A REVIEW OF BIODIESEL PRODUCTION FROM NON-EDIBLE RAW MATERIALS USING THE TRANSESTERIFICATION PROCESS WITH A FOCUS ON INFLUENCE OF FEEDSTOCK COMPOSITION AND FREE FATTY ACIDS

RENATA N. VILAS BÔAS [1,*] AND MARISA F. MENDES [1]

[1]Department of Chemical Engineering, Federal Rural University of Rio de Janeiro 23.897-000- Seropédica - RJ, Brazil.

ABSTRACT

The main resources needed for an alternative fuel are availability and renewability, that is, less dependence on restricted raw materials accompanied by no or less pollution. Due to being eco-friendly and non-toxic to nature, biodiesel is attracting more and more interest. Biodiesel has many important technical advantages compared to petroleum diesel, such as inherent lubricity, low toxicity, derivation of renewable and domestic raw materials, biodegradability, insignificant sulfur content, and lower exhaust emissions. However, they have some important disadvantages that include the high cost of the raw material, lower storage and oxidative stability, lower volumetric energy content, lower low-temperature operability, and in some cases, higher NOx exhaust emissions. One of the major challenge obstacles is the high cost of refined vegetable oil as raw material, which consists of almost 70% of the total production costs. Therefore, in order to reduce the cost of biodiesel, non-edible sources such as residual cooking oil (WCO), algae oil, non-edible vegetable oil, and residual fats are commonly used for the production of biodiesel due to its low cost and don't affect the food chain. The most common method used in the production of biodiesel is the transesterification of vegetable oils and animal fats. Production and process are influenced by several factors, such as temperature and reaction time, the molar ratio of alcohol to oil, and type and concentration of catalyst. Therefore, this review focuses on the recent discovery of the transesterification of inedible sources for biodiesel, the influence of the composition of the raw material on the quality of biodiesel, and the possible solutions to its disadvantages for the production of biodiesel.

Keywords: Alternative feedstocks, Biodiesel, Fatty acid FAME, Transesterification.

1. INTRODUCTION

Biodiesel is defined by ASTM International as a fuel composed of monoalkyl esters of long-chain fatty acids derived from renewable vegetable oils or animal fats that attend the requirements of ASTM D6751[173]. Vegetable oils and animal fats are mainly composed of triacylglycerols (TAG) consisting of long-chain fatty acids chemically linked to glycerol (1,2,3-propanotriol). The chemical process by which biodiesel is prepared is known as the transesterification reaction and involves a TAG reacting with short-chain alcohol normally in the presence of a catalyst at an elevated temperature to form alkyl fatty acid esters (FAAE) and glycerol as a by-product[1,2].

The second and third generation of biodiesel is produced from non-edible foods from crops (vegetable oil and algae) and waste oil (residual animal oil and WCO), respectively. In addition, the feasibility of using a wide range of raw materials, process optimization, and cost reduction for biodiesel production has been a challenge for more than 20 years. This led to the search for low-cost alternatives, such as non-edible resources and raw materials of animal origin[3]. Therefore, the use of waste oil sources (WCO and animal fats) is increasing for the production of biodiesel on an industrial scale, which makes the production process more sustainable[4,5].

Biodiesel has been perceived as a potential source of renewable sources and environmentally friendly energy in the future, replacing the exhaustible diesel derived from petroleum. A significant amount of research conducted worldwide for the production of biodiesel due to its vast advantages compared to conventional diesel. For example, biodiesel is superior to diesel in terms of sulfur content, flash point, aromatic content, and biodegradability[6,7]. However, the raw material for the production of biodiesel is derived from renewable sources, which are abundant and inexhaustible. Therefore, the production of biodiesel guaranteed the sustainability of human development and the energy source in the future[8].

Despite the bright prospect of biodiesel as a sustainable source of energy, its marketing efforts have been very limited worldwide. One of the biggest obstacles is the high cost of refined vegetable oil as a raw material, which consists of almost 70% of the total production costs[9,10]. Therefore, in order to reduce the cost of biodiesel, low-quality residues or oils/fats that are cheap and readily available are being used as raw materials. However, the challenge of using this cheap raw material is the presence of impurities, such as water and free fatty acids (FFA), which are common components in residual oils/fats[8,11]. The interaction of FFA with water in the presence of an alkaline catalyst in the biodiesel production process has limited the use of low-grade, cheap, recycled raw material, or whatever can significantly reduce biodiesel costs[12].

Subsequently, the limitations of the homogeneous catalytic reaction led researchers to focus on alternative technologies in the production of biodiesel.

According to West et al.[13], the solid acid-catalyzed process for the production of biodiesel is more efficient than homogeneous acid and alkaline catalysis and supercritical processes. The study also emphasized as having the lowest capital investment with the highest return on investment, through a technically simple process. Thus, numerous solid acid catalysts have been developed to overcome the disadvantages of homogeneous catalysts currently used in the industry. The numerous problems identified in relation to the catalyst the production of biodiesel stimulated research both in industry and academia to explore better options with greater emphasis on better catalyst systems and flexible raw materials.

This article discusses various non-edible raw materials used for the production of biodiesel with its benefits, disadvantages, and characterization. It also describes the different biodiesel production processes with a primary focus on the transesterification process. In addition to providing a description of the properties and quality assessment of biodiesel in relation to the raw material used. This review will help researchers to analyze and compare different generations of biodiesel.

2. NON-EDIBLE SOURCES FOR BIODIESEL PRODUCTION

Biodiesel can be obtained from different raw materials, such as vegetables, algae, microbial oil, and animal fats, thus obtaining a biofuel with different purities and compositions[1]. The main stage for the production of biodiesel is the selection of raw material because it influences on several factors, such as biodiesel purity, cost, composition, and conversion. The availability and type of raw material source are the main parameters for classifying biodiesel as edible, non-edible, and based on residual origins[14].

Inedible oils can be seen as important future sources for the production of biodiesel compared to edible oils (Figure 1), which are competitive to people's food needs. They can be obtained from crops grown on land in remote areas and degraded forests. In addition, they can also be grown in areas of agricultural fields, irrigation channels, and roadside[15]. The selection of raw materials for the production of biodiesel is also dependent on regions, taking into account the country's availability and economic aspect. As an example, we have canola oil, which is widely used as a raw material in Canada and soy oil, which is used as a raw material in Brazil and the USA. Coconut and palm oils are widely used in Indonesia and Malaysia as a raw material for biodiesel. Among the oils that have been used a lot before as a raw material for biodiesel, we have sunflower oil, rapeseed oil, soybean oil, and mustard oil, but due to the unfavorable results of being widely used in food plants, there was a slowdown in use as raw materials for biodiesel[16].
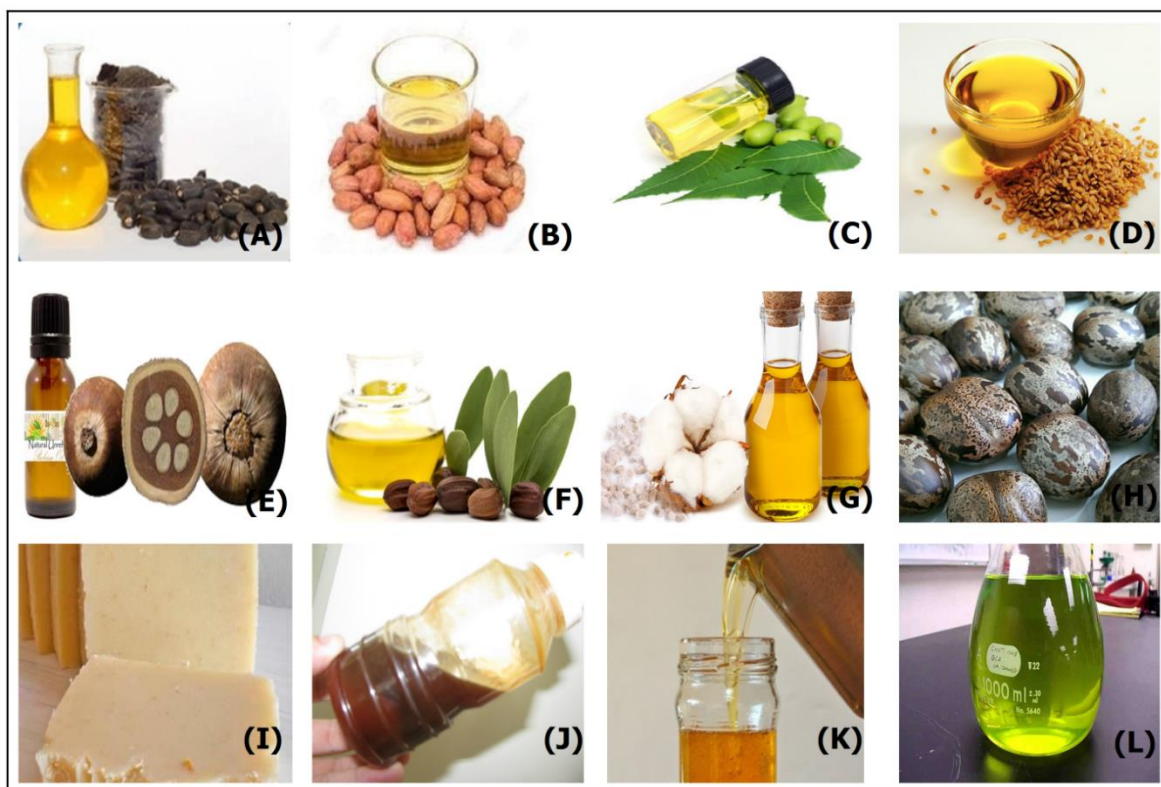
*Corresponding author email: revilasboas@ufrrj.br

Figure 1. Non-edible sources used in biodiesel production: (A) Jatropha oil, (B) Karanja oil, (C) Neem oil, (D) Linseed, (E) Babassu oil, (F) Jojoba oil, (G) Cottonseed Oil, (H) Rubber tree seed, (I) Animal tallow, (J) Distillate from soybean oil deodorization, (K) Cooking oil residues, (L) Algal oil.

The use of edible oils as raw materials for biodiesel faces several problems, due to the use of these raw materials directly affecting the food chain. From numerous researches, it can be concluded that the consumption of non-edible oil as a raw material for biodiesel has many benefits, for example, it is biodegradable, has a low amount of sulfur, with no effect on the food chain, low aromatic content and availability. Some advantages and disadvantages of non-edible oils are shown in Table 1.

Table 1. The advantages and disadvantages of non-edible oils[132,178].

Advantages	Disadvantages
▪ Tolerant and adaptability to different environmental conditions for cultivation.	▪ The toxic compounds made it unfavorable for human consumption.
▪ No competition with agricultural crops, human food, and animal feed products.	▪ The production cost is high due the high content of free fatty acids (FFAs).
▪ Higher production rate and quality of biodiesel.	
▪ Generation of useful by-products. ▪ Non-edible oils are preferred because of their liquid nature portability, ready availability, renewability, higher heat content, lower sulfur content, lower aromatic content, and biodegradability. ▪ Due to their high potential for conversion to biodiesel, they can generate rural employment.	

