



Current Technologies and Future Trends for Biodiesel Production: A Review

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Received: 5 March 2022 / Accepted: 29 June 2022 / Published online: 4 August 2022
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Abstract

Increasing use of rapidly developing technology in daily life, people's commitment to comfortable living and rising prosperity increases the need for energy day by day and makes energy essential for human beings. Today, the level of energy consumption has become an indicator of economic development and power for countries, and the sharing of existing energy resources has been one of the main factors that play a role in the formation of the world politics and conjuncture. The majority of the total energy consumption in the world consists of fossil fuels, which are burned in the internal combustion engines (ICE) in the transport sector. The disadvantages of fossil fuel use in ICEs lead researchers to work on new engine designs that will increase combustion efficiency and reduce harmful emission gas output, and to develop renewable and green fuels that can be used in these engines. Biodiesel is the most suitable alternative to petroleum diesel used as conventional fuel in compression ignition engines (diesel engines), which is the most widely used ICE in the transportation sector. In this review paper, a general view of the biodiesel production technologies is addressed to focus on the most valuable strategy, mainly, for ICEs in transportation industry sector. After reviewing a wide range of data, it has been observed that microwave assisted biodiesel production technology is not well-known in low-income countries and should be emphasized about its RandD technology in these countries. This technology has advantages to solve aforementioned problems. The main objective of this paper is to present and discuss the current and future technologies for biodiesel production. Biofuels, in general, are initially presented, then an emphasis is placed on the processes for obtaining biodiesel, on raw materials origins and characteristics and on biodiesel properties when used as fuel. Finally, biodiesel production methods from past to present are discussed. A special focus is given to microwave technology as an emerging solution for biodiesel production.

Keywords Biodiesel · Vegetable oil · Transesterification · Fatty acid methyl esters · Microwave

Abbreviations

ASTM American society for testing and materials

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BD	Biodiesel
CO	Carbon monoxide
CO ₂	Carbon dioxide
DIN	Deutsches institut für normung
EN	European norm
EU	European union
ICE	Internal combustion engine
FAME	Fatty acid methyl ester
FFA	Free fatty acid
NF	Nanofluid
NO _x	Nitrogen oxides
NP	Nanoparticles
WBA	World bioenergy association



1 Introduction

While the importance of energy is increasing day by day, the search for solutions for two main problems in energy production and consumption continues within the scope of clean and sustainable energy policies. The first of these problems is that fossil fuels, which have the largest share among the sources, used in energy production, cause environmental damages and cause irreversible climate changes. The second major problem is the limited availability of fossil fuels reserves and their rapid depletion.

In particular, the introduction of environmental restrictions on energy consumption, such as the Kyoto agreement and the 2017 Carbon agreement, and the lack of a stable energy policy in the world despite the increasing need for energy are of concern. For this purpose, RandD studies with a vision of energy policy should be spread around the world by taking the use of sustainable, domestic and renewable energy sources as an example. However, there is a need to focus on the development of new fuels/systems that reduce emissions of harmful species and the efficient use of existing energy sources [1].

Biodiesel, usually produced from renewable energy sources such as vegetable oils, does not have a high toxic effect in nature. Biodiesel could be used as a fuel alternative in diesel engines to reduce emissions of pollutants as carbon monoxide (CO), hydrocarbons (HC), particulate matter (PM), sulfur oxides (SO_x), and to increase combustion efficiency [2–5]. The use of biodiesel as an alternative fuel has been investigated by many researchers and the studies on the engine performance, combustion characteristics and exhaust emission values of biodiesels produced from different raw materials are still being investigated by using experimental and numerical methods (Computational Fluid Dynamics tools for simulations) [6–8]. The most important reason why biodiesel usage, which has many advantages compared to diesel, is still not widespread at the desired level today is the high production cost compared to diesel [9, 10]

Current research topics include the search for different raw materials (waste oil, animal fat, etc.) to reduce the biodiesel cost production, in addition to use more efficient new technologies (microwave, ultrasonic heating, etc.) to improve the production processes [11]. In scientific literature, it was stated that biodiesel production using microwave technology was quite fast compared to conventional production methods and also some increase in product yield was observed [12–14]. However, the limited penetration depth and safety conditions were considered to be the main reason why the microwave could not be used in the production of large-scale commercial biodiesel. Studies on this subject are continuing, but large volume biodiesel reactors with microwave technology have not yet emerged in the industrial sector.

2 Methodology

In the following sections, a general view of biofuels is initially presented, then, their advantages and disadvantages are displayed, and finally, their production methods from past to present are discussed. A special focus has been given to microwave technology as an emerging solution in biodiesel production.

3 General View of Biofuels

Renewable energy is the energy obtained by using the existing energy flow in the natural processes that operate continuously. Therefore, there is no risk of extinction of the source. As it is obtained through natural processes, the negative impact on the environment is negligible. The most important renewable energy sources are geothermal, wind, solar, hydropower and biomass. Nowadays, countries or international communities put into effect legal and encouraging RandD studies in order to increase the utilization rate of the most suitable renewable energy sources in relation to their economic, geographical and social characteristics. For example, the European Union (EU) has been working on privatizing energy policies and establishing a competitive market since 1990 in order to increase the energy supply security and to minimize the energy production/use environmental impacts [15]. Energy policies in the EU have been determined since 1995 according to White Paper, Kyoto Protocol and Green Book reports. In order to prevent climate change, a package known as 20–20–20 was adopted in the European Parliament on 17 December 2008. In this package, the energy targets in the EU by 2020 have been determined. According to this:

- 20% of the energy used is renewable. This ratio is 35% for electrical energy.
- It was decided to reduce the greenhouse gas emission level by 20% from its 1990 level.
- 20% improvement in energy efficiency is targeted. In addition, renewable energy production which is targeted to be reached in 2020 is stated as 550–600 TWh.

Biomass has the greatest energy potential, among the sources of renewable energy. According to WBA Global Bioenergy Statistics 2018 of the World Bioenergy Association [16], globally, bioenergy is the principal renewable energy source in the world. In 2016, the total primary energy supply of biomass resources constituted 70% of the share among all renewable energy sources.

Biomass energy sources are all substances of plant and animal origin with carbohydrate compounds. Using biomass energy sources, three basic biofuels can be produced: Biogas,

Biodiesel and Bioethanol. The most widely used renewable alternative fuels in common areas are biogas, bioethanol and biodiesel, respectively.

3.1 Biogas

Biogas is a type of gas obtained by decomposition of biomass under anaerobic conditions and is produced only from organic raw materials containing carbohydrate, protein, fat, cellulose and hemicellulose as the main component. Domestic, industrial and agricultural product wastes and animal manure are the main raw materials used in biogas production. Similar to natural gas, the main components of biogas are methane (CH_4) and carbon dioxide (CO_2) gases. By removing CO_2 in the crude biogas, a purified biogas is obtained, of which 98% is composed of CH_4 . Biogas is a renewable biofuel that can be used directly in electricity generation, heat generation and vehicle fuel. Biogas can be used wherever natural gas is used as an alternative fuel to natural gas or mixed with natural gas [17]

3.2 Bioethanol

Bioethanol is a biofuel that can be extracted from plants such as corn, sweet sorghum, sugar beet, wheat, sugar cane, potatoes, woody waters or agricultural wastes and domestic wastes containing cellulose. Besides the transportation sector, it can be used in heat and electricity production, cogeneration applications and also in the production of chemicals. Bioethanol can be used by blending with gasoline, with any proportion in dedicated spark ignition engines, as it is a common practice in Brazilian cars (flex fuel vehicles) or in certain proportions without making any changes in existing gasoline engines [18].

3.3 Biodiesel

Biodiesel is a biofuel, for diesel engines, obtained from renewable energy sources such as vegetable or animal oils. Biodiesel can be used in conventional diesel engines without any modifications, and it is, generally, mixed with petroleum fuels. The chemical structure of the biodiesel consists of methyl or ethyl esters containing medium length C_{16} – C_{18} fatty acid chains unlike diesel and contains about 11% oxygen by weight. The most important advantages of biodiesel are engine lubrication improvement, biodegradability, low toxicity, low emission profile and production from renewable sources [19].

Biodiesel is generally described as a mono alkyl ester of fatty acids chain obtained by reacting vegetable, animal or waste oils, a monohydric alcohol (methanol, ethanol, etc.) and a catalyst. The word “bio” means that the fuel is renewable and biological, and the term “diesel” specifies it is

dedicated to diesel engine. Biodiesel is defined as the ester of the raw material (oil source) reacted according to the type of alcohol used in its production. It is called methyl ester if a methyl alcohol is used and ethyl ester if an ethyl alcohol is used. For example, canola oil methyl ester, soybean oil methyl ester, canola oil ethyl ester, soybean oil ethyl ester and so on. Biodiesel can be used in diesel engine in pure form and as a mixture with diesel in various ratios. The percentage of biodiesel in the mixture is expressed as “BXX”. “XX” herein refers to the ratio of biodiesel used in the mixture to the volume percentage. For example, B20 refers to a mixture of 20% by volume of biodiesel and 80% diesel, B100 refers to pure biodiesel, and B0 to pure gasoline fuel. In general, it is an alternative, renewable, clean and environmentally friendly diesel fuel that can be used without any changes in diesel engines. Biodiesel is superior to diesel in terms of emissions, cetane number and flash point. Lubrication of biodiesel is one of the important properties. In low sulfur diesel fuels, it is possible to increase the reduced lubrication using biodiesel [20].

In addition, biodiesel, especially in rural agricultural countries contributes to the economic structure, to the strengthening of job opportunities and to the development of the industry as well.

