycerides, 8 monoglycerides, their methyl esters, potassium salts of the fatty acids, potassium methoxide, water, etc.

The studies on this subject [24, 25] indicate the following general guidelines:

- For longer reaction times, the concentration of triglycerides diminishes the concentration of esters, increases and the concentration of mono- and diglycerides increases to a maximum and then decreases.
- Most of the chemical reaction takes place during the first minutes.
- The absence of mono- and diglycerides at the beginning of the chemical reaction and the increase and reduction of their concentration during the reaction confirm that the production of esters from the triglycerides takes place in three steps, as represented in the equations below:

$$\mathrm{TG} + \mathrm{MOH} \xrightarrow{\mathrm{KOH}} \mathrm{DG} + \mathrm{ME} \tag{2.2}$$

$$\mathrm{DG} + \mathrm{MOH} \xrightarrow{\mathrm{KOH}} \mathrm{MG} + \mathrm{ME} \tag{2.3}$$

$$\mathrm{MG} + \mathrm{MOH} \xrightarrow{\mathrm{KOH}} \mathrm{G} + \mathrm{ME} \tag{2.4}$$

where MOH indicates methanol, ME are the methyl esters, TG, DG and MG are tri-, di- and monoglycerides, respectively, and G is the glycerin.

Several methods, with different levels of equipment complexity and training requirements, have been devised to analyze samples that are mixtures of fatty acids and esters from mono-, di-, and triglycerides obtained from transesterification of vegetable oils. A list is presented in Box. 2.5.

It must be noted that thin layer chromatography (TLC) provides essentially qualitative information about the sample composition, as distinct from the other methods in Box 2.5, that can be used for quantitative analysis. However, the simplicity, speed and low cost of TLC make it quite attractive as a technique for process optimization and routine checks, especially in small- and medium-scale production plants, and also for training purposes.

2.3.3.1 Catalysts

The catalysts used for the transesterification of triglycerides may be classified as basic, acid or enzymatic, as indicated in Box 2.3 [38, 39].

Basic catalysts include sodium hydroxide (NaOH), potassium hydroxide (KOH), carbonates and their corresponding alcoxides (for instance, sodium methoxide or ethoxide). There are many references on basic catalysts in the scientific literature [26, 40–51].

Acid catalysts include sulfuric acid, sulfonic acids and hydrochloric acid; their use has been less studied [26, 52–57].

Heterogeneous catalysts that have been considered for biodiesel production include enzymes [39], titanium silicates [58], and compounds from alkaline earth metals [59], anion exchange resins [59] and guanidines in organic polymers [60]. Lipases are the most frequently used enzymes for biodiesel production [61–64].

2.3.4 Separation of the Reaction Products

The separation of reaction products takes place by decantation: the mixture of fatty acids methyl esters (FAME) separates from glycerin forming two phases, since

Box 2.5 Analytical Methods for Mixtures of Fatty Acid and Esters

Thin Layer Chromatography [26]
Gas Chromatography (GC) [27–29]
High Performance Liquid Chromatography (HPLC) [29–33]
Gel Permeation Chromatography [34]
Nuclear Magnetic Resonance (NMR) [35, 36]
Infrared (IR) Spectroscopy [36, 37]

they have different densities; the two phases begin to form immediately after the stirring of the mixture is stopped. Due to their different chemical affinities, most of the catalyst and excess alcohol will concentrate in the lower phase (glycerin), while most of the mono-, di-, and triglycerides will concentrate in the upper phase (FAME). Once the interphase is clearly and completely defined, the two phases may be physically separated. It must be noted that if decantation takes place due to the action of gravity alone, it will take several hours to complete. This constitutes a "bottleneck" in the production process, and in consequence the exit stream from the transesterification reactor is split into several containers. Centrifugation is a faster, albeit more expensive alternative.

After the separation of glycerin, the FAME mixture contains impurities such as remnants of alcohol, catalyst and mono-, di-, and triglycerides. These impurities confer undesirable characteristics to FAME, for instance, increased cloud point and pour point, lower flash point, etc. In consequence a purification process is necessary for the final product to comply with standards. This will be discussed in the next section.

2.3.5 Purification of the Reaction Products

The mixture of fatty acids methyl esters (FAME) obtained from the transesterification reaction must be purified in order to comply with established quality standards for biodiesel. Therefore, FAME must be washed, neutralized and dried.

Successive washing steps with water remove the remains of methanol, catalyst and glycerin, since these contaminants are water-soluble. Care must be taken to avoid the formation of emulsions during the washing steps, since they would reduce the efficiency of the process. The first washing step is carried out with acidified water, to neutralize the mixture of esters. Then, two additional washing steps are made with water only. Finally the traces of water must be eliminated by a drying step. After drying, the purified product is ready for characterization as biodiesel according to international standards.