However, there are some raw materials in increasing use that can also be used to produce biodiesel such as tallow oil, animal fats, fish oil and microalgae etc[14]. Therefore, the main sources of biodiesel production are divided into two different categories (edible and non-edible) as shown in Figure 2.
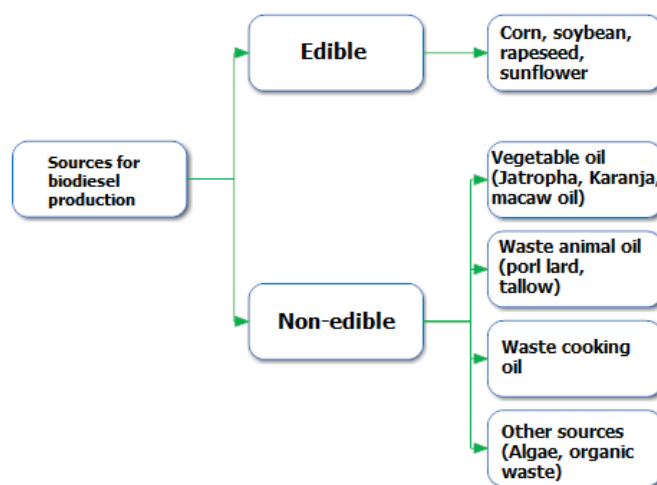

Figure 2. Different sources for biodiesel production[4].

The selection of raw material can be done through the analysis of various parameters of the raw material, such as fatty acid composition (Table 2), adequacy, chemical composition and physical properties[1]. Raw materials that do not compete with the food chain for the production of biodiesel can be categorized mainly into three main groups:

1) Non-edible vegetable oils: Jatropha oil (*Jatropha curcas*)[17], Karanja oil (*Pongamia pinnata*)[18], Neem oil (*Azadirachta indica*)[19], Linseed (*Linum usitatissimum*)[20], Rubber seed (*Hevea brasiliensis*)[21], Cotton seed (*Gossypium*)[22], Jojoba oil (*Simmondsia chinensis*)[23], Babassu (*Orbignya* sp.)[24] and Castor oil (*Ricinus communis*)[25].

2) Waste oil (vegetable and animal): Cooking oil waste[26], Soybean oil deodorization distillate[27], Animal tallow[28], Chicken fat[29], Fish oil[30] and Lard[31].

3) Algal oil.

Table 2. Fatty acid compositions of some animal fats and fatty acid compositions of various non-edible feedstock[14,179].

Feedstock	% (by weight)							
	12:0 (lauric)	**14:0 (myristic)**	**16:0 (palmitic)**	**16:1 (palmitoleic)**	**18:0 (stearic)**	**18:1 (oleic)**	**18:2 (linoleic)**	**18:3 (linolenic)**
FAC of animal fats								
Chicken fat	–	0.5	24	5.8	5.8	38.2	23.8	1.9
Duck tallow	–	-	17	-	4	59.4	19.6	-
Mutton fat	0.2	3	27	2	24.1	40.7	2	-
Fish oil	-	6.3	12.1	8.1	1.1	11.9	4.2	0.9
Lard	-	1.7	23.2	2.7	10.4	42.8	19.1	64.7
FAC of non-edible feedstock								
Jatropha	-	0.1	15.1	0.9	7.1	44.7	31.4	0.2
Karanja	-	-	3.7-7.9	-	2.4-8.6	44.5-71.3	10.8-18.3	-
Neem	–	0.2-0.26	14.9	0.1	20.6	43.9	17.9	0.4
Linseed	–	-	4.4	0.3	3.8	20.7	15.9	54.6
Rubber seed	–	2.2	10.2	-	8.7	24.6	39.6	16.3
Cotton seed	-	-	28	-	11	13	58	0
Jojoba	-	-	16	-	6.5	43.5	34.4	0.0
Babasu	48.8	17.2	9.7	-	4	14.2	1.8	-
Castor	–	-	1.1	0	3.1	4.9	1.3	0.6

Each oil raw material will have a different fatty acid composition. The fatty acid composition of the raw material and alcohol play important roles in determining the properties of biodiesel, including viscosity, melting point, heat of combustion and oxidation stability[32,33]. According to Knothe[34], the properties of fatty acids that affect the properties of biodiesel are: degree of unsaturation, length and branching of the chain. For example, oil-based raw materials, such as soybean oil and rice bran oil, have low oxidation stability due to the high amount of linoleic acid for having double bonds in the carbon chain[33].

2.1 Vegetable oil

Different types of edible and non-edible vegetable oils are used for the production of biodiesel in several countries. The United States exports edible oil that uses soy for the production of biodiesel, while European countries use rapeseed oil as a raw material for the production of biodiesel. Tropical countries, such as Malaysia, use palm oil or coconut oil, while India uses inedible vegetable oils, such as Jatropha, Simarouba and Karanja[35]. In Australia, papaya seed oil and fruit kernel oil are popular inedible vegetable oils for the production of biodiesel[36]. Due to economic issues and pressure on food security, the use of non-edible oils is preferable to edible vegetable oils[4,37].

2.1.1 Jatropha (Jatropha curcas)

Jatropha is an oilseed plant and is grown in semi-arid and marginal areas. Shrubs can be collected twice a year and are usually not seen by cattle and remain productive for 30 to 50 years. The seeds can be obtained from the plant after 1 year of planting and its productivity is higher after 5 years of planting[38]. The Jatropha plant belongs to the *Euforbiaceae* family and the maximum plant height is up to 5–7 m[39]. The countries India, Argentina, United States, Paraguay, Brazil, Africa, Bolivia and Mexico are home to the jatropha crop[40,41]. In India, Jatropha tree has been recognized as one of the main sources of biodiesel, where about 64 million hectares of area are classified as uncultivated or waste area. The seeds of the Jatropha plant have approximately 20 to 60% oil[14]. The density and viscosity value of Jatropha oil are 916 kg.m-3 (at 15 °C) and 37.28 mm².s-1 (at 40 °C), respectively[42]. Jatropha has mainly unsaturated components, such as oleic (34.3 - 44.7%) and linoleic acid (31.4 - 43.2%), some saturated components, such as palmitic acid (13.6 - 15.1%) and stearic acid (7.1 - 7.4%)[43].

Jatropha as an inedible vegetable oil has been considered as a commercially viable alternative to edible oil for the production of biodiesel due to its physicochemical characteristics[44]. Different methods, such as traditional methods (using the simple hand held machine) and advanced methods, such as oil presses (yield of 1 liter of biodiesel for every 4 kg of seed) have been used for the extraction of Jatropha oil[45]. Salar-García et al.[46] used Jatropha oil to produce biodiesel and reached the maximum yield of FAME (99.5%) and 100% conversion at a temperature of 325 °C in a reaction time of 90 min.

2.1.2 Karanja (Pongamia pinnata)

The main producing countries of Karanja are Southeast Asia, Australia, China and the USA[174]. It belongs to the legume family, and the maximum height of the Karanja plant is 15 to 25 m. After 3 to 4 years, the flowering of the plantation begins and matures 4 to 7 years after planting. The Karanja plant has 9 to 90 kg of seeds in a single plant. It has a huge inconsistency in the amount of oil in Karanja seeds (25-40%)[14,47]. The density and viscosity values for Karanja oil are 933 kg/m³ (at 15 °C) and 39.9 mm²/s (at 40 °C) respectively[42]. Karanja oil has stearic acid (2.4–8.9%), linoleic acid (10.8-18.3%) and oleic acid (44.5-71.3%)[48]. A recent study using Karanja oil obtained 97% biodiesel through the transesterification process at a reaction temperature of 65 °C using 1% (m/m) KOH in a molar ratio of methanol to oil of 6:1 in a reaction time of 2 h[4,49].

2.1.3 Neem (Azadirachta indica)

The main Neem producing countries are in parts of Bangladesh, Australia, India, Japan, Burma, Sri Lanka, Indonesia and Pakistan. Neem belongs to the *Meliaceae* family, and can be grown in all types of sand, such as limestone, dry, alkaline, saline, shallow, rocky and clayey. The Neem plant can reach a maximum height of 12 to 18 m. For the cultivation of the Neem plant, between 140 and 120 cm of rain are required annually. The age of the Neem plant is around 150 to 200 years and, after 15 years of planting, it shows greater productivity. The amount of oil is 20 to 30% in the Neem seed[14,50]. Some of the physical properties, such as density and viscosity of Neem oil, are 929 kg.m-3 (at 15 °C) and 38,875 mm².s-1 (at 40 °C), respectively[42]. Nem oil mainly contains a large amount of unsaturated fatty acids, such as oleic acid (25 to 54%) and linoleic acid (6 to 16%) and saturated parts like stearic acid (9 to 24%)[51].

2.1.4 Linseed (Linum usitatissimum)

Linseed (*Linum usitatissimum* L.) belongs to *Linaceae* and is an annual dicotyledonous crop[52]. The main linseed producing countries are Argentina, India, Europe and Canada. Linseed is the seed of linen (*Linum usitatissimum*), belongs to the *Linaceae* family, from which linseed oil is extracted. Linseed oil is considered a drying oil and is frequently used in varnishes and paints[52]. Although linseed oil is edible, its use is very limited due to its strong odor and taste. Physical properties such as density and viscosity are 924 kg.m^{-3} (at 15 °C) and 26.24 mm^2.s^{-1} (at 40 °C), respectively[42]. It has a high composition of unsaturated fatty acids such as linolenic acid (46.10–51.12%), oleic acid (20.17–24.05%) and linoleic acid (13.29–14.93%) and saturated part contains palmitic acid (5.85–6.21%) and stearic acid (5.47-5.63%)[14,53].

2.1.5 Rubber seed (Hevea brasiliensis)

The rubber tree that is widely used as a natural source of rubber has reported that its seeds are rich in oil. Although there are variations in the oil content of seeds from different countries, the average oil yield has been reported to be 40%[54]. The main producer country of rubber seeds is Brazil and some other producing countries are Indonesia, Malaysia, Thailand and India. It belongs to the Euphorbia family. The rubber tree can reach a height of up to 34 m[55]. The growth of the rubber plant requires an environment without frost and rain. Its seeds have about 50 to 60% oil[14,56]. Physical properties such as density and viscosity of rubber seed oil are 917 kg.m^{-3} (at 15 °C) and 42.54 mm^2.s^{-1} (at 40 °C), respectively[42]. Rubber seed oil has a high amount of unsaturated fatty acids, such as linolenic acid (16.3%), linoleic acid (39.6%) and oleic acid (24.6%)[57].

2.1.6 Cotton seed (Gossypium)

Cotton (*Gossypium arboreum*) belongs to the *Malvaceae* family, or mallow. The seed contains oil seeds surrounded by a hard black outer shell that produces fibers and linters, 20-25% high quality proteins, carbohydrates and other constituents, such as vitamins, minerals, lecithin, sterols, etc. The oil has good lubricating properties and was reported by Ertugrul and Filiz[58] as being a good additive for lubricating oil. However, the refined oil is edible and the by-product is used for animal feed. The crude oil is black and is usually refined and bleached to remove impurities and the black color to produce marketable light yellow oil[59].

The main cotton producing countries are Europe, China and the United States. The main species of cotton plants are *Gossypium herbaceum* and *Gossypium hirsutum*, widely used in the production of cottonseed oil. Cotton plants can reach up to 1.2 m in height. This oil has a density in the range of 917 to 933 kg.m^{-3} (at 15 °C) and viscosity of 34.79 mm^2.s^{-1} (at 40 °C), respectively[42]. Cotton seeds contain oil contents in the range of 17 to 25%. Cottonseed oil has fatty acid, such as oleic from 19.2 to 23.26%, palmitic from 11.67 to 20.1% and linoleic acid from 55.2 to 55.5%[60].