4 Biodiesel Production

The most important factor for sustaining biodiesel production with domestic resources is the supply of raw materials. When the countries that are the biggest biodiesel producers in the world are examined, it is seen that they choose the raw materials used in biodiesel production from the oils grown in their own countries and which have more food supply. In this title, the situation of biodiesel in the EU, USA and other rapidly developing countries that have a say in biodiesel production and directs the sector is summarized. With the biofuels directive 2003/30/EC published in the EU [21], which is the largest producer of biodiesel in the world (see Fig. 1), in 2010, 5.75% of the fuel used in the transportation sector across the EU was targeted to be supplied from biofuels. In 2009, this target was revised to 10% by 2020 with a new directive. In order to achieve these goals, energy agriculture is economically supported, and tax deduction is applied to biodiesel fuel in EU countries. Biodiesel production capacity increased by 360% between 2006 and 2009 with the incentives prepared in EU and increased by 4–5% on average in 2010 and after. Low crude oil prices, high vegetable oil prices, rising imports and the financial crisis since 2008 are cited as the reasons for this decline. Although the increase in biodiesel production rate has decreased slightly, EU biodiesel production capacity has continuously increased and continues to increase over the years. The latest data presented are up to 2015 and when the

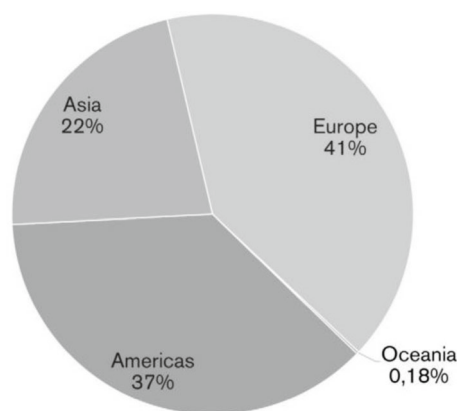


Fig. 1 Liquid biodiesel production in 2016 [16]

EU's biodiesel production for the last 10 years is analyzed, the annual production increased from 3,673,700 tons of oil in 2006 to 11,076,800 tons of oil in 2015. Germany, which is the largest producer of biodiesel in the EU member states with 28 members, realized 24.97% of EU total biodiesel production alone in 2015. The most widely used biodiesel raw material in the EU is canola (rapeseed) oil [16].

Various techniques are used in the production of renewable diesel fuel from oils. These are usually; Direct use of oils, microemulsion, pyrolysis (separation) and transesterification (reesterification) and biodiesel production methods. These techniques are discussed below.

4.1 Microemulsion Method

This method, used to reduce the viscosity of oils, is to form a microemulsion of the oil with short chain alcohols such as methanol, ethanol or 1-butanol. The microemulsion is the equilibrium distribution of optically isotropic liquid microstructures having dimensions between 1–50 nm and is normally formed by the combination of two immiscible liquids and one or more amphiphiles (active substances). Although positive results such as decreases in viscosity of the fuels obtained by this method and improved spray characteristics have been recorded [22], their volumetric thermal values and cetane numbers are lower due to alcohol content than diesel. In addition, microemulsions tend to degrade the mixture at low temperatures. The high latent evaporation temperatures of alcohols have a cooling effect on the combustion chamber. This has the effect of reducing the heavy carbon build-up around the injector orifices and the exhaust valves [23].

4.2 Pyrolysis

Pyrolysis or cracking is the process of breaking the chemical bonds of one substance to form smaller molecules and

converting it into another substance by applying heat energy in an oxygen-free environment. The equipment required for pyrolysis is quite expensive, but it is considered as the most economically reasonable process to produce biodiesel with lower GHG emissions⁴⁹ [23].

Furthermore, while pyrolysis products are chemically similar to diesel fuel and petroleum-derived gasoline [24], the oxygen removal during the thermal treatment eliminates the using of an oxygen fuel environmental benefit.

According to Mahanta and Shrivastava [25], pyrolyzed vegetable oils contain acceptable quantities of water, sulfur, sediment; however, ash as well as carbon residue amounts, and spillage points are unacceptable. Therefore, the motor tests of pyrolyzed vegetable oils are limited to short-term tests.

4.3 Transesterification

Transesterification is a chemical process used to transform the triglycerides of oils or fats into methyl or ethyl esters using an alcohol, generally methanol or ethanol.

Transesterification is considered as the main convenient method to produce biodiesel from oil and fat feedstock types [26, 27]. Thus, transesterification is the most frequently used method, for commercial purposes, to transform vegetable oils into an environmentally friendly and clean fuel i.e., biodiesel [28].

The most widely used method in biodiesel production is the transesterification reaction in the presence of catalyst [29]. The main reasons for this are as follows:

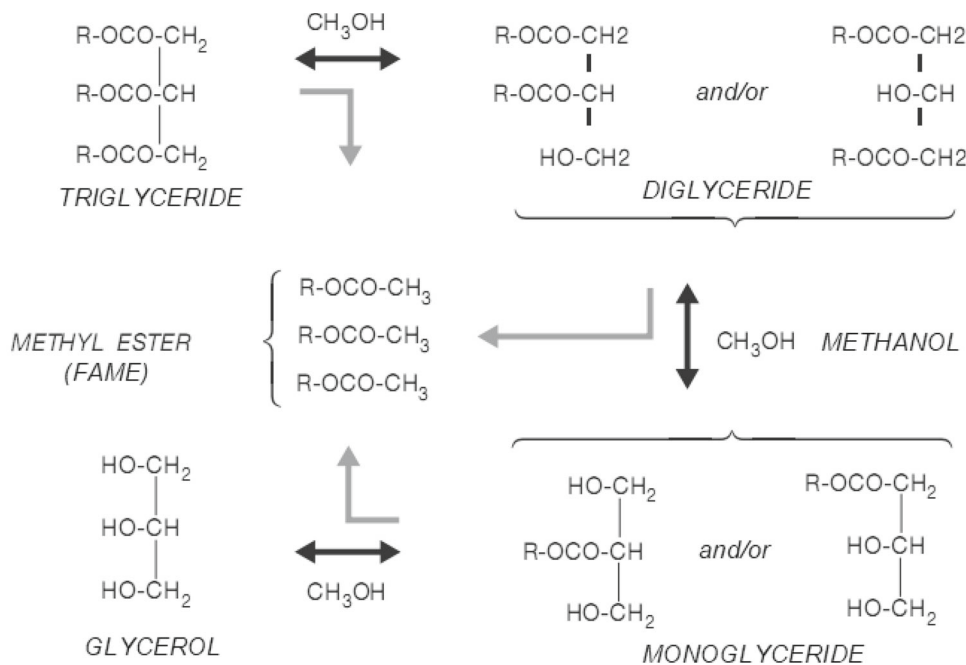
- Realization at low pressures and temperatures,
- High conversion in short reaction times,
- Direct biodiesel is obtained without intermediate/side components.

In the three reaction steps of transesterification, theoretically, in the presence of catalyst, 1 mol of triglyceride and 3 mol of methanol, respectively: 1 mol of diglyceride + 1 mol of FAME, 1 mol of monoglyceride + 1 mol of FAME and 1 mol of glycerol and 1 mol of FAME are obtained (Fig. 6).

The transesterification reaction breaks down the triglyceride, the essential component of the oil, to remove the high viscosity and viscous glycerol from the oil structure and to re-esterify the fatty acids with a short chain alcohol such as methanol. Catalyst is used to accelerate the reaction. As a result, glycerol-based triesters, is transformed to FAMES, also called biodiesel, whose molecular weight is reduced by three times and viscosity by about eight times. In addition, the volatility of the reaction is improved somewhat.

As shown in Fig. 2, a 3:1 molar ratio is sufficient in a theoretical transesterification reaction. However, since transesterification is a reversible equilibrium reaction, it is

Fig. 2 Development of transesterification reaction



required to either use more alcohol than in theory or to remove one of the products from the mixture in order to advance the reaction to the desired products. Therefore, molar ratio greater than 3:1 is generally used in transesterification reactions. In the literature, when 100% excess alcohol (6:1 molar ratio) is used, reaction rate and ester conversion are maximized; it is stated that increasing the alcohol ratio more than a certain value does not improve the ester conversion and makes the separation of glycerol difficult and requires extra process and cost to remove residual alcohol from the product at the end of the reaction [30].

Due to its economic and physico-chemical advantages (short-chain and polar alcohol) in the transesterification reaction, the most preferred alcohol is methyl alcohol, also known as methanol. Methanol reacts rapidly with triglycerides, and the catalysts used in the reaction are more readily soluble in methanol than other alcohols. Apart from methanol, different types of alcohol can also be used, such as ethanol, butyl alcohol and isopropyl alcohol. However, it is stated that the reaction conditions change, and the production of biodiesel becomes difficult in the presence of different alcohols. In addition, no significant difference was found in the engine performance of biodiesel produced from different alcohols.

In transesterification, base (NaOH, KOH, alkali metal alkoxides), acid (H₂SO₄, HCl) or enzymatic catalysts can be used as catalysts. Acid and enzyme catalysts are much slower than base catalysts. When the same amount of acid and base catalyst is used as the catalyst for vegetable oils transesterification in the presence of methyl alcohol, the reaction can be up to 4000 times faster for the base catalyst [31]. In addition to

all these advantages of base catalysts, the base catalyst should not be used if the FFA content is above 0.5% (acid value is 1 mg KOH/g). Because FFAs react with base catalyst, they consume the catalyst and cause the formation of soap which reduces ester conversion and prevents the decomposition of ester, glycerol and wash water. In addition, soaps increase the viscosity and lead to gel formation. In these cases, the oil is pretreated (esterification). When the FFA value of the oil falls below 0.5% with the pretreatment process, transesterification process is started for high-speed biodiesel production.

5 Biodiesel Raw Materials

Vegetable oils, animal oils, algae and bacteria, waste oils and oil refining waste are used as biodiesel raw materials [32]. Vegetable oils are the most preferred among these raw materials. The production of biodiesel from waste, non-renewable and animal oils is advantageous compared to the use of vegetable oils in terms of biodiesel raw material costs. However, the production process from these oils is more difficult than from vegetable oils, as it usually requires many additional processes and esterification. Furthermore, there is a possibility that the biodiesel produced may not meet the relevant fuel standards.

Since biodiesel standards are based on the most produced oil seeds in that country (canola, soybean oil, etc.), the fuel performance and cold flow characteristics of the biodiesel are mostly based on these oil sources. Although various types of oils are used to produce biodiesel, the chemical structure

Table 1 Some vegetable oils acid compositions [33]

Oil Type	Fatty acid composition (mass%)									
	14:0	16:0	18:0	20:0	22:0	24:0	18:1	22:1	18:2	18:3
Sunflower	0	6	3	0	0	0	17	0	74	0
Rapeseed	0	3	1	0	0	0	64	0	22	8
Soybean	0	12	3	0	0	0	23	0	55	6
Corn	0	12	2	–	0	0	25	0	6	–
Cotton	0	28	1	0	0	0	13	0	58	0

Table 2 Some vegetable oils properties [34]

Oil Type	Viscosity (38 °C, mm ² /s)	Higher heating value (MJ/kg)	Pour point. (°C)	Flash Point. (°C)	Density (g/cm ³)
Sunflower	33.9	39.6	– 15.0	274	0.9161
Rapeseed	37.0	39.7	– 31.7	246	0.9115
Soybean	32.6	39.6	– 12.2	254	0.9138
Corn	34.9	39.5	– 40.0	277	0.9095
Cotton	33.5	39.5	– 15.0	234	0.9148

of the oils is similar because the basic structure of the oils consists of 90–98% triglycerides, small amounts of di and monoglycerides and glycerol. Fuel properties of biodiesels produced from different raw materials vary mainly according to carbon chain lengths and unsaturation rates of raw fatty acids used (see Tables 1 and 2). In the case of transesterification process, Triglyceride is prepared by esterifying 3 mol of fatty acids with 1 mol of glycerol; likewise, diglyceride and monoglyceride are formed by esterification of 2 mol and 1 mol of fatty acids with 1 mol of glycerol, respectively. Fatty acids are called free fatty acids (FFAs) if they are free and not bonded. On average, the mass of glycerol in a triglyceride molecule is about 41 g and the masses of fatty acid radicals are about 650–790 g. Therefore, it can be said that fatty acid radicals, which make up 94–96% by mass of triglyceride molecules, will significantly affect the chemical and physical properties of fats.