An alternative to the purification process described above is the use of ion exchange resins or silicates.

Glycerin as obtained from the chemical reaction is not of high quality and has no commercial value. Therefore, it must be purified after the phase separation. This is not economically viable in small scale production, due to the small glycerin yield. However, purification is a very interesting alternative for large-scale production plants, since, in addition to the high quality glycerin, part of the methanol is recovered for reutilization in the transesterification reaction (both from FAME and glycerin), and thus lowering biodiesel production costs. The steady increase of biodiesel production is fostering research for novel uses of glycerin in the production of high-value-added products.

It must be noted that the stages of the biodiesel production process (summarized in Box 2.4) are the same for all the production scales (laboratory, pilot plant, small-, medium-, and large-scale industrial). However, the necessary equipment will be significantly different [2].

2.4 Glycerin

Glycerin is the usual name of 1,2,3-propanetriol; it is also referred to as glycerol, glycerin or glycyl alcohol. Chemically an alcohol, it is a liquid of high viscosity at room temperature, odorless, transparent, colorless, of low toxicity and sweet taste. The boiling point of glycerin is high, 290°C (563 K), and its viscosity increases noticeably at low temperature, down to its freezing point, 18°C (291 K). It is a polar substance that can be mixed with water and alcohols, and is also a good solvent. Glycerin is hygroscopic and has humectant properties.

Until the last years of the nineteenth century, glycerin was a product of candle manufacturing (from animal fat) and it was used mainly in the production of nitroglycerin for explosives. Later, separation processes from soap were developed and most glycerin was obtained as a sub-product of the soap industry. Since mid-century, synthetic glycerin can also be obtained using raw materials from the petrochemical industry.

At present, glycerin is obtained as a sub-product of soap or biodiesel production, and it is purified to eliminate the contaminants, mainly partially dissolved soap or salt (for the sub-product of soap production), or catalyst and methanol (from biodiesel production).

2.4.1 Uses

Even though the main use of glycerin was traditionally in the soap industry, about the middle of the twentieth century more than 1,500 uses for glycerin had been identified. These include the manufacture, conservation, softening and moisturizing of an ample variety of products [65]. Some of the uses of glycerin are:

- As an additive in the manufacture of soaps, to improve their properties
- In the manufacture of nitroglycerin for the production of explosives
- In the food industry, for the manufacture of sweets, soft drinks, and pet foods and in the conservation of canned fruit
- Due to its moisturizing and emollient properties, in the cosmetics industry for the manufacture of creams and lotions
- In the chemical industry, for the fabrication of urethane foams, alkydic resins and cellophane, among other uses
- In the pharmaceutical industry, for the manufacture of ointments, creams and lotions
- In the manufacture of certain inks
- For the lubrication of molds.

In the last years, glycerin production has increased, due to the steady growth of biodiesel production. Several academic and industrial research groups are actively pursuing new applications for glycerin, particularly in connection with polymers and surfactants [65]. It must be noted that the uses of glycerin are in principle similar to those of other widely used poliols (glycol, sorbitol, pentaerythritol, etc.), thus opening the technological possibility of replacing these poliols in new applications. Of course, these substitutions will take place if economically viable, and will depend on the prices of glycerin and the poliols involved.

The main research objective is the production of high-value-added products using glycerin, for instance, as a substrate for protein production from single-cell organisms, as a raw material for the production of detergents and bioemulsifiers, for the production of other poliols by fermentation (such as 1,2-propanediol or 1,3-propanediol), or for the production of other biofuels (bioethanol, biogas, hydrogen).

2.5 Concluding Remarks

There are significant advantages in the use of biodiesel as a replacement of diesel fuel and in blends.

The vegetable oils used as raw materials can be obtained from different oil crops that may be grown in a wide variety of environments, some of which are not adequate for traditional agricultural production. Microalgae grown in ponds and photobiological reactors have also great potential for the production of oils for biodiesel production. Moreover, used cooking oils and fat residues from the meat processing industry may also be employed in biodiesel production.

The production process has the same stages, irrespective of the production scale, although the differences in equipment may be significant. After the treatment of the raw materials, the transesterification reaction (usually with methanol and a basic catalyst) produces a mixture of fatty acids methyl esters (FAME) with glycerin as a co-product. The mixture of methyl esters must be separated from the glycerin and purified in order to comply with the requirements set by international standards for biodiesel.

In large-scale production plants, glycerin is usually recovered and purified since it is a valuable substance, with many applications in the pharmaceutical, cosmetics and chemical industries.

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