2.1.7 Jojoba (Simmondsia chinensis)

Mexico, California, Arizona and India are the main producers of Jojoba plant. The jojoba plant belongs to the *Simmondsiaceae* family. The main product obtained from the Jojoba plant is the oil obtained from its seeds. The maximum height of the plant is 1 to 2 m. The leaf profile of the Jojoba plant is oval and has a width of approximately 1.5 to 3 cm, and is greyish green in color[14,61]. The density and viscosity value of Jojoba oil is 868 kg.m^{-3} (at 15 °C) and 24.89 mm^2.s^{-1} (at 40 °C), respectively[42]. The seeds of the Jojoba plant have about 40 to 50% oil, being in their composition linoleic fatty acids, about 25.2-34.4% and oleic acid with approximately 43.5-66% oil content Jojoba[62]. Unlike vegetable oils and animal fats, jojoba oil is not a triglyceride, but a mixture of chain esters (97-98% by weight) of fatty acids and alcohols, and is therefore more appropriately referred to as a wax[63].

2.1.8 Babassu (Orbignya sp.)

The babassu palm (*Orbignya* sp) belongs to the Arecaceae family. Its fruit consists of a fibrous outer part (epicarp), a fibrous-starch intermediate (mesocarp), and a woody inner part (endocarp), where the almonds are found[64]. Maranhão is the largest producer of babassu nut in Brazil. It is responsible for the production of almost 80% of the national production, corresponding to 120 thousand tons in the base year of 2005[64]. Babassu oil has a high percentage of saturated fatty acids, 91%, composed mainly of lauric acid (48%), myristic acid (16%), palmitic acid (10%), stearic acid (2%), and others (5 %). They also present 19% of unsaturated fatty acids, mainly oleic (14%) and linoleic acids (5%)[65].

2.1.9 Castor (Ricinus communis)

Extracts from castor oil seeds usually contain 40-55% oil, a very high potential compared to most other commonly used oilseeds (soy: 15-20% (w/w), sunflower: 25-35% (w/w), rapeseed: 38-46% (w/w) and palm: 30-60% (w/w))[66]. In addition, the cost of cultivation can be 50% less than the cost of cultivating rapeseed and 25% of the cost of cultivating jatropha. Moreover, castor beans are not suitable for human consumption, so the use as an energy source does not compete with food production.

Castor oil contains about 80-90% of branched fatty acids from ricinoleic acid and about 10% of unbranched fatty acids, mainly oleic and linoleic acids. Such a composition brings a disadvantage for its use in the production of biodiesel, since its viscosity is about 7 times higher than that of other vegetable oils[67]. To avoid this disadvantage, castor oil biodiesel, when mixed with petrodiesel, makes use of effective standards specifications[68]. It is the presence of the hydroxyl group (-OH) linked to the hydrocarbon chain in the ricinoleic acid of the castor oil molecule that makes castor oil chemically very different from other oils; especially its high viscosity and polarity making it extremely valuable for the industrial production of coatings, plastics and cosmetics[69,70].

2.2 Waste oil (vegetable and animal)

2.2.1 Waste cooking oil

The cooking oil residue is widely used to produce biodiesel due to its low cost and high availability[71]. The cooking oil residue is composed of TGs or glycerides that may contain animal fat or vegetable oil. Font de Mora et al.[72] classified the residue of cooking oil into yellow and brown grease, obtained from palm oil, canola, corn, sunflower and other oils used in food preparation. The cooking oil residue can also be classified based on the source from which it is collected, such as restaurants, coffee shops and homes. Alkali and acid-based catalysts can be used to produce biodiesel from waste[4,73].

Researchers recently focused their studies on optimizing biodiesel production using cooking oil waste as a basis for developing new catalysts. For example, Hamze et al.[74] evaluated the effects of catalyst load, reaction temperature and catalyst concentration on the molar ratio on the biodiesel yield produced from cooking oil residue. Maximum biodiesel yield (99.38% by weight) was obtained under ideal conditions of 1.4% (m/m) of catalyst, reaction temperature of 65 °C and 7.5:1 of the molar ratio of the concentration of the catalyst in relation to oil. However, the most important parameter was the concentration of the catalyst.

2.2.2 Soybean oil deodorization distillate

The deodorization distillate is a by-product formed in the last stage of the vegetable oil refining process. It consists of deodorizing the oil to remove compounds responsible for bad odor and taste. Due to the conditions used in the distillation process, the obtained distillate also contains sterols, tocopherols, squalene, free fatty acids, triglycerides, diglycerides, monoglycerides, and sterile esters[75]. This by-product is harmful to the environment when it cannot be used to benefit industrial activities[76]. Due to the high content of free fatty acids, this by-product becomes a potentially cheap raw material for the production of biodiesel. For example, Vilas-Bôas et al.[77] evaluated the effect of distillate from vegetable oil deodorization as a source of lipid raw material in biodiesel production, in which a maximum conversion of 88% was obtained under ideal conditions of 5% (w/w) of chemical catalyst, reaction temperature of 70 °C and a molar ratio of 45:1 alcohol/oil. However, there are few reports in the literature on the production of biodiesel using soy oil deodorization distillate as a raw material.

2.2.3 Animal tallow

In Brazil, animal tallow is considered the second-largest raw material after soy oil for the production of biodiesel[78]. In addition, tallow-derived biodiesel produces between 17% and 35% impact of diesel with low sulfur content, which can be considered an environmental advantage. Chavarria-Hernandez et al.[79]

showed that cattle and poultry FFA can be used as a potential low-cost source for biodiesel production in Mexico. Considering that animal fat can be used as a viable raw material for the production of biodiesel and is available on the international market at low prices, this will make biodiesel competitive with petro-diesel[4,80]. As reported by Sander et al.[81], biodiesel produced from animal fat sources met the standard specifications for biodiesel fuel in terms of free glycerin content.

Bolonio et al.[82] suggested that biodiesel from animal fat can be produced through a two-step process: 1) hydrolysis of raw animal fat into free fatty acids, and 2) reaction of free fatty acids with ethanol. Suwannapa and Tippayawong[83] used a two-step process for the production of biodiesel from beef tallow. The optimal conditions were: microwave irradiation time of 30 min, the molar ratio of oil to methanol of 1:12, H_2SO_4 loading at 1.35% in the first stage, followed by microwave irradiation time of 25 min, and in the second stage, a molar ratio of oil to methanol of 1:9 was used, and loading of NaOH to 0.62%, which resulted in 99% biodiesel yield. On the other hand, Punsuvon et al.[84] used biodiesel production in two stages by acid and alkaline esterifications and obtained 86.10% FAME yield under optimal conditions at a reaction temperature of 60 °C, using 2.40% sulfuric acid in methanol for a molar ratio of animal fat of 6:1 in a reaction time of 1.5 h.

2.2.4 Waste chicken fat

Residual chicken fat has been used as a source of raw material for the transesterification reaction for the production of biodiesel. The fat content in chicken is about 10% by weight, which is very high and its cost is low. Commercial chicken meat has been reported to have relatively high levels of polyunsaturated lipids compared to organic chicken[85]. The researchers reported that chicken fat constitutes about 25% to 35% saturated and 40% to 75% unsaturated fatty acids. Palmitic acid, together with stearic acid, linoleic acid, and oleic acid, is the main fatty acids in chicken fat[86,87].

Studies in the literature show that under optimal conditions in the molar ratio of methanol to FFA of 30:1, a quantity of solid catalyst of 25%, reaction temperature of 90 °C and reaction time of 3 h, a yield of 93.7% biodiesel[4,88]. According to a recent study by Abid et al.[89], a 97.5% biodiesel yield was obtained in a two-stage extraction of lipids from chicken skin under ideal conditions at a reaction temperature of 65 °C, a reaction time of 30 min, at a proportion 1:3 methanol to oil and 1% H_2SO_4.

2.2.5 Waste Fish Oil

Waste fish oil is another potential inedible source for the production of biodiesel. The fishing industry generates a large amount of waste and its indiscriminate disposal poses a threat to the environment[90]. In 2016, world fish production was around 171 million tons, of which 88% was destined for human consumption and the rest was used for non-food products[91]. Approximately 76 million tons of fish waste (heads, tails, fins, viscera, and skin) were generated that year. These residues form the fishing industry contain approximately 40% and 65% of oil, which can be converted into biodiesel by chemical catalysis[92,93].

Fadhil et al.[94] obtained in their studies a high biodiesel yield (96%) from residual fish oil, in which it was obtained from the transesterification of fish oil under the optimized condition of a 6:1 molar ratio (methanol in oil), 0.50% KOH (w/w), at 32 °C for 60 min of reaction. Otherwise, reports of a mixture of two inedible sources (castor and residual fish oil) were used for the production of

biodiesel[95]. In which obtained biodiesel with a yield of 95.20% in an optimum condition of 8:1 molar ratio of methanol to oil, 0.50% (w/w) KOH, 30 min reaction at a temperature of 32 °C, in which the mixing ratio of the two sources used was 50:50%.

2.2.6 Lard pork

Lard is a by-product of the pork industry with other limited uses and a low market price. Due to its high availability, the pork industry in Greece consumes around 120 M kg of pork[96], and in appropriate waste management schemes, an additional increase in production is expected. Lard is widely used as a raw material in the animal feed industry. However, the increased risk of animal disease has had a detrimental effect on the use and prices of this raw material of animal origin. Therefore, currently, the biodiesel industry has shown itself to be an alternative market for the use of this raw material, which also contributes to the sustainability of the use of biodiesel[97].

2.3 Algae oil

Micro and macroalgae are grown in natural and artificial environments, as need light, carbon dioxide, nutrients, and other inorganic substances to grow[98]. Better efficiency in the production of algae biomass was achieved through the cultivation of microalgae in an open and closed system in the treatment of wastewater[99]. After harvesting, algae can be used as an inedible source for biodiesel production[100]. Its lipid content (40-80% dry weight) is 15-300 times higher than in other cultures[175]. In general, the most significant advantages of producing biodiesel from microalgae are less land use and a high accumulation of TGs of 20 to 50%[4,101].

The transesterification process is the predominant method for commercially producing biodiesel from algae and this biodiesel can be mixed with petroleum diesel[102]. In addition, the production of biodiesel from algae using the transesterification method is more economical than biodiesel produced from vegetable oils and animal fats[103]. It is well documented that a wide range of microalgae species, such as *Chlorella minutissima*, *Chlorella vulgaris*, has been used for the production of biodiesel[104]. In addition, transesterification can reduce the viscosity of FAME for the production of biodiesel from algae[4,105].

In the extraction of oil from algae, pretreatment is one of the crucial steps to accelerate the lipid extraction process, which improves the lipid yield of algae. Pre-treatment methods include enzymatic hydrolysis, ultrasound, high-pressure homogenization, microwaves, ball bearing, and chemical methods, such as microwaves[106]. In the pretreatment stage, it involves cell disruption, drying, particle size reduction, followed by lipid extraction by different methods and removal of cellular debris and solvents. After pre-treatment, the drying step is carried out to reduce the water content in the algae and can be carried out using different methods such as solar or steam[4,107].

The most important step in the production of biodiesel from algae is the lipid extraction process. et Wang al.[108] studied the effects of liquid/solid ratio, acid concentration, and reaction temperature on lipid extraction. The results showed that the ideal condition is the use of formic acid of 5.57 g/g and HCl of 0.1 g/g, liquid/solid ratio of 10:1, and reaction temperature of 100 °C. The total lipid yield was 45.6%, while the FAME yield of *Chlorella prototecoides* was 85.8%[4]. Table 3 shows recent results on the production of biodiesel from different microalgae species.

Table 3. Recent results on the production of biodiesel from different species of algae[4].