Biodiesel has the highest thermal value among biological materials. Vegetable oils are therefore the closest biological substances to conventional liquid fuels and have higher heat energy than non-fat biomaterials. Oily biological materials enable a sustainable biodiesel production with its renewable structure. Other advantages of vegetable oils include the ability to grow oil seed plants as biodiesel sources in many climatic zones, ease of processing, utilization of residues and by-products formed after processing. There are more than 4000 types of plants extracted from the world. These products differ according to agricultural inputs and cultivation techniques. The most suitable and commercially preferred vegetable oils for biodiesel production are soy,

canola, sunflower (high oleic type), palm and cottonseed oil, which generally contain monounsaturated fatty acids. Table 3 presents the carbon, hydrogen, oxygen and heating values of some vegetable oils and diesel. According to this, carbon and hydrogen values of vegetable oils are similar to diesel, oxygen values are higher and thermal values are lower.

The following sections are devoted to briefly introduce sunflower, soybean and canola oils, which are widely used in biodiesel production worldwide as raw materials.

5.1 Sunflower

Sunflower oil is a type of oil obtained from the seeds of *Helianthus annuus* plant which has a grain rate of 35–50%. Most sunflower cultivation countries worldwide are Russia, Ukraine, Argentina, Hungary, France, Spain, India, and Turkey. Fatty acid composition of sunflower oil; genetic structure, planting time, growing area-climate conditions, harvest time and varies according to the nutritional status of the plant. Sunflower oil is the third most produced oil after soybeans and rapeseed oils in the world rankings. The Worldwide sunflower seed production in 2020/2021 was near 50 million metric tons [35].

5.2 Soybean

Soybean oil is produced from soybean seeds with a grain content of 18–20%. It has a wide range of consumers worldwide. Soybean oil accounts for 90% of the total oilseed production in the US [36] and Europe, and 80% in Canada. Soybean

Table 3 Basic components of diesel fuel and some vegetable oils [34]

	Unit	Diesel	Rapeseed (Canola)	Soybean	Olive oil
Carbon, C	%	86	77.7	77.8	77.6
Hydrogen, H	%	13	12.0	11.8	11.7
Oxygen, O	%	0.4	10.9	10.7	11.1
Sulfur, S	%	0.3	–	–	–
Lower Heating Value	MJ/kg	41.6	35.8	36.1	36.2

oil is the most widely used biodiesel raw material in the USA. Soybean oil is the most produced type of oilseed. In 2020/2021, more than 75 million metric tons of soybean oil was produced worldwide [35]. Indonesia and Malaysia are the major exporter of this type of oilseed [37].

5.3 Rapeseed

Rapeseed (*canola*) oil is obtained from the seeds of the rapeseed plant with a grain content of 30–42%. The erucic acid content of rapeseed oil containing less than 5% erucic acid was reduced to less than 2% as a result of the improvement of *B. napus* and *B. rapapures*. Canola oil has a higher rate of unsaturated fat than all liquid oils with 93% unsaturated fat. Canola oil is widely consumed throughout the world due to its relatively low price and a healthy type of oil. Canola plant can be considered as the most advantageous compared to other oil plants. Further, Rapeseed is composed of 6.3% saturated, 62.4% monounsaturated and 31.3% polyunsaturated fatty acids [38]. This composition content allows canola oil biodiesel cold flow properties to exhibit better cold flow properties than biodiesel from other plants [39]. The canola biodiesel conforms to the biodiesel fuel standards, making it the most widely used oil in Europe for biodiesel production [40].

6 Biodiesel Fuel Properties

Although biodiesel is largely diesel-like, it exhibits minor changes in some basic fuel properties due to physical and chemical structure differences. To give an example to the most important ones; therefore, the thermal value of biodiesel is slightly lower than diesel. This leads to loss of power as a result of combustion in the engine and an increase in specific fuel consumption values. Many studies [41–50] have been conducted on the effects of biodiesel fuels on the efficiency (emissions, performances) of compression ignition engines. All the studies showed a reduction of the engine power and an important rise of specific fuel consumption through the entire speed range [51].

The biodiesel density and viscosity are slightly higher than that of diesel fuel. The high viscosity and density of the fuel

adversely affect the injection rate at the injection tip and the disintegration of the fuel, i.e., atomization, and combustion. In addition, the density and viscosity of biodiesel are relatively high, allowing more fuel to be taken into the combustion chamber, resulting in less power loss in the engine compared to the difference in biodiesel—diesel thermal value [52]. Biodiesel cetane number is higher than diesel. This ensures that the biodiesel self-ignition capability is higher than that of diesel [53, 54]. The oxygen-containing structure of the biodiesel and the high cetane number compensate for the negative effects of high density and viscosity of the diesel fuel on combustion and increase the combustion efficiency, thus causing biodiesel to have an equivalent combustion characteristic with respect to diesel [55]. One of the most outstanding features of biodiesel compared to diesel is its high flash point. In engine performance, the flash point is usually related to the safety and storage of the fuel and did not create an effective change [56]. The most important two problems encountered in the biodiesel usage are its cold flow properties and its low oxidation stability. Cold flow properties and oxidation stability of biodiesel, which are worse than diesel, cause contamination of the injectors of the engine, fuel filter clogging deposits and deposits in the chamber of combustion as well as various the fuel system components [57]. With the addition of natural and synthetic additives, these properties of biodiesel can be improved and negative effects against the engine can be eliminated.

6.1 Biodiesel Fuel Specifications

Nowadays, most diesel engines use direct and high-pressure injection fuel technology. These engines are extremely affected by the quality of the fuel bundle than indirect spray engines. It is desirable that the biodiesel to be used should be as close to diesel as possible in terms of fuel properties. In diesel engines, various international quality standards have been established for the smooth use of biodiesel. The most widely used biodiesel standards in the world are EN 14,214 (EU) [58] and ASTM D6751 (USA) [59]. Developing engine technology requires some changes in the fuel used so that the fuel standards can be revised accordingly. Biodiesel standards in force today are EN 14,214: 2012 + A1: 2014 updated



Table 4 International biodiesel and diesel fuel standards [60]

Property	Unit	EN14214 (Biodiesel)	EN590 (Diesel)
Density	kg/m ³ (15 °C)	860–900	820–845
Kinematic viscosity	mm ² /s (40 °C)	3.5–5.0	2–4.5
Flash point	°C	101 min	55 min
Sulphated ash content	Weight, %	0.02 max	0.01
Cold filter clogging point	°C	–	– 15 Winter + 5 Summer
Sulfur	mg/kg	10 max	10 max
Carbon residue	Weight, %	0.30 max	0.30 max
Cetane number	–	51 min	51 min
Total pollution	mg/kg	24 max	24 max
Copper strip corrosion	3 h (50 °C)	No.1 max	No.1 max
Oxidation stability	hours (110 °C) g.m ³ , hour	8.0 min-	– 20–25
Water	mg/kg	500 max	200 max
Acid value	mg KOH/g	0.50 max	–
Number of Iodine	–	120 max	–
Monoglyceride content	weight, %	0.7 max	–
Diglyceride content	weight, %	0.2 max	–
Triglyceride content	weight, %	0.2 max	–
Free glycerol	weight, %	0.02 max	–
Total glycerol	weight, %	0.25 max	–
Ester content	weight, %	96.5 min	7 max (V/V)
Linolenic acid methyl ester	weight, %	12 max	–
Phosphorus content	mg/kg	10 max	10 max
Group 1 Metals (Na + K)	mg/kg	5 max	5 max
Group 2 Metals (Ca + Mg)	mg/kg	5 max	–

for the EU in 2013 and ASTM D6751-12 updated for the US in 2012.

Table 4 provides a comparison of EN 14,214 biodiesel standards and EN 590 diesel fuel standards (up to 7% biodiesel content allowed) for diesel in force in the EU.

7 Pros and Cons of Biodiesel

7.1 Advantages of Biodiesel

The properties of biodiesel are highly affected by the oil source and alcohol type. Therefore, the ignition, combustion and emissions levels of each biodiesel vary slightly. Generally speaking, the oxygen-containing structure of biodiesel significantly reduces the formation of HC, CO and soot emissions by providing the necessary oxidant in the combustion zones [61, 62]. The structure of conventional diesel containing aromatic compounds and sulfur causes soot and particle emissions to occur. An increase in particle and soot (smoke darkness) emissions occurs in proportion to the amount of

aromatics added to the diesel. The fact that biodiesel contains, typically, no aromatic and sulfur compounds, results in a significant reduction in polyaromatic hydrocarbon (PAH) and soot emissions [63].

The general view in the literature is that HC, CO and soot emissions are significantly reduced, and NO_x emissions increase slightly when biodiesel is used [64].

The high amount of oxygen in biodiesel composition enhances the combustion process resulting in more complete combustion reactions, which leads to lower pollutant emissions of CO and soots. But a rise in NO_x values has been observed, due to higher temperatures and oxygen content [65, 66] (see Fig. 3).

Biodiesel, which is generally obtained from oilseed plants, is not considered to increase the greenhouse effect because it converts CO₂ by photosynthesis and accelerates the carbon cycle. The CO₂ released into the atmosphere by burning the produced biodiesel is consumed by the oil plant to be used in biodiesel production. In this opinion, biodiesel produced and used as a fuel serves as a natural sink that traps CO₂ emissions and contributes to the solution of greenhouse effect caused



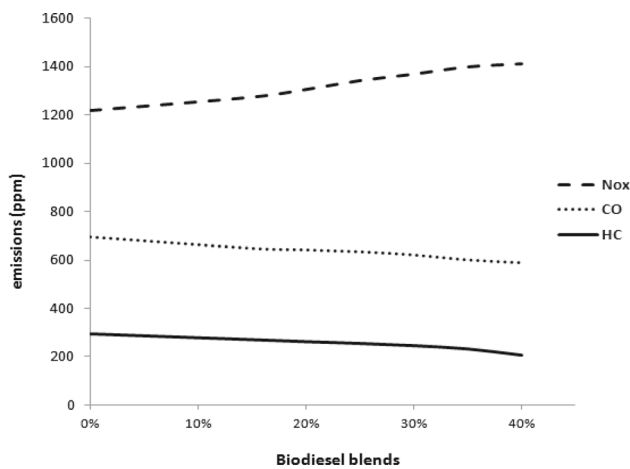


Fig. 3 Average impacts of biodiesel blends on exhaust emissions [65]

by CO₂ emissions and global warming problems. Biodiesel is evaluated in terms of environment and safety; it is a non-toxic fuel for acute oral toxicity and has 10 times less toxicity than table salt. Biodiesel has been found to cause a very mild irritation of 4% on human skin after 24 h, which is less than the effect of soap-water solution. Tests for the determination of aquatic toxicity showed that the 96-h lethal concentration (LC) test results were slightly greater than 1000 mg/L. The lethal concentration at these levels is considered insignificant. In terms of biodegradability, biodiesel can be broken down 4 times faster and easier in 28 days than diesel.

7.2 Disadvantages of Biodiesel

As it is a solvent and organic-based fuel, storage conditions of biodiesel are of great importance. Biodiesel should be kept in clean and dry tanks, avoiding excessive heat. Also, the place to be stored in should be dark and not exposed to sunlight. The rate of oxidation of biodiesel exposed to light increases; oxidized biodiesel resins and causes blockages in the injector [67]. Biodiesel has a dissolving effect on copper-containing metals (bronze, brass) and tin, lead, galvanized, and zinc coated surfaces. Biodiesel contact with these materials will cause sediment formation. Copper strip corrosion shows the corrosion effect of biodiesel on metal. Soft steel, stainless steel, fluorinated polyethylene and fluorinated polypropylene can be selected as the tank material in the warehouses where biodiesel will be stored [68]. The use of certain elastomers, natural and butyl rubbers in storage, transport and motor materials is inconvenient, since biodiesel is a good solvent and disintegrates them. For use above the B20 ratio, the use of biodiesel compatible viton B-type elastomeric materials is also recommended [69].

When used as a fuel, it has been reported that biodiesel significantly reduces the engine performance compared to pure diesel fuel operation. [70–72] For example, Boubahri

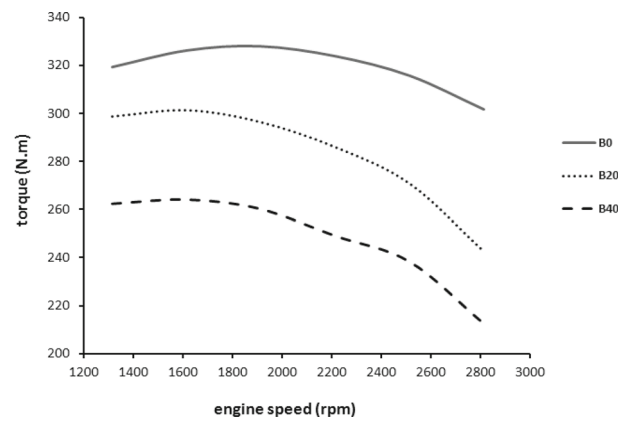


Fig. 4 Torque versus speed for different biodiesel blends [66]

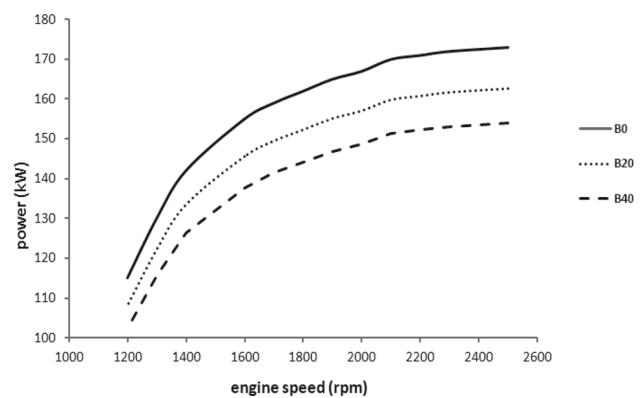


Fig. 5 Power versus speed for different biodiesel blends [66]

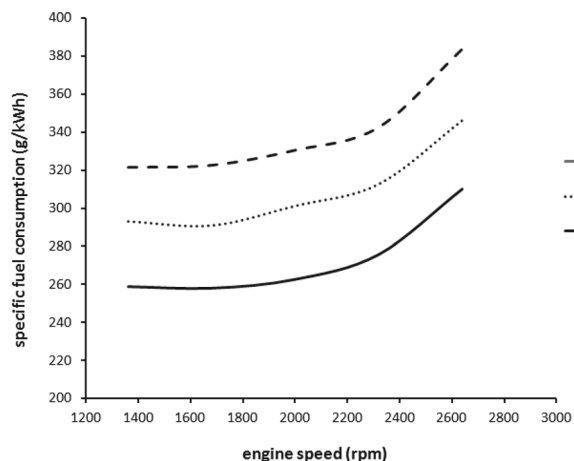


Fig. 6 Specific fuel consumption versus speed for different biodiesel blends [66]

et al. [66] have obtained approximately a 5% diminution of engine torque and power (see Figs. 4 and 5), comparatively to pure diesel fuel, for each 10% of methyl ester (ME) added to diesel fuel. However, an increase in fuel consumption was

observed (see Fig. 6): approximately 6% for each 10% of ME added to diesel fuel.

The following figures present the effect of biodiesel blends (from B0 to B40) on the performance (torque, power and fuel consumption) of V8 cylinders diesel engine, at various engine speeds. B0 refers to pure diesel fuel and BX refers to biodiesel blend with X% the volumetric content of biodiesel in pure diesel fuel [39].

To overcome the disadvantages of using BD on engine performances, researchers have investigated several solutions. One of the promising solutions is the adding of nanoparticles (NPs) to the BD fuels. Sateesh et al. [73], Gavhane et al. [74], and Soudagar et al. [75, 76] reported that these BD nanofluids (NFs) prepared using, for example, aluminum oxide (Al₂O₃) NPs, zinc oxide (ZnO) NPs, strontium-zinc oxide NPs (Sr@ZnO), multi-walled carbon nanotubes (MWCNT), etc. additives improve engine performance and reduces emissions. A notable increase in the brake thermal efficiency and a decrease in NO_x emissions was generally recorded.

8 Conventional Technologies for Biodiesel Production

Under this section, biodiesel production studies using conventional thermal heating, basic catalysts (NaOH, KOH, CH₃ONa, CH₃OK) and methanol are discussed due to their high efficiency and low cost in commercial biodiesel production.

Dias et al. [77] investigated the effects, on fuel quality, of different base catalyst species (KOH, NaOH and CH₃ONa); refined soybean, sunflower, and waste frying oils used to produce, by transesterification, various biodiesel samples. In general, for all types of catalysts, the yield of refined oils (highest 97%) was higher than that of waste frying oil (highest 92%). According to the results of the experiment, in order to ensure the viscosity limit value of EN 14,214 standard of 5 mm²/s, it is sufficient to use 0.6% KOH by mass in refined oils and this ratio has increased to 0.8% KOH in waste frying oil. However, it has been reported that 0.4% NaOH or CH₃ONa should be used in refined oils to achieve this viscosity value and that both catalysts should be used at a rate of 0.6% for waste frying oil. In the experiments, the highest ester content was obtained using 1.2% KOH. In his study, Fedai [78] examined optimum reaction conditions for biodiesel production using canola oil. The samples produced for this purpose; ester content, linolenic, mono-, di-, triglyceride, free and total glycerol amounts, viscosity, density, filter obstruction point, and flash point of cold were analyzed and their changes according to reaction parameters were investigated. According to the results of the study, optimum reaction conditions in canola oil methyl ester production were determined as 55 °C, 25% (by volume) methanol, 1.05% (by

mass) NaOH and 1 h reaction time. The amount of ester in biodiesel produced under these conditions was reported to be 99.22%. Vicente et al. [79] have used, in their studies, sunflower oil for the production of biodiesel. NaOH, KOH, CH₃ONa and CH₃OK catalysts, used in all transesterification reactions, have obtained biodiesel samples with nearly 100% ester content. The researchers found that only the methoxide catalysts (CH₃ONa and CH₃OK) in biodiesel yielded close to 100% product yield and that the yields were slightly lower due to side reactions such as saponification when using KOH and NaOH. The fastest completed reaction in the experiments continued for 30 min at 65 °C using 6:1 molar methanol and 1% by mass NaOH. Çildir and Çanakçı [80] used sunflower, corn and rapeseed oil in the transesterification reactions of various vegetable oils. They observed the effects of various reaction parameters such as the amount of alcohol and catalyst ester conversion efficiency, kinematic viscosity, density, yield point, acid value and the flash point. Methanol was used as alcohol and NaOH was used as catalyst. According to the test results, the highest ester conversion rate (99.65% of corn oil methyl ester); was obtained at temperature 60 °C, NaOH 0.3% of the oil mass and methanol:oil ratio 6:1 (molar). The duration of the reaction was 60 min. Also, in the production of methyl esters of corn, rapeseed and sunflower oil, it was found that viscosity and flash points of esters decreased as oil/alcohol molar ratio increased, density decreased with increasing catalyst amount, but saponification increased when catalyst amount was above 1% of the oil mass. Azcan and Danişman [81] produced biodiesel from cottonseed oil by transesterification method both by conventional method in heated magnetic stirrer and under microwave radiation using microwave synthesis unit. In the microwave synthesis unit, the highest conversion efficiency (92.7%) and the highest ester content (99.7%) were obtained by reaction at 60 °C reaction temperature, 1.5% KOH (mass) and 6:1 molar methanol:oil. 91.4% conversion efficiency and 99.9% ester content were achieved by conventional methods under the same reaction conditions. Sabudak and Yıldız [82] used a biodiesel reactor with a volume of 50 L in the study of pilot scale biodiesel production. In this study, first of all, collected restaurant oils were pretreated and the FFA values were reduced to the appropriate level for transesterification. The resulting raw material was then reacted in the transesterification reaction with 20% by weight of methanol (average 6:1 molar methanol:oil) and 1% by mass of CH₃ONa at 58 °C for 1 h. In the fuel analyzes carried out after different purification processes, the density of 885 g/cm³ (15 °C) and 4.4088 mm²/s (at 40 °C) viscosity values of biodiesel produced after purification with pure water are in compliance with EN 14,214 standards. Methyl ester content was found to be below the standard value of 95.6%. Meher et al. [83] identified optimum reaction conditions for biodiesel production