Species	Pretreatment type	Catalyst type	CL (%)	T (°C)	RT (h)	MR	LC (mg L^{-1} d^{-1})	Yield (%)
Nannochloropsis oculata	Sonication and biphasic solvent	Heterogeneous nanocomposite of Mn-ZnO capped with poly ethylene glycol (PEG)	3.5	60	4	15:1	-	87.5
Lactuca	Ultrasound and autoclave	Waste clay doped with zinc oxide	8	55	0.8	9:1	-	97.43
Acutodesmus obliquus	Microwave	Immobilized *C. rugosa* lipase	15	50	8	3:1	57.03	95.36
Chlorella vulgaris	-	Calcium oxide (CaO) derived from chicken egg shell waste	1.39	70	3	10:1	-	92.03

* CL is catalyst loading. LC is lipid content. MR is molar ratio (alcohol/oil). RT is reaction time. T is temperature.

3. BIODIESEL PRODUCTION PROCESSES

Vegetable oils cannot be used in engines due to high viscosity, low volatility and the presence of unsaturation in the carbon chain[109]. To overcome these problems, several methodologies have been developed for the production of biodiesel. The most used methods: direct mixing (dilution), pyrolysis, micro-emulsion and transesterification[110]. Transesterification is the most common method for converting triglycerides to methyl or ethyl esters, as the conversion efficiency is greater when compared to other methods[111]. Researchers report in their studies that transesterification is highly suitable for low investment production[112].

3.1 Direct use and blending of oils

In the direct mixture (dilution), crude oil is mixed with diesel in a certain proportion, but problems such as high viscosity, high acidity, presence of free fatty acids and formation of dreg are seen as obstacles to use as fuel[113]. Therefore, the use of vegetable oils in diesel engines requires significant modifications, including changing the types of injectors, otherwise, the operating time will decrease, thus increasing maintenance costs due to increased wear and the risk of major engine failures[114].

3.2 Pyrolysis

Pyrolysis is also known as thermal cracking. The term pyrolysis refers to a chemical change due to the application of thermal energy in the presence of a catalyst and in the absence of air or nitrogen. The substrates used for the pyrolysis method in the production of biodiesel are vegetable oils, animal fats, fatty acids or fatty acid methyl esters. Singh and Singh[115] reported that the pyrolysis process is effective, simple and free pollution. It was also found that the cetane number of pyrolyzed vegetable oil or fat was lower than that of diesel. In addition, pyrolyzed vegetable oils have an acceptable amount of sulfur, carbon residues and pour point[116]. The pyrolysis process can be divided into three subclasses by operational condition: conventional pyrolysis, rapid pyrolysis, and instant pyrolysis, according to the reaction rate, residence time and heating rate. The main product of slow pyrolysis is solid coal, while the main products of fast and instant pyrolysis are biofuels or liquid fuels[117].

3.3 Microemulsification

The microemulsion method is widely used to improve the high viscosity, low liquidity and other disadvantages of biodiesel fuels[118]. Microemulsions involve a mixture of oils with emulsifying agents used, such as alcohol, mainly methanol, ethanol, propanol or butanol to form a microemulsion biodiesel fuel. The main obstacle associated with the use of microemulsions is the formation of carbon deposits in the engine and incomplete fuel[113]. The microemulsion method is activated by a simple and direct reduction in the viscosity of biodiesel. However, when the combustion engine or fuel produced by the microemulsion method for a long time, problems can occur, such as a composition of large amounts of carbon, incomplete fuel and increased lubricant viscosity[118].

3.4 Transesterification

Transesterification is a process catalyzed by exchanges the alkoxy group of an ester for alcohol like methanol or ethanol (acyl acceptor), thus converting triglycerides into methyl or ethyl esters and glycerol[119,120]. In addition to being one of the main approaches to the production of biodiesel because it is simple compared to other types of production methods as oil microemulsion, pyrolysis or catalytic cracking.

Rudolf Diesel, the diesel engine pioneer, conducted experiments with crude peanut oil in the diesel engine in the late 1890s. However, the use of crude vegetable oil in the diesel engine is considered too viscous for combustion, causing inconsistency during the ignition cycle that causes damage to the engine. Therefore, transesterification aims to reduce the viscosity of the fuel without changing the caloric value of the fuel generated[116,121].

In the transesterification process, a source of triglycerides, such as oil or fat, is used to react with methanol or ethanol in the presence of a catalyst. As mentioned before, the conversion consists of breaking the glycerides into a simpler form, thus forming the methyl or ethyl ester. In general, the glycerol produced is considered to be a by-product however, the glycerol can be refined to a greater purity due to its commercial value in the pharmaceutical, food and cosmetic industry[121,122].

4. CATALYTIC AND NON-CATALYTIC TRANSESTERIFICATION PROCESS

The type of catalyst used in transesterification changes is a critical element that affects biodiesel production. It can be chemical compounds, such as bases and/or enzymes, depending on the method (Table 4) used for the production of biodiesel[119]. The general process involves three consecutive and reversible steps that produce intermediate monoglyceride molecules[119,123] (Figure 3).
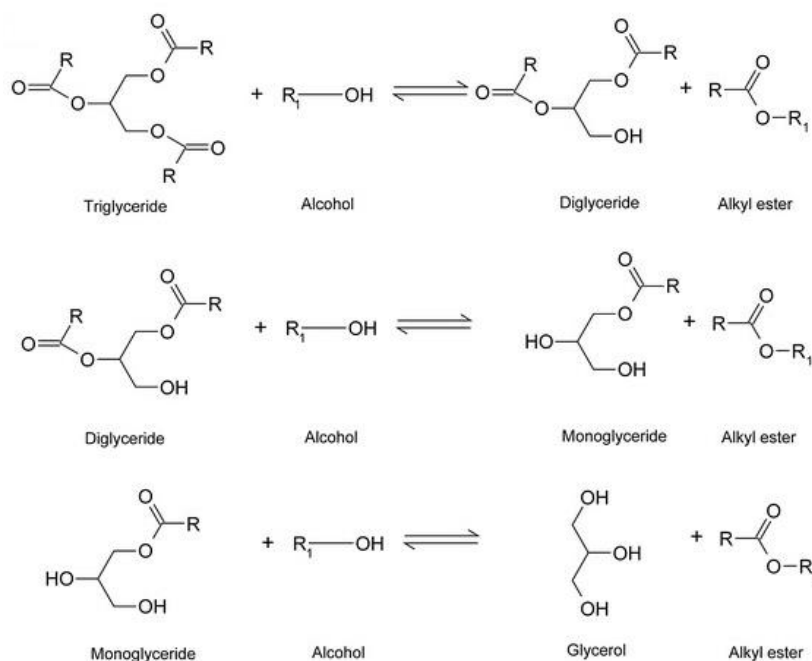

Figure 3. Step-by-step reactions for biodiesel production (R is a small alkyl group, R1, R2 and R3 are fatty acid chains)[152,180].

Table 4. Advantages and disadvantages at different types of catalysts used in the biodiesel production.

Type	Example	Advantages	Disadvantages	References
Alkali Homogeneous	NaOH, KOH	High catalytic activity, low cost, favorable kinetics, modest Preferred method for low-grade feedstock	Low FFA requirement, anhydrous conditions, saponification, emulsion formation, more wastewater from purification, disposable Hazardous for the environment compared to heterogeneous catalysts Hydroscopic nature (NaOH, KOH)	Leung et al. (2010); Ruhul et al. (2015); Norjannah et al. (2016)
Heterogeneous	CaO, $CaTiO_3$, $CaZrO_3$, $CaO–CeO_2$, $CaMnO_3$, $Ca_2Fe_2O_5$, KOH/Al_2O_3, KOH/NaY, Al_2O_3/KI, ETS-10 zeolite ZnO/I_2, ZrO_2/SO_4^{2-}, TiO_2/SO_4^{2-}, carbon-based solid acid catalyst, carbohydrate-derived catalyst, niobic acid, sulphated zirconia, Amberlyst-15, NafionNR50	Noncorrosive, environmentally benign, recyclable, fewer disposal problems, easily separation, higher selectivity, longer catalyst lifetimes Catalyze esterification and transesterification simultaneously, recyclable, eco-friendly	Low FFA requirement, anhydrous conditions, more wastewater from purification, high molar ratio of alcohol to oil requirement, high reaction temperature and pressure, diffusion limitations, high cost Low acid site concentrations, low microporosity, diffusion limitations, high cost	Leung et al. (2010); Norjannah et al. (2016)
Acid Homogeneous	Concentrated sulphuric acid	Catalyze esterification and transesterification simultaneously, avoid soap formation	Equipment corrosion, more waste from neutralization, difficult to recycle, higher reaction temperature, long reaction times, weak catalytic activity	Leung et al. (2010); Norjannah et al. (2016)
Non-catalyzed reaction	Supercritical alcohol	Super-fast reaction, high yield, can convert FFA, no catalyst, easy product purification, no waste	High temperature and pressure, high cost of reactor, high alcohol to oil molar ratio	Norjannah et al. (2016)
Enzymes	*Candida antarctica* fraction B lipase, *Rhizomucor mieher* lipase	Avoid soap formation, nonpolluting, easier purification Tolerate free fatty acids and water content High possibility to reuse and regenerate the catalyst	Expensive, denaturation Long process time due to very slow reaction rate	Leung et al. (2010); Ruhul et al. (2015); Norjannah et al. (2016)

4.1 Alkali based catalysts

The reaction catalyzed by homogeneous alkaline catalysts, using sodium hydroxide (NaOH) or potassium hydroxide (KOH): Among alkaline catalysts, potassium hydroxide and sodium hydroxide are the most investigated homogeneous basic catalysts for the transesterification of vegetable oils[124]. Sun et al.[125] reported the use of KOH as a catalyst to convert methyl alcohol and cotton oil into biodiesel. The conditions used were molar ratio 1:6 of alcohol/oil, the residence time of 6 min, reaction temperature of 60 °C and different concentrations of catalyst. It was concluded that an increase in the KOH concentration from 0.40% wt to 1% wt led to an increase in the conversion of methyl ester from 86% to 99.3%, but at concentrations above 1% wt of KOH the conversion decreased to 94.80%. This reduction in conversion was attributed to the saponification of the oil with an increase in the KOH concentration from 1.0 to 1.2 wt%. Similarly, the influence of the amount of catalyst was investigated in the transesterification of soybean oil with three different KOH concentrations of 0.6, 1.2 and 1.8% wt. The results obtained indicated that the percentage of methyl ester increased when the concentration of the catalyst increased from 0.6 to 1.2% wt, while a small decrease in the proportion of methyl ester was observed when using a KOH concentration of 1.8% wt[126]. In contrast, experiments carried out with a NaOH catalyst were conducted in different concentrations of NaOH from 0.25 to 1% wt in the transesterification of canola oil in a small column reactor. The residence time, methanol/oil molar ratio (6:1), temperature and reaction pressure were kept constant for each concentration of catalyst. The results showed that the use of higher concentrations of the catalyst obtained a higher conversion of triglycerides. However, in reactions with concentrations above 0.75%, there were insignificant differences in conversion[127]. However, some researchers suggest that homogeneous alkaline catalysts are suitable only for raw materials with a low content of free fatty acids (AGL)[128]. If the AGL content is greater than 6% wt, the basic catalyst is unsuitable for the synthesis of biodiesel. Thus, it is recommended that AGL content should be less than 2% wt[129]. In contrast, the homogeneous basic catalyst is slowly gaining popularity in the production of biodiesel for the following reasons[130]: a low reaction temperature is required to synthesize biodiesel at atmospheric pressure; high conversion of biodiesel may be possible under ideal conditions; widely available and economical; easy handling when compared to solid catalysts.