from tropical *Pongamia pinnata* oil, which is generally produced in the shadow of Asia. Optimum production efficiency according to working outputs were 6:1 molar methanol:oil and 1% mass KOH. Under these conditions, biodiesel was produced from *Pongamia pinnata* oil with 96% conversion efficiency. Özsezen [84], in his study, designed a conventional biodiesel reactor with a capacity of 100 L, heated by electric resistance, and produced biodiesel for use in motor tests. Waste palm oil was used as raw material in the study (50 kg). The reactant and production parameters used in this study were: alcohol:oil molar ratio 6:1 methanol (1134 g), KOH up to 1% by mass (500 g) of the oil and at 60 °C and 240 min, respectively, reaction temperature and time. The fuel properties of the biodiesel sample purified by washing four times using distilled water at 60 °C were measured as 875 g/cm³ (15 °C) density, 4.401 mm²/s (40 °C) kinematic viscosity and 96.5% ester content. In their study on the determination of optimum transesterification parameters for pilot scale biodiesel production from mustard oil, Bouaid et al. [85] used methanol as alcohol and KOH as catalyst. The reactor tank of the pilot scale plant is designed with a volume of approximately 200 L. Optimum reaction data at the end of the study are 1.5% KOH by mass, 6:1 methanol:oil ratio (molar), 25 °C as reaction temperature and 60 min reaction time. It was found that the biodiesel produced under these conditions contained 97.1% methyl ester by mass and also important fuel properties such as viscosity, density, water content and acid value were in compliance with EN 14,214 biodiesel standards. Alptekin et al. [86] carried out biodiesel production by transesterification method from different vegetable and animal oils in pilot scale biodiesel reactors. In the works, after the pre-treatment of waste oils, corn oil was directly transesterified reaction. From refined corn oil, they produced methyl ester at reaction temperature of 60 °C. in the presence of 1% by mass of KOH and 6:1 molar methanol with a yield of 91% conversion after 120 min of reaction. The fuel produced has a density of 886 g/cm³ at 15 °C, a 4.18 mm²/s kinematic viscosity at 40 °C as well as a higher heating value of 39.878 kJ.kg⁻¹.

9 New Biodiesel Production Technologies

Despite the many advantages of biodiesel, the high cost of production is shown as the biggest factor limiting the usage rate in industry [87]. To reduce this cost, researchers are focusing on various aspects of the production process by using new raw materials, testing recoverable and renewable catalysts and applying non-conventional techniques such as plasma, ultrasonic, microwave-assisted methods for getting rapid conversions [88, 89].

According to Palm et al. [90] these non-conventional techniques can reduce significantly the reaction time as well as improve the biodiesel production yields.

In the following, these new technologies will be briefly discussed. A particular emphasis will be placed on microwave technique as the most promising method, economically and technically.

9.1 Plasma-Assisted BD Production Method

Plasma is defined as an ionized gas constituted by electrons at high-energy levels, free radicals, positive ions, and ultraviolet light [91], making it suitable for biological dissociation.

Non-thermal plasma (NTP) is mostly used to produce very high concentrations of the chemically active species at ambient temperature and pressure.

NTP is generally applied using corona discharge plasma technology which is more suitable for lab-scale usage. For industrial applications, requiring high energy, plasma jets are more appropriate thanks to their versatility and low-cost operation [92].

In biodiesel production, plasma has been used to operate transesterification at low temperature. A high biodiesel conversion yield, near 98%, has been reported by several authors [93, 94].

9.2 Ultrasound-Assisted BD Production Method

Ultrasound application in biodiesel production has gained great interest in the last years due to the high homogenization of the reagents by acoustic cavitation. This phenomenon increases the reaction speed by increasing the medium temperature. Consequently, the amount of catalyst is reduced, and the reaction duration drops from hours to few minutes [95].

Typically, the ultrasonic frequency ranges between 20 and 50 kHz at a relatively high power (usually more than 200 W). Recently, more economical ultrasonic devices have been developed. Giving satisfactory conversion yields, this equipment's require powers less than 50 W [96].

According to Shinde and Kaliaguine [97], it was reported that the conversion rate of oil into FAME is better under ultrasound than using mechanical stirring. Stavarache et al. [98] showed that using high ultrasonic frequency (40 kHz), the transesterification reaction speed increases rapidly, with a positive effect on biodiesel yield. Shinde et al. [99] performed a parametric study of ultrasound-assisted biodiesel production, they found that the effect of ultrasonic waves on the reaction conversion rate is concentrated in the small volume at the vicinity of the sonotrode tip.

Recently, Oliveira et al. [100], applied a high frequency (from 1 to 3 MHz) and low power (from 6 to 9 W) ultrasound to produce biodiesel from soybean oil. They concluded that



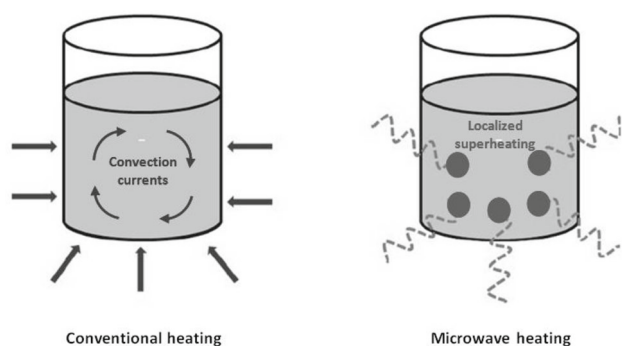


Fig. 7 Comparison of conventional heating versus microwave heating

the increase in either ultrasonic power or frequency increases the reaction conversion rate.

9.3 Microwave Assisted Technology

Microwave is one of the most effective methods to produce biodiesel, in very concise time, with high production yields [27, 101]. It was indicated that the reaction times of 60 to 240 min, required in conventional technique, are reduced to 0.5 to 7 min, and higher conversion efficiencies can be obtained by conducting transesterification reactions in microwave synthesis units instead of conventional heating systems [102].

Several studies demonstrated that biodiesel production with conventional heating needs more power than microwave-assisted heating. Soltani et al. [103] explained this by the fact that, in this method, the heat is not applied directly to the reactants but through the material surface of the reactor and it is transferred by molecule to molecule from outside. While in microwave systems thermal energy is directly transferred into molecules interior of the reactants and the heat is distributed uniformly throughout the fluid as shown in Fig. 7.

Microwave-assisted biodiesel production, which does not currently have large scale production potential, is described below.

In the chemical reactions carried out using microwave, many important advantages are observed, such as very short reaction time, reduced side reactions and improved selectivity (inertness of non-polar substances to the microwave). Thanks to these advantages, microwave systems are becoming increasingly widespread and improved, despite that how the microwave-induced effects that are advantageous for chemical reactions and the operating mechanisms are still unknown [104].

According to a recent study of Khedri et al. [105] biodiesel production using microwave technology could be affected by several parameters, including power of the microwave system, temperature of the reaction, stirring velocity, catalyst

type and concentration, alcohol type and alcohol:oil molar ratio as well as water and free fatty acids oil contents.

The effects most emphasized by the researchers are generally discussed under four main headings:

9.3.1 Super Heating Effect

When the solvents interact with microwaves, it is observed that they boil at atmospheric pressure at 13–25 °C higher than normal boiling points compared to conventional heating (thermal). The effect of this increase is defined as the super heating effect. Overheating is thought to be the main source of increased reaction rates [106]. In conventional heating, heat energy is usually first transmitted to the wall of the reaction vessel. Conventional boiling is related to the presence of bubbles and the presence of cavities/scratches on the inner surface of the container. The mass of liquid in the container holds air bubbles in the cavities. As the pressure in the air bubbles increases, the bubble begins to grow and once the forces holding the bubbles on the ground are defeated, the bubbles are separated from the cavity and boiling begins. In microwave heating, all the material in the container heats up by absorbing the microwave energy. The formation of bubbles in the container wall is delayed by heating (due to penetration) from the inside out. Therefore, the temperature of the liquid rises above the normal boiling point, but no boiling occurs. In these conditions, the onset of boiling at transient temperatures is called a delayed boiling point. For example, methanol boiling at 65 °C with conventional heating under normal conditions, begins to boil at 84 °C under microwave irradiation. This value is called the delayed boiling point of methanol.

9.3.2 Hot-Point/Hot-Spot Effect

The hot-spot effect is defined as the thermal microwave effect caused by overheating. Even at low temperatures, it is considered that there are hot spots in the reaction mixture that occur locally continuously and disappear. With the mixing of the mixture, the formation of these spots continues to emerge, albeit to some extent. It is assumed that the reaction rate increases due to the increase in temperature value at these points. On the other hand, this effect is an unproven assumption because the hot spot temperatures cannot be measured, and a mathematical approach to this effect has not yet been developed. In relation to the hot spot assumption, Berlan et al. [107] showed that the Diels–Alder reactions occur much faster than microwave heating and conventional heating at the same hot value and explained this rate increase by the hot spots formed in the reaction mixture and the overheating of the solvent [106]. The chemical reactions of the microwave showed that the acceleration of 6–40 times was caused by the formation of hot spots of many ions.

9.3.3 Kinetic Effect (Specific Effect)

Several theories have been formulated about the existence of non-thermal microwave effects and the sources of these effects. For example, it has been found that the speed of some organic and inorganic reactions carried out with microwave power of 560 W is higher than that of conventional reactions with the same temperature. The researchers stated that this increase cannot be achieved by increasing the temperature under microwave radiation, the effect of the microwave on the reaction is very complex and this effect is mostly observed in unstable systems. Non-thermal effects of microwaves are studied under the name of kinetic effects. In recent years, kinetic studies have been carried out with precise temperature measurements in order to investigate non-thermal effects in order to determine the reason for accelerating the chemical reactions of microwaves. Since the results of the studies on the subject are variable, there is no clear consensus on the existence of specific microwave effect [108]. This is because; the same temperature values under microwave irradiation are faster reactions than thermal conditions, as well as other reactions at the same temperature in both microwave and thermal conditions are proceeding at equal speeds. In order to compare the reactions carried out by microwave and thermal methods, it has been found that it must be in exactly equal conditions. To this end, studies using isothermal systems have gained speed and importance in recent years.

9.3.4 Screening Effect of Microwave Energy (Lattice Effect)

A solvent that increases the polarity of the medium (ϵ'') is usually added to the reaction mixture for decomposition reactions of azobisisobutyronitrile (AIBN). The AIBN molecules encapsulated by the added solvent were less able to absorb the microwave because the solvent was substantially absorbed, so that the reaction was carried out by the heat transmitted by the heated solvent. As a result, a reaction rate close to the thermal reaction rate was formed under microwave radiation. The different microwave reactions in which the solvent is added have different microwave effects and different reaction rates have been described as the shielding of the microwaves by the solvent.

10 Microwave Assisted Transesterification for Biodiesel Production

In the following section, biodiesel production using transesterification reactions, under microwave radiations are discussed.

In their study, Azcan and Danışman [86] carried out biodiesel production from cottonseed oil by transesterification method both by conventional method in heated magnetic

stirrer and under microwave radiation using microwave synthesis unit. In the microwave synthesis unit, the highest conversion efficiency (92.7%) and the highest ester content (99.7%) were obtained by reaction at 60 °C reaction temperature, 1.5% KOH and 6:1 molar methanol:oil; 91.4% conversion efficiency and 99.9% ester content were achieved by conventional methods under the same reaction conditions. In another study by Azcan and Danışman [109] investigated the effects of catalyst rate, reaction temperature and time on biodiesel production by transesterification method using microwave heating system from rapeseed oil. As a result of the study, optimum reaction conditions where 93.7% conversion efficiency and 97.8% ester content were obtained; 1.0% by weight of the basic catalyst, 6:1 molar methanol, 50 °C reaction temperature and 5 min reaction time. Duz et al. [110] started lab station using microwave heating in a laboratory-scale chemical synthesis reactor with 1% for NaOH:oil ratio (mass), 1:10 for oil:methanol molar ratio and 6 min reaction time as a result of their transesterification process with 98.4% methyl ester content of safflower oil and viscosity, density, cloud point, flash point, such as cetane number have obtained biodiesel in accordance with EN and ASTM standards of basic fuel properties. Sherbiny et al. [111] obtained methyl ester from jatropha oil with high FFA value in microwave synthesis unit. In their studies, the researchers primarily used the esterification method, a pre-treatment method, to make jatropha oil suitable for use in transesterification. In the second stage of the study, the reactant contents of the FFA values were 1:7.5 oil:methanol molar ratio and 1.5% KOH transesterification reaction and they completed biodiesel production at 65 °C temperature in 2 min. They were able to produce biodiesel with similar fuel properties in 60 min by using conventional heating methods under the same reaction conditions. Kumar et al. [112] produced biodiesel under laboratory conditions using *Pongamia pinnata* oil, microwave heating system, 1:6 oil:alcohol ratio (molar), 60 °C heating temperature and different catalyst ratios and reaction times. The researchers stated that 1% KOH by mass and 97% conversion in 10 min reaction time, 0.5% NaOH and 96% conversion efficiency were obtained in 5 min reaction time. Encinar et al. [113] compared conventional heating and microwave irradiation transesterification reactions in soybean biodiesel production. The researchers used 6:1 molar ratio methanol, 1% KOH by mass, to produce 96.6% ester content biodiesel with a density of 0.879 g/cm³ and a viscosity of 4.23 mm²/s after 60 min at a temperature of 65 °C; They achieved to produce biodiesel with similar properties (96.5% ester content, 0.881 g/cm³ density and 4.41 mm²/s viscosity) after 3 min reaction with 200 W output power in microwave unit.

Another biodiesel production study using microwave-assisted heating from *Pongamia pinnata* oil was presented by Venkatesh et al. [114]. In this study, firstly the oil with high FFA value was subjected to pre-treatment by using H₂SO₄



and the oil which reached the appropriate FFA value was converted to biodiesel in the presence of KOH and methanol. As a result, optimum reaction conditions (89.9% conversion yield); The molar ratio of 9.3:1 methanol:oil was determined as 1.33% KOH by mass and a 150 s reaction time. Chen et al. [115] produced biodiesel using a microwave synthesis unit, from waste cooking oil. In their parametric study, 6:1 molar methanol, 0.75 mass % CH_3ONa were reacted with waste oil under microwave irradiation for 3 min to obtain 97.7% conversion efficiency. In the conventional production carried out under the same reaction conditions, the highest conversion efficiency (96.6%) was obtained in 90 min reaction time. Hernando et al. [116] produced methyl esters from rapeseed and soybean in their transesterification reaction in a continuous flow microwave synthesis unit. They stated that the reaction conditions should be 60 °C reaction temperature, 1.13% NaOH, 15:1 molar methanol and 1 min reaction time in order to obtain the highest biodiesel product yield (97%). In order to make comparisons, the researchers carried out biodiesel production with conventional methods under similar conditions and reported that microwave technology is a much faster and effective method for biodiesel production. Boldor et al. [117] tried to determine the optimum reaction parameters and reactant species to produce biodiesel from soybean and rice husk oils using a batch microwave system. Ethanol and methanol were used at reaction temperatures of 60, 70 and 80 °C, during 5-, 10-, 15-, and 20-min reaction times and in the presence of 0.15–0.18% by mass of catalyst. A 96% conversion rate was obtained in all reactions. The 20-min transesterification reaction carried out at 80 °C reaction temperature resulted in the highest conversion from oil to biodiesel, and the fuel obtained from the measurements was found to comply with ASTM standards. In these reaction parameters, soybean oil was converted to biodiesel by 98.64% with methanol and 98.32% with ethanol; rice husk oil was converted to 98.82% with methanol and 97.78% with ethanol. In this study, it has been found that the use of methanol in microwave biodiesel production is a more suitable alcohol type than ethanol with its higher conversion efficiency and lower cost.

11 Future Trends on Biodiesel Production Techniques

The combination of microwaves and ultrasounds to produce biodiesel has been recently reported in several studies [118–120]. Simultaneous use of both techniques has been stated to reduce reaction time and improve the efficiency of biodiesel production [121]. Martinez-Guerra and Gude [122] investigated microwave and ultrasound effects on biodiesel production, both separately and simultaneously. This study was performed under 100 W microwave radiations, for 2 min,

using waste oils and methanol as raw materials. As a result, a maximum biodiesel conversion efficiency of 98% has been reached when microwave and ultrasound were combined using 0.75 wt% of sodium hydroxide as catalyst and 6:1 as methanol:oil ratio. Accordingly, Chipurici et al. [123] focused on the production of biodiesel using acoustic cavitation (hydrodynamic or ultrasonic) or continuous flow systems supported by microwaves. The goal is to design end-user small or medium-sized farm-scale equipment that can produce enough fuel for agricultural machinery using locally produced renewable or waste raw materials.

Supercritical alcohol transesterification is a promising solution to cut down the high cost of biodiesel production since there is no need for catalysts [27]. Thus, the complexity and the costs related to the separation and recuperating of the catalyst are eliminated. Furthermore, there is no saponification reactions and no need for rinsing water. According to Deshpande et al. [124], the supercritical transesterification reaction is very fast, occurring in few minutes versus hours in the traditional method, and the biodiesel yields is higher.

Saka and Kusdiana [125] were the pioneers of using this technology in biodiesel production. They used supercritical methanolysis of rapeseed oil at a pressure ranging from 448 to 648 bars and a temperature near 450 °C. The reaction time was 4 min and the yields reached 95%. After that, several studies have conducted on this technology [126–129] and demonstrated the feasibility of this technology.

On the other hand, supercritical transesterification requires very high temperatures and pressures conditions which reduces the life of the equipment used and considerably increases investment costs. [124]

According to Singh et al. [130] the high energy consumption is the main downside of the supercritical transesterification process.

Supercritical transesterification technology is a very promising biodiesel production method; however, it still needs optimization and improvements to make it more cost-effective and to bring it to the commercial level. To overcome the limitations of this technique, attempts are made to combine it with other methods such as microwave. Patil et al. [131] demonstrated the feasibility of microwave mediated supercritical transesterification, but more efforts are needed.

12 Conclusions

This paper presents a comprehensive review on biodiesel production technologies. This general view was addressed to focus on the most valuable strategy to be adopted by developing countries in order to increase their energy supply security and to minimize the environmental impacts of fossil fuels by using a new generation substituting fuel. Many aspects of biofuels, especially of biodiesels, have been

emphasized in this review. The origins of biodiesel fuels, their properties, their advantages and disadvantages and their production techniques have been discussed. The scientific literature in relation with conventional and new methods of biodiesels production has been examined. The efficiency of these methods was discussed in detail. A special emphasis has been given to the microwave assisted technology. This novel technic was recently discussed in several studies and publications. All of these studies have proven the high conversion efficiency and the low production time of microwave technique compared to conventional heating methods. However, there is a big lack of information about many aspects of this novel technic that must be unveiled, mainly in industrial applications. Indeed, most of these studies are limited to laboratory-scale experiments, but large-scale studies are not covered. So, it is important, in future, to more study microwave assisted biodiesel production systems on a large scale in terms of providing new environmental solutions.