4.2 Acid catalysts

Several heterogeneous catalysts that are characterized as acid catalysts based on the concepts of Lewis and Bronsted, are being used for the transesterification of oils for the production of biodiesel[131]. Heterogeneous acid catalysts are considered less active when compared to basic heterogeneous catalysts, and normally, the reaction temperature required to complete the transesterification process is higher. However, there are several positive results compared to the basic heterogeneous catalyst. For example, it is capable of conducting esterification and transesterification simultaneously for oils with low cost and high content of AGL; can be easily separated from the product; eliminate the washing step of the final product; greater biodiesel conversion; requires a small amount of catalyst; it's easily regenerated and recycled[132,133]. While the use of a homogeneous acid catalyst during the transesterification process for the production of biodiesel requires additional processing downstream to remove residual inorganic components, causing a higher production cost[134].

4.3 Enzyme catalyzed

In enzyme-catalyzed reactions, the necessary raw materials are oil and acyl acceptor (usually alcohol) in the presence of an enzyme catalyst, usually a lipase. The advantages of using enzymes as a catalyst in the production of biodiesel are the high specificity of the enzyme towards the substrate, a wide range of substrate, complete catalysis of free fatty acids, high product quality, lower reaction temperatures, low alcohol/oil ratio and without saponification. However, the enzyme in biodiesel production is not widely used due to its high cost, low reaction rates, enzyme inhibition and loss of activity[33,135]. There are several factors that can affect the conversion of the biodiesel produced into enzymatic reactions. Factors include lipase specificity and efficiency, lipase immobilization, substrate fatty acid composition and types of acyl acceptor. In addition, operational conditions change from enzyme to enzyme to achieve the ideal activity such as enzyme quantity, temperature, reaction time, agitation and others[136].

4.4 Non-catalytic

Biodiesel can be produced by the transesterification reaction under supercritical conditions without using any catalyst. Reaction rates are high (50-95%) and advanced reactions can occur within the first 10 minutes[176]. However, reaction under supercritical conditions require high temperatures and pressures, approximately 250-400 °C and 12 psi, respectively[177]. For this reason, this type of reaction consumes more energy and increases the cost of production. In contrast, the supercritical conditions in the absence of catalysts offer some advantages, such as greater production efficiency, ecologically viable and availability of use of a wide variety of raw materials[137]. Supercritical in methanol, ethanol, propanol, and butanol have been shown to be the best procedures for the transesterification of triglycerides without the use of a catalyst[130,138].

5. PROCESS PARAMETERS FOR TRANSESTERIFICATION REACTION

5.1 Effect of molar ratio

The catalytic performance of a specific catalyst is used to determine the molar ratio between alcohol (methanol or ethanol) and oil (raw material) in the transesterification reaction[134]. In a process in which the transesterification reaction is reversible, the excessive amount of alcohol determines the formation of biodiesel. Consequently, the disproportionate use of alcohol during the biodiesel process is not recommended, as it can decrease the yield due to the dilution effect of the catalyst due to the insolubility of the alcohol in the oil and, therefore, wasting materials. In addition, in the recovery of unreacted alcohol at the end of the reaction, a greater amount of energy is required, thus increasing the cost of the process[12].

Amani et al.[133] reported a 90% conversion of biodiesel using a molar ratio of 20:1 (methanol/oil) and conversion 65% to a molar ratio of 30:1, drastically reducing the yield when there was an increase in the molar ratio. This study is compared with the results of Phan and Phan[139], where conversion 88% of biodiesel in the molar ratio of 8:1 (methanol/oil) was reported and followed by a reduction to 82% when the molar ratio was increased to 12:1 methanol/oil[12,139]. However, it can be concluded that among the reports that in a molar ratio between alcohol and oil, the use of excess alcohol is necessary, but the disproportionate use of alcohol during the process can also decrease the conversion, in addition to the waste of reagents and increasing the cost of the process.

5.2 Effect of catalyst concentration

The concentration of catalysts has a direct connection to the production of biodiesel. It is understood that the conversion of biodiesel generally increases with the concentration of the catalyst, but after an optimum value, the conversion can decrease or remain constant with the additional increase of the catalyst[140]. In previous studies, Meher et al.[141] investigated the effect of the concentration of basic homogeneous catalyst (KOH) using concentrations of 0.25%, 0.5%, 0.75%, 1.25% and 1.5% in the following reaction conditions, such as temperature 65 °C, molar ratio of 6:1 M under agitation of 600 rpm. The conversion obtained in 2h of reaction using 0.25% of catalyst was about 55%. However, when there was an increase in the concentration of the catalyst, consequently there was also an increase in the conversion of biodiesel. However, at concentrations greater

than 1% of catalyst, there was a decrease in conversion where it was concluded that the best conversion was in the use of 1% KOH where a conversion of 96% was obtained in 2 h. Other similar reports were also obtained by Meher et al.[142] with results obtained in 97% conversion of biodiesel using 1% KOH in 3 h of reaction.

5.3 Effect of temperature

The temperature considerably influences the reaction and conversion in the production of biodiesel. At higher reaction temperature, the viscosity of the oils may decrease. This results in a higher reaction rate and a reduction in reaction time[143]. During the starting of the reaction, the process normally retard due to the mingling and distribution of methanol with high viscosity oil. The reaction temperature normally depends on the type of alcohol used and the temperature is maintained below the boiling point of alcohol to maintain the alcohol level constant in the reaction flask[144]. However, Leung and Guo[145] investigated that when the reaction temperature increases beyond the ideal level, the biodiesel conversion decreases because a higher reaction temperature can accelerate the saponification reaction of the triglycerides. The reaction temperature must be lower than the boiling point of the alcohol, in order to ensure that the alcohol does not vaporize. Depending on the oil used, the ideal temperature ranges from 50 °C to 60 °C[146].

5.4 Stirrer Speed

The mixture of reagents is very important to reach the conclusion of the transesterification reaction and, consequently, it will increase the yield of the product[147,148]. Therefore, in addition to agitation increasing the collision between the particles and the diffusion of one reagent into another, it will also increase the complete mixture of the catalyst with reagents causing a higher reaction rate. In addition, increasing the agitator speed will decrease the reaction time[149] and increase the conversion[150]. In that case, it is necessary to optimize the agitator speed according to the different types of raw materials based on their physical properties. When using an enzymatic catalyst or heterogeneous catalyst, the reagents must diffuse from the liquid to the surface of the catalyst and also to the internal surface of the catalyst[147]. Kumari et al.[151] found that there is an increase in conversion, increasing the agitator speed from 100 to 200 rpm. But at 250 rpm, there was no significant increase in conversion due to shear in the enzyme molecules. Therefore, it was suggested that 200 rpm was the ideal speed for biodiesel production by an enzymatic reaction.

6. INFLUENCE OF FEEDSTOCK COMPOSITION ON BIODIESEL QUALITY

Biodiesel can be used as a substitute for diesel due to its similar properties. In addition, biodiesel emits less toxic gases, is renewable, biodegradable, non-toxic, has good lubricity, and is free of sulfur and aromatics. As a disadvantage, it has an increase in nitrogen oxide emissions, probably due to the higher temperature reached inside the combustion chamber compared to traditional diesel[152]. Since it is produced from renewable and sustainable raw materials, the quality and profile of biodiesel fatty acids are largely dependent on the nature of the raw material. Each raw material has a different chemical composition; therefore, when the raw material changes, the properties of the biodiesel produced also change. Therefore, the biodiesel produced must be characterized by the raw material used, which must satisfy the ranges defined for fuel properties by ASTM and EN before its commercialization[153,154]. Some of the important biodiesel properties that are directly influenced by biodiesel composition have low-temperature operability, storage and oxidative stability, energy content, cetane number, viscosity, and exhaust emission[132].

Low temperature operability is determined based on three parameters such cloud point, pour point, and cold filter plugging point. Cloud point refers to the minimum temperature at which enough crystals (0.5 μm ≤ diameter) appear so that they are visible to the naked eye, and if the temperature is further reduced, these crystals agglomerate and hinder the free pouring of biodiesel known as pour point. The length and degree of unsaturation of the carbonic chains of fatty acids present in the raw material largely influence the low-temperature property of biodiesel. In the case of excessive saturated compounds, it has bad properties at low temperatures. While, in unsaturated compounds with the same length of the carbon chain and in excess, biodiesel obtains better low-temperature properties[132,155].

Regarding the oxidative stability property, it is one of the valuable factors that help in the assessment of the quality of biodiesel. Oxidative stability is a measurement indication in relation to oxidation, caused by reactivity with air and also serves as an indication for the use of antioxidants[156]. Oxidation occurs because of the presence of chains of unsaturated fatty acids and the double bond in a molecule, which reacts immediately with oxygen in the air after exposure[157]. The chemical composition of biodiesel makes it more susceptible to oxidative degradation than the degradation of fossil diesel. The Rancimat method (EN ISO 14 112) is the oxidative stability specification in ASTM D6751 and EN 14 214[9].

Another property that is influenced by the composition of biodiesel is the energy content, also known as the heat of combustion, and is the amount of thermal energy released when a specific amount of fuel is burned. It is measured according to the standard method of ASTM D240. The energy content of a fuel is largely dependent on its chemical composition, and biodiesel produced from biomass has less energy content compared to fossil diesel. Pure fossil diesel with mixtures of biodiesel such as B20 and B100 were tested, and the results obtained were 46.7, 43.8, and 38.1 MJ.kg^{-1}[65]. The lower energy content in biodiesel can be attributed to the fact that it contains oxygenated compounds. In addition, FAME saturation and unsaturation also affect the energy content of biodiesel. As the degree of unsaturation increases, the energy from biodiesel decreases. On the other hand, longer chains of saturated compounds have higher energy content. Thus, the energy content reflects its dependence on the composition of biodiesel, which in turn varies from raw material to raw material[132].

On the other hand, the cetane number (CN) is known as an ignition signal or the ability to self-ignite quickly after fuel is injected. Ignition quality is always associated with a higher CN value[66]. For the use of biodiesel, CN is one of the most important parameters considered during the selection procedure of methyl esters[158]. CN increases with increasing fatty acid chain length and increased saturation. A higher CN represents the shortest time between ignition and the start of fuel injection in the engine's combustion chamber[9,159]. Biodiesel has a higher CN than conventional petroleum diesel oil, which indicates greater combustion efficiency.

Due to the high value of the kinematic viscosity of vegetable oils and animal fats, they are processed through the transesterification reaction to produce biodiesel. The result is biodiesel with lower viscosity, an important factor for the injection of the engine[9]. Therefore, viscosity describes the flow capacity of fuel. This characteristic plays an important role in the operation of fuel injection and spray atomization equipment, especially at low temperatures, in which case the increase in viscosity affects the fluidity of the fuel. The viscosity of biodiesel is 10-15 times greater than diesel derived from fossil fuels. This occurs because it has a great chemical structure, and consequently a great molecular weight[66]. At low temperatures, biodiesel becomes highly viscous or can even solidify. The high viscosity of biodiesel can affect the volume flow and the characteristics of the injection spray on the engine. It can also compromise the mechanical integrity of the injection pump drive system. The maximum acceptable viscosity limit according to ASTM D445 is 1.9-6.0 mm^2.s^{-1} and 3.5-5.0 mm^2.s^{-1} according to EN ISO 3104[9,160].

Exhaust the engine after the combustion of the fuel is another important aspect and depends on the type and composition of the fuel being burned. Engine emission involves NOx nitrogen oxides, HC hydrocarbons, PM particulate matter, and COx carbon oxides. When burning biodiesel, PM, HC, and CO are reduced by 48%, 77% and 48%, respectively, but NOx increases by 12%. NOx emissions are dangerous for the environment, especially in sensitive areas such as public parks and urban centers[161]. Therefore, the chemical composition of biodiesel influences NOx emission; there are reports that, by decreasing the length of the ester chain or increasing the number of double bonds in the carbon chain, NOx emission is increased[162]. Thus, the composition of the raw material has a great influence on the emission of exhaust gases. In general, it can be concluded that the quality of biodiesel depends on the type and characterization of the raw material[132].

7. INFLUENCE OF FREE FATTY ACIDS ON BIODIESEL PRODUCTION

In order to reduce the cost of biodiesel, low-quality residues or oils/fats that are cheap and readily available can be used as a raw material. However, the challenge of using this cheap raw material is the presence of impurities, such as water and free fatty acids (FFA), which are common components in residual oils/fats[163]. Therefore, the quality of the raw material determines mainly the type of catalyst or process that is required to produce biodiesel that meets the biodiesel standards established by ASTM D6751 or EN 14214. If the raw material contains a significant percentage of FFA (> 3 wt.%), the use of typical homogeneous alkaline-based catalysts, such as sodium or potassium hydroxide will not be effective, that is, it will obtain results from an unwanted, in which the catalyst reacts with FFA to form soap (sodium salt of fatty acid) and water, thus irreversibly extinguishing the catalyst and resulting in an undesirable mixture of FFA, unreacted TAG, soap, DAG, MAF, biodiesel, glycerol, and water[2,128]. In fact, base-catalyzed transesterification will not occur or be significantly delayed if the FFA content of the raw material is 3 wt.% or more[164]. For example, biodiesel yield is obtained with homogeneous alkaline-based catalysts in cases where the FFA content of the raw material is 0.5 wt.% or less[165]. Another complex factor with a high content of FFA present in the raw material is the production of water after the reaction with homogeneous alkaline-based catalysts. Water is particularly problematic because, in the presence of any remaining catalyst, it can participate in the hydrolysis of biodiesel to produce additional FFA and alcohol[2].

A common approach in cases where the FFA content of raw material is above 1 wt.% is to perform a pre-esterification of the raw material using mineral acid as a catalyst to decrease the FFA content. In which, the FFA are esterified to FAME under established temperature, excess of methanol, and the addition of sulfuric acid as a catalyst[166]. After the reduction of FFA content, the pre-esterified is followed by a transesterification reaction in the presence of homogeneous alkaline-based catalysts to produce biodiesel. The two-step procedure promptly allows the use of low-cost raw materials with high FFA content for the production of biodiesel[148].

Despite the additional costs associated with the production of the integrated two-stage system, the process is being increasingly applied to produce biodiesel from low-cost raw materials with high FFA content with good results[128]. Table 5 shows some examples of biodiesel produced from raw materials with high FFA content. Other potential strategies for the production of biodiesel from raw materials with a high content of FFA include purification of raw materials, such as refining, bleaching, and deodorization to remove FFA and other undesirable compounds, when present[167]. However, refining the raw material increases production costs, such as the demand for equipment, time, and necessary manpower[2].

Table 5. Examples of biodiesel production from feedstocks high in free fatty acids (FFA)[2].

Feedstock	FFA (wt %)	Pretreatment method	Catalyst for transesterification	Yield (wt %)
Pongamia pinnata	Up to 20	H_2SO_4	KOH	97
Jatropha curcas	14/<1	H_2SO_4	KOH	99
Nicotiana tabacum	35/<2	H_2SO_4	KOH	91
Hevea brasiliensis	17/<2	H_2SO_4	NaOH	N.R. b
Heterotrophic microalgal	8.97a	None	H_2SO_4	N.R. b
Acid oil	59.3	None	H_2SO_4	95
Waste cooking oil	7.25/<1a	H_2SO_4	NaOH	90 c

a Acid value (mg KOH/g) was given instead of FFA. In cases where two values are given, the first value is prior to pretreatment and the second is after.
b Not reported.
c Conversion to esters (wt %) is provided instead of yield.

8. ADVANTAGES AND DISADVANTAGES OF BIODIESEL

Biodiesel is the only alternative fuel with a low concentration property to mixtures of biofuels. In addition to being able to be produced from renewable seed plantations, such as soy, rapeseed, and sunflower. The risks of handling, transporting, and storing biodiesel are low to those associated with petroleum diesel. That is, biodiesel is safe to be handled and transported because it is biodegradable and has a high flash point compared to petroleum diesel. Biodiesel can be used alone or mixed in different proportions with petroleum diesel. The most common blend is a blend of 20% biodiesel with 80% petroleum diesel, also known as B20 in recent scientific research. However, future commercial

applications in Europe provide for a maximum increase of 5.75% in biodiesel[160,168].

Biodiesel still provides significant reductions in particulate and carbon monoxide emissions compared to petroleum diesel oil. Therefore, biodiesel is an ecological fuel with low levels of unwanted emissions and is therefore considered environmentally useful. Using biodiesel as an alternative fuel is a way of minimizing global air pollution and, in particular, reducing the levels of potential or probable carcinogens[160,169]. Biodegradable fuels such as biodiesel have an increasing potential application and are environmentally friendly. Biodiesel is non-toxic and degrades about four times faster than petroleum diesel[170]. Biodiesel also has good lubricating properties compared to petroleum diesel oil. This is very important to reduce wear on the engine and the injection system[171]. As a result, the use of biodiesel can extend the service life of diesel engines.

On the other hand, there are some disadvantages to using biodiesel as a substitute for petroleum diesel. The first disadvantage would be in slightly higher fuel consumption due to the lower calorific value of biodiesel. Nitrous oxide (NOx) emissions are also slightly higher than diesel fuel. The freezing point is higher than that of diesel fuel, and this can be inconvenient in cold climates. In addition, biodiesel is less stable than diesel oil and therefore long-term storage (more than six months) of biodiesel is not recommended. It should be noted that these disadvantages are significantly reduced when biodiesel is used in mixtures with diesel oil[172].

CONCLUSION AND FUTURE SCOPE

The wide range of raw materials available for biodiesel production represents one of the most important advantages of biodiesel production. Selecting the best raw material is vital to ensure low cost in the production of biodiesel. In addition, non-edible raw materials, such as Jatropha oil, microalgae oil, and cooking oil residues are considered promising and sustainable for the production of biodiesel, yet, it does not compete with food and agriculture. Biodiesel is produced from oil using different techniques, that is, direct use and blending of oils, pyrolysis, micro emulsification, transesterification, etc. Among these conversion techniques, transesterification is the most economical and the biodiesel produced from this technique has properties comparable to diesel oil. The present review summarizes that the energy demand of the future cannot be met by a single source of raw material; a mixture of different sources of raw materials will be preferred for the production of biodiesel. In future research, they should focus on the identification of non-edible raw materials for the production of high-yield biodiesel. There are ample research opportunities available in the area of reducing the cost of producing biodiesel without affecting fuel quality. Improvement in photon to fuel conversion efficiency (PFCE) for biodiesel production will be the main area of future work[14].

ACKNOWLEDGMENT

REFERENCES

1. I. Ambat, V. Srivastava, M. Sillanpää, *Renew Sustain Energy Rev*. 90, 356-369, (2018).
2. B. R. Moser *Biodiesel production, properties, and feedstocks*. In: Biofuels. Springer, New York, 2011.
3. M. Rehan, J. Gardy, A. Demirbas, U. Rashid, W. M. Budzianowski, D. Pant, *Bioresour. Technol.* 250, 17–25, (2018).
4. S. Rezania, B. Oryani, J. Park, B. Hashemi, K. K. Yadav, E. E. Kwon, J. Hur, J. Cho, *Energy Convers Manag*. 201, 112155, (2019).
5. I. S. A. Manaf, N. H. Embong, S. N. M. Khazaai, M. H. A. Rahim, M. M. Yusoff, K. T. Lee, *Energy Convers Manag*. 185, 508–17, (2019).
6. M. R. Monteiro, C. L. Kugelmeier, R. S. Pinheiro, M. O. Batalha, A. Da Silva, A. César, *Renew Sustain. Energy Ver.* 88, 109-122, (2018).
7. A. Demirbas, *Energy Convers Manag.* 4(15-16), 2271-2282, (2006).
8. K. T. Tan, K. T. Lee, A. R. Mohamed, *J. Supercrit. Fluids* 53(1-3), 88-91, (2010).
9. V. K. Mishra, R. Goswami, *Biofuels* 9(2), 273-289, (2017).
10. X. Meng, G. Chen, Y. Wang, *Fuel Process Technol*. 89(9), 851-857, (2008).
11. C. Dalla Rosa, M. B. Morandim, J. L. Ninow, D. Oliveira, H. Treichel, J. V. Oliveira, *J. Supercrit. Fluids* 47(1), 49-53, (2008).
12. N. Mansir, Y. H. Taufiq-Yap, U. Rashid, I. M. Lokman, *Energy Convers. Manag.* 141, 171-182, (2017).
13. A. H. West, D. Posarac, N. Ellis, *Plant. Bioresour. Technol.* 99(14), 6587-6601, (2008).
14. D. Singh, D. Sharma, S. L. Soni, S. Sharma, P. K. Sharma, A. Jhalani, *Fuel* 262, 116553, (2020).
15. P. Verma, M. P. Sharma, *Renew Sustain. Energy Rev.* 62, 1063-1071, (2016).
16. N. Kumar, K. V. Anand, M. P. Reddy, *Acta Physiol. Plant.* 32(5), 917-924, (2010).
17. R. Anr, A. A. Saleh, M. S. Islam, S. Hamdan, M. A. Maleque, *Energy Fuels* 30(1), 334-343, (2016).
18. M. R. Uddin, K. Ferdous, S. K. Mondal, M. R. Khan, M. A. Islam, *Oil. Chem. Eng. J.* 29(1), 24-28, (2017).
19. B. Gurunathan, A. Ravi, *Bioresour. Technol.* 190, 424-428, (2015).
20. A. Demirbas, *Biomass Bioenergy.* 33(1), 113-118, (2009).
21. A. Arumugam, D. Thulasidharan, G. B. Jegadeesan, *Renew Energy* 116, 755-761, (2018).
22. M. Mourshed, S. K. Ghosh, M. W. Islam, *Int. J. Ambient. Energy* 1-11, (2020).
23. G. Sarojini, P. Kannan, G. Pravin, *J. Environ. Biol.* 40(4), 802-806, (2019).
24. K. S. Moreira, L. S. Moura Júnior, R. R. Monteiro, A. L. De Oliveira, C. P. Valle, T. M. Freire, J. Dos Santos, *Catalysts* 10(4), 414, (2020).
25. F. Halek, A. Delavari, A. Kavousi-rahim, *Clean Technol. Environ. Policy*, 15(6), 1063-1068, (2013).
26. R. Yahyaee, B. Ghobadian, G. Najafi, *Renew. Sust. Energ. Rev.* 17, 312-319, (2013).
27. X. Yin, X. Duan, Q. You, C. Dai, Z. Tan, X. Zhu, *Energy Convers. Manag.* 112, 199-207, (2016).
28. F. Toldrá-Reig, L. Mora, F. Toldrá, *Appl. Sci.* 10(10), 3644, (2020).
29. J. Abraham, R. S. Kumar, F. Xavier, D. Mathew, *Int. Agric. Eng. J.* 9(12), 1190-1193, (2015).
30. D. Papargyriou, E. Broumidis, M. De Vere-Tucker, S. Gavrielides, P. Hilditch, J. T. Irvine, A. D. Bonaccorso, *Renew. Energy* 139, 661-669, (2019).
31. I. Lawan, Z. N. Garba, W. Zhou, M. Zhang, Z. Yuan, *Renew. Energy* 145, 2550-2560, (2020).
32. R. C. Rodrigues, G. Volpato, M. A. Z. Ayub, K. Wada, *J. Chem. Technol. Biotechnol.* 83(6), 849-854, (2008).
33. B. Norjannah, H. C. Ong, H. H. Masjuki, J. C. Juan, W. T. Chong, *RSC Adv.* 6(65), 60034-60055, (2016).
34. G. Knothe, *Fuel Process. Technol.* 86(10), 1059-1070, (2005).
35. M. Takase, T. Zhao, M. Zhang, Y. Chen, H. Liu, L. Yang, X. Wu, *Renew. Sustain. Energy Rev.* 43, 495-520, (2015).
36. M. Anwar, M. G. Rasul, N. Ashwath, M. N. Nabi, *Energy Rep.* 5, 280-297, (2019).
37. V. B. Veljković, M. O. Biberdžić, I. B. Banković-Ilić, I. G. Djalović, M. B. Tasić, Z. B. Nježić, O. S. Stamenković, *Renew. Sustain. Energy Rev.* 91, 531-548, (2018).
38. H. C. Ong, A. Silitonga, H. Masjuki, T. Mahlia, W. Chong, M. Boosroh, *Energy Convers. Manag.* 73, 245–255, (2013).
39. O. Kibazohi, R. S. Sangwan, *Biomass Bioenergy.* 35, 1352–1356, (2011).
40. W. M. J. Achten, L. Verchot, Y. J. Franken, E. Mathijs, V. P. Singh, R. Aerts, *Biomass Bioenergy.* 32, 1063–1084, (2008).
41. K. Openshaw, *Biomass Bioenerg.* 19, 1–15, (2000).
42. D. Singh, D. Sharma, S. L. Soni, S. Sharma, D. Kumari, *Fuel* 253, 60–71, (2019).
43. I. Reksowardojo, I. Lubis, W. Manggala, T. Brodjonegoro, T. Soerawidjaja, W. Arismunandar, *Training* 2007, 11–19, (2013).
44. S. Thapa, N. Indrawan, P. R. Bhoi, *Environ. Technol. Innov.* 9, 210-219, (2018).
45. M. A. Kalam, J. U. Ahamed, H. H. Masjuki, *Renew. Sustain. Energy Rev.* 16(6), 3999-4007, (2012).
46. M. J. Salar-García, V. M. Ortiz-Martínez, P. Olivares-Carrillo, J. Quesada-Medina, A. P. De Los Ríos, F. J. Hernández-Fernández, *J. Supercrit. Fluids* 112, 1-6, (2016).
47. S. K. Karmee, A. Chadha, *Bioresour. Technol.* 96, 1425–1429, (2005).
48. S. Bajpai, P. K. Sahoo, L. M. Das, *Fuel* 88, 705–711, (2009).
49. R. L. Patel, C. D. Sankhavara, *Renew. Sustain. Energy Rev.* 71, 464-474, (2017).
50. M. I. Al-Widyan, M. Al-Muhtaseb, *Energy Convers. Manag.* 51, 1702–1707, (2010).