References

- Janaun, J.; Ellis, N.: Perspectives on biodiesel as a sustainable fuel. *Renew. Sust. Energy Rev.* **14**, 1312–1320 (2010)
- Aggarwal, H. D., Chowdhury, S. N., Mukerji, and Verman, L. C.: Indian vegetable oils as fuel for diesel engine, *Bull. Indian Ind. Res., Council of Scientific and Industrial Research, New Delhi, India* (1952)
- Goering, C., Schrock, M., Kaufman, K., Hanna, M., Harris, F., and Marley, S.: Evaluation of vegetable oil fuels in engines, *ASAE Paper No. 87–1586* (1987)
- Nascimento, M.A.R.; Sierra, R.; Silva Lora, G.A.: Performance and emission experimental evaluation and comparison of a regenerative gas microturbine using biodiesel from various sources as fuel. *J. Energy Resour. Technol.* **133**(2), 022204 (2011)
- Soudagar, M.E.M.; Khan, H.M.; Khan, T.M.Y.; Razzaq, L.; Asif, T.; Mujtaba, M.A.; Hussain, A.; Farooq, M.; Ahmed, W.; Shahapurkar, K.; Alwi, A.; Ibrahim, T.M.; Ishtiaq, U.; Elfakhany, A.; Ali Baig, M.A.; Goodarzi, M.S.; Safaei, M.R.: Experimental analysis of engine performance and exhaust pollutant on a single-cylinder diesel engine operated using *Moringa Oleifera* biodiesel. *Appl. Sci.* **11**, 7071 (2021). <https://doi.org/10.3390/app11157071>
- Giuffrè, A.M.; Tellah, S.; Capocasale, M.; Zappia, C.; Latati, M.; Badiani, M.; Ounane, S.M.: Seed oil from ten Algerian peanut landraces for edible use and biodiesel production. *J. Oleo Sci.* **65**(1), 9–20 (2016). <https://doi.org/10.5650/jos.ess15199>
- Giuffrè, A.M.; Capocasale, M.; Zappia, C.; Sicari, V.; Pellicanò, T.M.; Poiana, M.; Panzera, G.: Tomato seed oil for biodiesel production. *Eur. J. Lipid Sci. Technol.* **118**(4), 640–650 (2016). <https://doi.org/10.1002/ejlt.201500002>
- Ramadhas, A.S.; Jayaraj, S.; Muraleedharan, C.: Biodiesel production from high FFA rubber seed oil. *Fuel* **84**, 335–340 (2005)
- Sadeghinezhad, E.; Kazi, S.N.; Sadeghinejad, F.; Badarudin, A.; Mehrali, M.; Sadri, R.; Safaei, M.R.: A comprehensive literature review of bio-fuel performance in internal combustion engine and relevant costs involvement. *Renew. Sustain. Energy Rev.* **30**, 29–44 (2014). <https://doi.org/10.1016/j.rser.2013.09.022>
- De Araújo, C.D.M.; de Andrade, C.C.; Silva, E.D.S.; Dupas, F.A.: Biodiesel production from used cooking oil: a review. *Renew. Sustain. Energy Rev.* **27**, 445–452 (2013)
- Karmakar, A.; Karmakar, S.; Mukherjee, S.: Properties of various plants and animals feedstocks for biodiesel production. *Biores. Technol.* **101**, 7201–7210 (2010)
- Motaseemi, F.; Ani, F.N.: A review on microwave-assisted production of biodiesel. *Renew. Sustain. Energy Rev.* **16**(7), 4719–4733 (2012). <https://doi.org/10.1016/j.rser.2012.03.069>
- Nomanbhay, S.; Ong, M.Y.: A review of microwave-assisted reactions for biodiesel production. *Bioengineering* **4**(2), 57 (2017). <https://doi.org/10.3390/bioengineering4020057>
- Wilson A.B. and Dobrev A.: (2015) Energy supply and security, European Parliamentary Research Service, 2019, PE 630.275
- World Bioenergy Association, Global Bioenergy Statistics 2018, www.worldbioenergy.org
- Thangavelu, S.K.; Ahmed, A.S.; Ani, F.N.: Review on bioethanol as alternative fuel for spark ignition engines. *Renew. Sustain. Energy Rev.* **56**, 820–835 (2015). <https://doi.org/10.1016/j.rser.2015.11.089>
- Atelge, M.R.; Senol, H.; Djaafri, M.; Hansu, T.A.; Krisa, D.; Atabani, A.; Eskicioglu, C.; Muratçobanoğlu, H.; Unalan, S.; Kalloum, S., et al.: A critical overview of the state-of-the-art methods for biogas purification and utilization processes. *Sustainability* **13**, 11515 (2021). <https://doi.org/10.3390/su132011515>
- Chincholkar, S.P.; Srivastava, S.; Rehman, A.; Dixit, S.; Lanjewar, A.: Biodiesel as an alternative fuel for pollution control in diesel engine. *Asian J. Exp. Sci.* **19**(2), 13–22 (2005)
- Guo, S.; Yang, Z.; Gao, Y.: Effect of adding biodiesel to diesel on the physical and chemical properties and engine performance of fuel blends. *J. Biobased Mater. Bioenergy* **10**, 34–43 (2016). <https://doi.org/10.1166/jbmb.2016.1566>
- Bhattacharyya, S.; Reddy, C.S.: Vegetable oils as fuels for internal combustion engines. *J. Agric. Eng. Res.* **57**, 157–166 (1994)
- Directive 2003/30/EC of the European Parliament and of the Council of 8 May 2003 on the promotion of the use of biofuels or other renewable fuels for transport.
- Wijesekara, R.G.; Nomura, N.; Sato, S.; Matsumura, M.: Pre-treatment and utilization of raw glycerol from sunflower oil biodiesel for growth and 1, 3-propanediol production by *Clostridium butyricum*. *J. Chem. Technol. Biotechnol.* **83**(7), 1072–1080 (2008)
- Vignesh, G.; Barik, D.: Chapter 6 - toxic waste from biodiesel production industries and its utilization. In: Debabrata, B. (Ed.) *Woodhead publishing series in energy, energy from toxic organic waste for heat and power generation*. Woodhead Publishing (2019)
- Ma, F.; Hanna, M.A.: Biodiesel production: a review. *Bioresour. Technol.* **70**, 1–15 (1999)
- Mahanta, P., Shrivastava, A.: (2004), Technology development of biodiesel as an energy alternative. Available from: <http://newagepublishers.com/samplechapter/001305.pdf>
- Gebremariam, S.N.; Marchetti, J.M.: Biodiesel production technologies: review. *AIMS Energy* **5**(3), 425–457 (2017). <https://doi.org/10.3934/energy.2017.3.425>
- Salahelddeen, M.; Mariod, A.A.; Aroua, M.K.; Rahman, S.M.A.; Soudagar, M.E.M.; Fattah, I.M.R.: Current state and perspectives on transesterification of triglycerides for biodiesel production. *Catalysts* **11**, 1121 (2021). <https://doi.org/10.3390/catal11091121>
- Jaichandar, S.; Annamalai, K.: The Status of biodiesel as an alternative fuel for diesel engine – an overview. *J. Sustain. Energy Environ.* **2**, 71–75 (2011)
- Giuffrè, A.M.; Capocasale, M.; Zappia, C.; Poiana, M.: Biodiesel from tomato seed oil: transesterification and characterisation of chemical-physical properties. *Agron. Res.* **15**(1), 133–143 (2017)
- Cheng, Z.Z.; Lin, S.S.; Lei, R.; Yan, X.C.; Nie, Y.J.: Synthesis of biodiesel from used cooking oils catalyzed by solid acid. *Adv. Mater. Res.* **236–238**, 496–500 (2011). <https://doi.org/10.4028/www.scientific.net/AMR.236-238.496>