51. M. H. Ali, M. Mashud, M. R. Rubel, R. H. Ahmad, *Proc. Eng.* 2056, 625–30, (2013).
52. F. Ullah, A. Bano, S. Ali, *Pol. J. Chem. Technol.* 15(1), 74-77, (2013).
53. S. Dixit, A. Rehman, *Renew. Sustain. Energy Rev.* 16, 4415–4421, (2012).
54. O. E. Ikwuagwu, I. C. Ononogbu, O. U. Njoku, *Ind. Crops. Prod.* 12(1), 57-62, (2000).
55. J. Ahmad, S. Yusup, A. Bokhari, R. N. M. Kamil, *Energy Convers. Manag.* 78, 266–275, (2014).
56. N. Usta, B. Aydoğan, A. Con, E. Uğuzdoğan, S. Ozkal, *Energy Convers. Manag.* 52, 2031–2039, (2011).
57. W. N. Ghazali, R. Mamat, H. H. Masjuki, G. Naja, *Renew. Sustain. Energy Rev.* 51, 585–602, (2015).
58. D. Ertugrul, K. Filiz, *Energ. Source* 26(7), 611-625, (2004).
59. E. I. Bello, A. A. Aladesuru, *Sci. Agric.* 11(1), 1-7, (2015).
60. C. Ilkilic, H. Yucesu, *Energy Sour.* 30, 742–53, (2008).
61. M. Y. E. Selim, M. S. Radwan, S. M. S. Elfeky, *Renew. Energy* 28, 1401–1420, (2003).
62. A. Kumar, S. Sharma, *Renew. Sustain. Energy Rev.* 15, 1791–1800, (2011).
63. L. Canoira, R. Alcantara, M. J. García-Martínez, J. Carrasco, *Biomass Bioenergy* 30(1), 76-81, (2006).
64. M. G. S. Da Silva, K. J. N. Ferreira, M. M. Teixeira, F. C. Silva, A. P. Maciel, *Rev. Univ. Vale Rio Verde* 12(2), 434-443, (2014).
65. J. S. Oliveira, R. Montalvao, L. Daher, P. A. Suarez, J. C. Rubim, *Talanta* 69(5), 1278-1284, (2006).
66. A. E. Atabani, A. S. Silitonga, I. A. Badruddin, T. M. I. Mahlia, H. H. Masjuki, S. Mekhilef, *Renew. Sustain. Energy Rev.* 16(4), 2070-2093, (2012).
67. I. B. Banković-Ilić, O. S. Stamenković, V. B. Veljković, *Renew. Sustain. Energy Rev.* 16(6), 3621-3647, (2012).
68. G. Knothe, S. C. Cermak, R. L. Evangelista, *Fuel* 96, 535-540, (2012).
69. S. T. Keera, S. M. El Sabagh, A. R. Taman, *Egypt. J. Pet.* 27(4), 979-984, (2018).
70. D. Da Costa Barbosa, T. M. Serra, S. M. P. Meneghetti, M. R. Meneghetti, *Fuel* 89(12), 3791-3794, (2010).
71. A. Talebian-Kiakalaieh, N. A. S. Amin, H. Mazaheri, *Appl. Energy* 104, 683–710, (2013).
72. E. F. Mora, C. Torres, A. Valero, *Sustainability* 7(5), 6321-6335, (2015).
73. S. E. Mahesh, A. Ramanathan, K. M. M. S. Begum, A. Narayanan, *Energy Convers. Manag.* 91, 442–450, (2015).
74. H. Hamze, M. Akia, F. Yazdani, *Process. Saf. Environ. Prot.* 94, 1–10, (2015).
75. A. R. S. Teixeira, J. L. C. Santos, J. G. Crespo, *Ind. Eng. Chem. Res.* 50, 2865-2875, (2011).
76. R. Piloto-Rodríguez, E. A. Melo, L. Goyos-Pérez, S. Verhelst, *Braz. J. Chem. Eng.* 31(2), 287-301, (2014).
77. R. N. Vilas-Bôas, L. L. Da Silva, L. D. Fernandes, B. L. Augusto, M. F. Mendes, *Catal. Lett.* 150, 3642–3652, (2020).
78. V. M. Sousa, S. M. Luz, A. Caldeira-Pires, F. S. Machado, C. M. Silveira, *Int. J. Life Cycle Assess.* 22(11), 1837-1850, (2017).
79. J. Chavarria-Hernandez, L. Ordóñez, L. F. Barahona-Pérez, M. Castro-Gomez, S. Paredes-Cervantes, *J. Chem. Technol. Biotechnol.* 92(5), 899-905, (2017).
80. S. M. S. Ardebili, A. Khademalrasoul, *J. Clean. Prod.* 204, 819-831, (2018).
81. A. Sander, M. A. Košćak, D. Kosir, N. Milosavljević, J. P. Vuković, L. Magić, *Renew. Energy* 118, 752-760, (2018).
82. D. Bolonio, P. Marco Neu, S. Schober, M. J. García-Martínez, M. Mittelbach, L. Canoira, *Energy Fuels* 32(1), 490-496, (2018).
83. P. Suwannapa, N. Tippayawong, *Chem. Eng. Commun.* 204(5), 618-624, (2017).
84. V. Punsuvon, R. Nokkaew, P. Somkliang, M. Tapanwong, S. Karnasuta, *Energ. Source* 37(8), 846-853, (2015).
85. M. Gürü, A. Koca, O. Can, C. Çınar, F. Sahin, *Renew. Energy* 35, 637–643, (2010).
86. F. Shafiq, M. W. Mumtaz, H. Mukhtar, T. Touqeer, S. A. Raza, U. Rashid, T. S. Y. Choong, *Catalysts* 10(6), 633, (2020).
87. S. Gugule, F. Fatimah, Y. Rampoh, *Anim. Prod.* 13, 115–121, (2011).
88. A. S. Rad, M. H. Nia, F. Ardestani, H. Nayebzadeh, *Waste Biomass Valorization* 9(4), 591-599, (2018).
89. M. Abid, A. Touzani, R. Benhima, *Int. J. Sustain. Eng.* 12(4), 272-280, (2019).
90. D. Castañeda, J. M. Lozano, H. Suárez, *Agron. Colomb.* 34(3), 403-414, (2016).
91. FAO, *Food and Agriculture Organization*. Available: http://www.fao.org. Acess in: January of 2018.
92. J. Ching-Velasquez, R. Fernández-Lafuente, R. C. Rodrigues, V. Plata, A. Rosales-Quintero, B. Torrestiana-Sánchez, V. G. Tacias-Pascacio, *Renew. Energy* 153, 1346-1354, (2020).
93. A. Wisniewski Jr, V. R. Wiggers, E. L. Simionatto, H. F. Meier, A. A. C. Barros, L. A. S. Madureira, *Fuel* 89(3), 563-568, (2010).
94. A. B. Fadhil, L. H. Ali, *Renew. Energy* 60, 481-488, (2013).
95. A. B. Fadhil, E. T. Al-Tikrity, M. A. Albadree, *Fuel* 210, 721-728, (2017).
96. GMRDF *Greek Ministry of Rural Development and Food. Statistics of agricultural policy*, in Greece, 2014
97. I. Sarantopoulos, E. Chatzisymeon, S. Foteinis, T. Tsoutsos, *Energy Sustain. Dev.* 23, 110-114, (2014).
98. Y. Zhao, J. Wang, H. Zhang, C. Yan, Y. Zhang, *Bioresour. Technol.* 136, 461–468, (2013).
99. E. S. Salama, M. B. Kurade, R. A. I. Abou-Shanab, M. M. El-Dalatony, I. S. Yang, B. Min, *Renew. Sustain. Energy Rev.* 79, 1189–1211, (2017).
100. S. Dickinson, M. Mientus, D. Frey, A. Amini-Hajibashi, S. Ozturk, F. Shaikh, *Clean. Technol. Environ. Policy* 19, 637–668, (2017).
101. H. M. Amaro, A. C. Guedes, F. X. Malcata, *Appl. Energy* 88, 3402–3410, (2011).
102. G. Huang, F. Chen, D. Wei, X. Zhang, G. Chen, *Appl. Energy* 87, 38–46, (2010).
103. M. Faried, M. Samer, E. Abdelsalam, R. S. Yousef, Y. A. Attia, A. S. Ali, *Renew. Sustain. Energy Rev.* 79, 893–913, (2017).
104. T. Suganya, M. Varman, H. H. Masjuki, S. Renganathan, *Renew. Sustain. Energy Rev.* 55, 909–941, (2016).
105. H. B. Bucy, M. E. Baumgardner, A. J. Marchese, *Algal. Res.* 1, 57–69, (2012).
106. A. Steriti, R. Rossi, A. Concas, G. Cao, *Bioresour. Technol.* 164, 70–77, (2014).
107. M. L. Menegazzo, G. G. Fonseca, *Renew. Sustain. Energy Rev.* 107, 87–107, (2019).
108. S. Wang, J. Zhu, L. Dai, X. Zhao, D. Liu, W. Du, *Energy* 115, 963–968, (2016).
109. V. K. Mishra, R. Goswami, *Biofuels*, 9(2), 273-289, (2018).
110. G. Baskar, R. Aiswarya, *Renew. Sustain. Energy Rev.* 57, 496-504, (2016).
111. J. C. Juan, D. A. Kartika, T. Y. Wu, T. Y. Y. Hin, *Bioresour. Technol.* 102(2), 452-460, (2011).
112. L. Lin, Z. Cunshan, S. Vittayapadung, S. Xiangqian, D. Mingdong, *Appl. Energy* 88(4), 1020-1031, (2011).
113. P. Verma, M. P. Sharma, *Renew. Sust. Energ. Rev.* 62, 1063-1071, (2016).
114. A. Abbaszaadeh, B. Ghobadian, M. R. Omidkhah, G. Najafi, *Energy Convers. Manag.* 63, 138-148, (2012).
115. S. P. Singh, D. Singh, *Renew. Sust. Energ. Rev.* 14(1), 200-216, (2010).
116. Y. C. Sharma, B. Singh, S. N. Upadhyay, *Fuel* 87(12), 2355–2373, (2008).
117. F. Motasemi, M. T. Afzal, *Renew. Sustain. Energy Rev.* 28, 317-330, (2013).
118. J. C. Ge, S. K. Yoon, N. J. Choi, *Appl. Sci.* 7(9), 881, (2017).
119. F. Moazeni, Y. C. Chen, G. Zhang, *J. Clean. Prod.* 216, 117-128, (2019).
120. L. R. Cavonius, N. G. Carlsson, I. Undeland, *Anal Bioanal. Chem.* 406(28), 7313e7322, (2014).
121. K. Y. Wong, N. Jo-Han, C. T. Chong, S. S. Lam, W. T. Chong, *Renew. Sustain. Energy Rev.* 116, 109399, (2019).
122. M. Aghbashlo, M. Tabatabaei, H. Rastegari, H. S. Ghaziaskar, *J. Clean. Prod.* 183, 1265-1275, (2018).
123. B. Kayode, A. Hart, *Biofuels* 1e19, (2017).
124. A. Tiwari, V. M. Rajesh, S. Yadav, *Energy Sustain. Dev.* 43, 143-161, (2018).
125. J. Sun, J. Ju, L. Ji, L. Zhang, N. Xu, *Ind. Eng. Chem. Res.* 47, 1398–1403, (2008).
126. B. Aghel, M. Rahimi, A. Sepahvand, M. Alitabar, H. R. Ghasempour, *Energy Convers. Manag.* 84, 541–549, (2014).
127. R. Jachuck, G. Pherwani, S. M. Gorton, *J. Environ. Monit.* 11, 642–647, (2009).
128. E. Lotero, Y. Liu, D. E. Lopez, K. Suwannakarn, D. A. Bruce, J. G. Goodwin, *Ind. Eng. Chem. Res.*, 44(14), 5353-5363, (2005).
129. P. K. Sahoo, L. M. Das, M. K. G. Babu, S. N. Naik, *Fuel* 86(3), 448-454, (2007).
130. A. M. Ruhul, M. A. Kalam, H. H. Masjuki, I. R. Fattah, S. S. Reham, M. M. Rashed, *RSC Adv.* 5(122), 101023-101044, (2015).
131. [131] H. Chen, B. Peng, D. Wang, J. Wang, *Front. Chem. Eng. China* 1, 11–15, (2007).
132. F. Jamil, L. Al-Haj, H. Ala'a, M. A. Al-Hinai, M. Baawain, U. Rashid, M. N. Ahmad, *Rev. Chem. Eng.* 34(2), 267-297, (2018).
133. H. Amani, Z. Ahmad, B. H. Hameed, *Appl. Catal. A: Gen.* 487, 16–25, (2014).

134. A. Madhawan, A. Arora, J. Das, A. Kuila, V. Sharma, *Biomass Convers. Biorefin.* 8(2), 485-496, (2018).
135. L. P. Christopher, H. Kumar, V. P. Zambare, *Appl. Energy* 119, 497-520, (2014).
136. J. Lu, L. Deng, R. Zhao, R. Zhang, F. Wang, T. Tan, *J. Mol. Catal. B Enzym.* 62(1), 15-18, (2010).
137. A. Madhawan, A. Arora, J. Das, A. Kuila, V. Sharma, *Biomass Convers. Biorefinery* 8(2), 485-496, (2018).
138. K. T. Tan, K. T. Lee, A. R. Mohamed, *Biomass Bioenergy* 33(8), 1096-1099, (2009).
139. A. N. Phan, T. M. Phan, *Fuel* 87, 3490–3496, (2008).
140. M. A. Hanif, S. Nisar, M. N. Akhtar, N. Nisar, N. Rashid, *Int. J. Energy Res.* 42(6), 2070-2083, (2018).
141. L. C. Meher, V. S. Dharmagadda, S. N. Naik, *Bioresour. Technol.* 97(12), 1392-1397, (2006).
142. L. C. Meher, S. N. Naik, L. M. Das, *CSIR* 913-918, (2004).
143. M. A. Hanif, S. Nisar, M. N. Akhtar, N. Nisar, N. Rashid, *Int. J. Energy Res.* 42(6), 2070-2083, (2018).
144. M. Kirubakaran, V. A. M. Selvan, *Renew. Sustain. Energy Rev.* 82, 390-401, (2018).
145. D. Y. C. Leung, Y. Guo, *Fuel Process Technol.* 87(10), 883-890, (2006).
146. D. Y. Leung, X. Wu, M. K. H. Leung, *Appl. Energy* 87(4), 1083-1095, (2010).
147. A. Gnanaprakasam, V. M. Sivakumar, A. Surendhar, M. Thirumarimurugan, T. Kannadasan, *Energy J.* 2013, 1-10, (2013).
148. M. Canakci, J. Van Gerpen, *Trans. ASAE* 46, 945–954, (2003).
149. S. T. Jiang, F. J. Zhang, L. J. Pan, *Braz. J. Chem. Eng.* 27(1), 137-144, (2010).
150. N. A. Adeyemi, A. Mohiuddin, T. Jameel, *Afr. J. Biotechnol.* 10(44), 8914–8929, (2011).
151. A. Kumari, P. Mahapatra, V. K. Garlapati, R. Banerjee, *Biotechnol. Biofuels* 2(1), 1-7, (2009).
152. A. L. De Lima, C. M. Ronconi, C. J. Mota, *Catal. Sci. Technol.* 6(9), 2877-2891, (2016).
153. L. Coniglio, J. A. Coutinho, J. Y. Clavier, F. Jolibert, J. Jose, I. Mokbel, V. Tschamber, *Prog. Energy Combust. Sci.* 43, 1-35, (2014).
154. A. Datta, B. K. Mandal, *Renew. Sust. Energ. Rev.* 57, 799-821, (2016).
155. F. Jamil, H. Ala'a, L. Al-Haj, M. A. Al-Hinai, P. Hellier, U. Rashid, *Energy Convers. Manag.* 117, 264-272, (2016).
156. A. E. Atabani, A. S. Silitonga, I. A. Badruddin, T. M. I. Mahlia, H. Masjuki, S. Mekhilef, *Renew. Sust. Energ. Rev.* 16(4), 2070-2093, (2012).
157. I. M. Atadashi, M. K. Aroua, A. A. Abdul, *Renew. Sust. Energ. Rev.* 14(7):1999–2008, (2010).
158. M. Balat, *Energy Convers. Manag.* 52(2), 1479–1492, (2011).
159. M. Lapuerta, O. Armas, J. Rodrıguez-Fernandez, *Prog. Energ. Combust. Sci.* 34(2), 198–223, (2008).
160. N. N. A. N. Yusuf, S. K. Kamarudin, Z. Yaakub, *Energ. Convers. Manag.* 52(7), 2741–2751, (2011).
161. M. Mofijur, H. H. Masjuki, M. A. Kalam, A. E. Atabani, *Energy* 55, 879-887, (2013).
162. M. M. Yasin, T. Yusaf, R. Mamat, A. F. Yusop, *Appl. Energy* 114, 865-873, (2014).
163. K. T. Tan, M. M. Gui, K. T. Lee, A. R. Mohamed, *J. Supercrit. Fluids* 53(1-3), 82-87, (2010).
164. M. Canakci, J. Van Gerpen, *Trans. ASAE* 42, 1203–1210, (1999).
165. M. Naik, L. C. Meher, S. N. Naik, L. M. Das, *Biomass Bioenerg* 32, 354–357, (2008).
166. U. Rashid, F. Anwar, *Fuel* 87, 265–273, (2008).
167. M. Zappi, R. Hernandez, D. Sparks, J. Horne, M. Brough, S. M. Arora, W. D. Motsenbocker *A review of the engineering aspects of the biodiesel industry. Mississippi Biomass Council*, M. S. Jackson, 2003.
168. A. Demirbas, *Energy Policy* 35, 4661–4670, (2007).
169. M. Canakci, A. N. Ozsezen, E. Arcaklioglu, A. Erdil, *Expert. Syst. Appl.* 36, 9268–9280, (2009).
170. A. Demirbas, *Energy Educ. Sci. Technol.* 21, 1–59, (2008).
171. C. Carraretto, A. Macor, A. Mirandola, A. Stoppato, S. Tonon, *Energy* 29, 2195–2211, (2004).
172. S. D. Romano, P. A. Sorichetti *Introduction to biodiesel production. In Dielectric Spectroscopy in Biodiesel Production and Characterization*, Springer, London, 2010, pp. 7-27.
173. ASTM *Standard specification for biodiesel fuel (B100) blend stock for distillate fuels*. In: Annual Book of ASTM Standards, ASTM International, West Conshohocken, Method D6751-08, 2008
174. P. T. Scott, L. Pregelj, N. Chen, J. S. Hadler, M. A. Djordjevic, P. M. Gresshoff, *Bioenergy Res.* 1, 2–11, (2008).
175. R. Shan, L. Lu, Y. Shi, H. Yuan, J. Shi, *Energy Convers. Manag.* 178, 277-289, (2018).
176. L. Wang, J. Yang, *Fuel* 86(3), 328-333, (2007).
177. S. Al-Zuhair, *Biofuels* 1(1), 57-66, (2007).
178. H. W. Aparamarta, S. Hapsari, S. Gunawan, R. I. Shiena, A. G. Ariandi, Y. H. Ju, *Mal. J. Fund. Appl. Sci.* 15(5), 767-771, (2019).
179. R. Selvaraj, R. Praveenkumar, I. G. Moorthy, *Biofuels* 10(3), 325-333, (2019).
180. H. Yun, M. Wang, W. Feng, T. Tan, *Energy* 54, 84-96, (2013).