31. Lam, M.K.; Jamalluddin, N.A.; Lee, K.T.: Chapter 23 - production of biodiesel using palm oil. In: Ashok, P.; Christian, L.; Claude-Gilles, D.; Edgard, G.; Samir, K.K.; Steven, R. (Eds.) In biomass, biofuels, biochemicals, biofuels: alternative feedstocks and conversion processes for the production of liquid and gaseous biofuels, 2nd edn. Academic Press (2019)
32. Banković-Ilić, I.B.; Stamenković, O.S.; Veljković, V.B.: Biodiesel production from nonedible plant oils. *Renew. Sustain. Energy Rev* **16**(6), 3621–3647 (2012)
33. Orsavova, J.; Misurcova, L.; Ambrozova, J.V.; Vicha, R.; Mlcek, J.: Fatty Acids composition of vegetable oils and its contribution to dietary energy intake and dependence of cardiovascular mortality on dietary intake of fatty acids. *Int. J. Mol. Sci.* **16**(6), 12871–12890 (2015). <https://doi.org/10.3390/ijms160612871>
34. Giakoumis, E.G.: Analysis of 22 vegetable oils' physico-chemical properties and fatty acid composition on a statistical basis, and correlation with the degree of unsaturation. *Renew. Energy* **126**, 403–419 (2018). <https://doi.org/10.1016/j.renene.2018.03.057>
35. Statista., 2022. "Worldwide oilseed production by type, 2020/2021 Statista", <https://www.statista.com/statistics/267271/worldwide-oilseed-production-since-2008/>, accessed on February 01, 2022
36. USDA, Economic Research Service, 2021, "Oil Crops Sector at a Glance", <https://www.ers.usda.gov/topics/crops/soybeans-oil-crops/oil-crops-sector-at-a-glance/>, accessed on February 01, 2022
37. OCDE/FAO, 2021, OECD-FAO Agricultural Outlook 2021–2030, in OCDE (eds.), Paris, <https://doi.org/10.1787/19428846-en>
38. Matthaus, B.; Özcan, M.M.; Al Juhaimi, F.: Some rape/canola seed oils: fatty acid composition and tocopherols Z *Naturforsch C. J. Biosci.* **71**(3–4), 73–77 (2016). <https://doi.org/10.1515/znc-2016-0003> (PMID: 27023318)
39. Hazrat, M.A.; Rasul, M.G.; Mofijur, M.; Khan, M.M.K.; Djavanroodi, F.; Azad, A.K.; Bhuiya, M.M.K.; Silitonga, A.S.: A Mini review on the cold flow properties of biodiesel and its blends. *Front. Energy Res.* **8**, 598651 (2020). <https://doi.org/10.3389/fenrg.2020.598651>
40. Farm Energy 2019, "Rapeseed and Canola for Biodiesel Production". <https://farm-energy.extension.org/rapeseed-and-canola-for-biodiesel-production/>. Accessed on February 01, 2022
41. Yoon, H.Y.; Park, S.H.; Suh, H.K.; Lee, C.S.: Effect of biodiesel-ethanol blended fuel spray characteristics on the reduction of exhaust emissions in a common-rail diesel engine. *J. Energy Resour. Technol.*, **132**, 042201–042207 (2010)
42. Cardone, M., Prati, M.V., Rocco, V., and Senatore, A.: 1998, Experimental analysis of performances and emissions of a diesel engine fuelled with biodiesel and diesel oil Blends, Proc. MIS—MAC V, Roma, pp. 211–225
43. De Vita, A., Alaggio, M., and Cavaliere, M.: (1999) Direct Injection Diesel Engines Fuelled with Diesel and Diesel Oil blends: Performances and Emissions, Proc. 54v ATI Congress, L'Aquila, Italy, pp. 547–556
44. Laforgia, D.; Ardito, V.: Biodiesel fuelled IDI engines: performances, emissions and heat release investigation. *Biores. Technol.* **51**, 53–59 (1995)
45. Singh, B.; Kaur, J.; Singh, K.: Production of biodiesel from used mustard oil and its performance analysis in internal combustion engine. *J. Energy Resour. Technol.* **132**, 031001–031004 (2010)
46. Schumacher, L.G.; Hires, W.G.; Borgelt, S.C.: Fuelling diesel engines with methyl-ester soybean oil, liquid fuels from renewable resources. *Proc. Altern. Energ. Conf.* **25**, 52 (1992)
47. Love, N.D.; Parthasarathy, R.N.; Gollahalli, S.R.: Rapid characterization of radiation and pollutant emissions of biodiesel and hydrocarbon liquid fuels. *J. Energy Resour. Technol.* **131**, 012202–012209 (2009)
48. Carrarotto, C., et al.: Biodiesel as alternative fuel: experimental analysis and energetic evaluations. *Energy* **29**, 2195–2211 (2004)
49. Moreno, F.; Munoz, M.; Morea-Roy, J.: Sunflower methyl ester as a fuel for automobile diesel engines. *Trans. ASABE* **42**, 1181–1186 (1999)
50. Che, M.S.; Idroas, M.Y.; Hamid, M.F.; Zainal, Z.A.: Performance and emissions of straight vegetable oils and its blends as a fuel in diesel engine: a review. *Renew. Sustain. Energy Rev* **82**, 808–823 (2018). <https://doi.org/10.1016/j.rser.2017.09.080>
51. Monirul, I.M.; Masjuki, H.H.; Kalam, M.A.; Zulkifli, N.W.M.; Rashedul, H.K.; Rashed, M.M.; Imdadul, H.K.; Mosarof, M.H.: A comprehensive review on biodiesel cold flow properties and oxidation stability along with their improvement processes. *R. Soc. Chem.* **5**(105), 86631–86655 (2005). <https://doi.org/10.1039/C5RA09555G>
52. Atabani, A.E.; Silitonga, A.S.; Ong, H.C.; Mahlia, T.M.I.; Masjuki, H.H.; Badruddin, I.A.; Fayaz, H.: Non-edible vegetable oils: a critical evaluation of oil extraction, fatty acid compositions, biodiesel production, characteristics, engine performance and emissions production. *Renew. Sustain. Energy Rev.* **18**, 211–245 (2013)
53. Bamgboye, A.I.; Hansen, A.C.: Prediction of cetane number of biodiesel fuel from the fatty acid methyl ester (FAME) composition. *Int. Agrophys.* **22**, 21–29 (2008)
54. Bezaire, N.; Wadumesthrige, K.; Simon Ng, K.Y.; Salley, S.O.: Limitations of the use of cetane index for alternative compression ignition engine fuels. *Fuel* **89**, 3807–3813 (2010)
55. Ramírez-Verduzco, L.F.; Rodríguez-Rodríguez, J.E.; del Rayo, A.; Jacob, J.: Predicting cetane number, kinematic viscosity, density, and higher heating value of biodiesel from its fatty acid methyl ester composition. *Fuel* **91**, 102–111 (2012)
56. Fu, J.: Flash points measurements and prediction of biofuels and biofuel blends with aromatic fluids. *Fuel* **241**, 892–900 (2018). <https://doi.org/10.1016/j.fuel.2018.12.105>
57. Hoekman, S.; Robbins, C.: Review of the effects of biodiesel on NOx emissions. *Fuel Process. Technol.* **96**, 237–249 (2012). <https://doi.org/10.1016/j.fuproc.2011.12.036>
58. DIN EN 14214. 2019. Liquid petroleum products-Fatty acid methyl esters (FAME) for use in diesel engines and heating applications-Requirements and test methods. European Standards
59. ASTM D6751-20a. (2020) Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels. American Society for Testing and Materials. DOI: <https://doi.org/10.1520/D6751-20A>
60. Jääskeläinen, H.E.: (2011) Biodiesel Standards and Properties, In: DieselNet technology guide. https://dieselnet.com/tech/fuel_biodiesel_std.php
61. Song, H.; Quinton, K.S.; Peng, Z.; Zhao, H.; Ladommatos, N.: Effects of oxygen content of fuels on combustion and emissions of diesel engines. *Energies* **9**, 28 (2016). <https://doi.org/10.3390/en9010028>
62. Kathirvelu, B.; Subramanian, S.; Govindan, N.; Santhanam, S.: Emission characteristics of biodiesel obtained from jatropha seeds and fish wastes in a diesel engine. *Sustain. Environ. Res.* **27**(6), 283–290 (2017). <https://doi.org/10.1016/j.serj.2017.06.004>
63. Bui, T.T.; Balasubramanian, D.; Hoang, A.T.; Konur, O.; Nguyen, D.C.; Tran, V.N.: Characteristics of PM and soot emissions of internal combustion engines running on biomass-derived DMF biofuel: a review. *Energy Sour., Part A: Recov., Utilization, Environ. Effects* (2020). <https://doi.org/10.1080/15567036.2020.1869868>
64. Xue, J.; Grift, T.; Hansen, A.: Effect of biodiesel on engine performances and emissions. *Renew. Sustain. Energy Rev.* **15**, 1098–1116 (2011). <https://doi.org/10.1016/j.rser.2010.11.016>

65. Boubahri, C. (2013) Etudes des performances d'un moteur à explosion interne fonctionnant en mélange de carburant, PhD thesis, National School of Engineers of Tunis
66. Boubahri, C.; Ennetta, R.; Said, R.; Bessrou, J.: Experimental study of a diesel engine performance running on waste vegetable oil biodiesel blend, *ASME. J. Energy Resour. Technol.* **134**, 032202 (2012)
67. Amara, A. B., Lecoite, B., Jeuland, N., Takahashi, T., Iida, Y., Hashimoto, H. and Bouilly, J.: (2014) Experimental Study of the Impact of Diesel/Biodiesel Blends Oxidation on the Fuel Injection System. *SAE International Journal of Fuels and Lubricants*, 7(3), 849–860. <http://www.jstor.org/stable/26273724>
68. Hoang, A.T.; Tabatabaei, M.; Aghbashlo, M.: A review of the effect of biodiesel on the corrosion behavior of metals/alloys in diesel engines. *Energy Sour, Part A: Recov., Utilization, Environ. Effects* **42**(23), 2923–2943 (2020). <https://doi.org/10.1080/15567036.2019.1623346>
69. Alves, S.M.; KaicDutra-Pereira, F.: Biodiesel compatibility with elastomers and steel. In: Jacob-Lopes, E.; Zepka, L.Q. (Eds.) *Frontiers in bioenergy and biofuels*. IntechOpen (2017)
70. Palani, Y.; Devarajan, C.; Manickam, D.; Thanikodi, S.: Performance and emission characteristics of biodiesel-blend in diesel engine: a review. *Environ. Eng. Res.* **27**(1), 200338 (2022). <https://doi.org/10.4491/eer.2020.338>
71. Murillo, S.; Miguez, J.L.; Porteiro, J.; Granada, E.; Moran, J.C.: Performance and exhaust emissions in use of biodiesel in outboard diesel engines. *Fuel* **86**, 1765–1771 (2007)
72. Allen Jeffrey, J.: Effectiveness of palm oil biodiesel on performance and emission characteristics in a compression Ignition engine. *Int. J. Sci. Eng. Technol. Res.* **6**, 546–550 (2017)
73. Sateesh, K.A.; Yaliwal, V.S.; Soudagar, M.E.M., et al.: Utilization of biodiesel/Al₂O₃ nanoparticles for combustion behavior enhancement of a diesel engine operated on dual fuel mode. *J Therm Anal Calorim* **147**, 5897–5911 (2022). <https://doi.org/10.1007/s10973-021-10928-7>
74. Gavhane, S.R.; Kate, M.A.; Pawar, A.; Safaei, M.R.; Soudagar, M.E.; Mujtaba Abbas, M.; Muhammad Ali, H.; Banapurmath, R.; Goodarzi, N.; Badruddin, I.A.; Ahmed, W.; Shahapurkar, K.: Effect of zinc oxide nano-additives and soybean biodiesel at varying loads and compression ratios on VCR diesel engine characteristics. *Symmetry* **12**, 1042 (2020). <https://doi.org/10.3390/sym12061042>
75. Soudagar, M.E.M.; Mujtaba, M.; Safaei, M.R.; Afzal, A.; Raju, V.D.; Ahmed, W.; Banapurmath, N.R.; Houssain, N.; Bashir, S.; Badruddin, I.A.; Goodarzi, M.; Shahapurkar, K.; Taqui, S.N.: Effect of Sr@ZnO nanoparticles and Ricinus communis biodiesel-diesel fuel blends on modified CRDI diesel engine characteristics. *Energy* (2020). <https://doi.org/10.1016/j.energy.2020.119094>
76. Soudagar, M.E.M.; Afzal, A.; Safaei, M.R., et al.: Investigation on the effect of cottonseed oil blended with different percentages of octanol and suspended MWCNT nanoparticles on diesel engine characteristics. *J. Therm. Anal. Calorim.* **147**, 525–542 (2022). <https://doi.org/10.1007/s10973-020-10293-x>
77. Dias, J.M.; Alvim-Ferraz, M.C.M.; Almeida, M.F.: Comparison of the performance of different homogeneous alkali catalysts during transesterification of waste and virgin oils and evaluation of biodiesel quality. *Fuel* **87**(17–18), 3572–3578 (2008). <https://doi.org/10.1016/j.fuel.2008.06.014>
78. Fedai, O.: (2006) Transesterifikasyon ile Kanola Yağı Metil Esteri Sentezinin Optimizasyonu Y.Lisans Tezi, Gazi Üniversitesi, Fen Bilimleri Enstitüsü, Ankara, Turkey
79. Vicente, G.; Martínez, M.; Aracil, J.: Integrated biodiesel production: a comparison of different homogeneous catalysts systems. *Bioresour. Technol.* **92**(3), 297–305 (2004). <https://doi.org/10.1016/j.biortech.2003.08.014>
80. Çildir, O.; Çanakci, M.: *An investigation of the effects of catalyst and alcohol amounts on the fuel properties of biodiesel from various vegetable oils* Çeşitli bitkisel yağlardan biyodizel üretiminde katalizör ve alkol miktarının yakıt özellikleri üzerine etkisinin incelenmesi. *J. Faculty Eng. Arch. Gazi Univ.* **21**, 367–372 (2006)
81. Azcan, N.; Danisman, A.: Alkali catalyzed transesterification of cottonseed oil by microwave irradiation. *Fuel* **86**, 2639–2644 (2007)
82. Sabudak, T.; Yildiz, M.: Biodiesel production from waste frying oils and its quality control. *Waste Manage.* **30**, 799–803 (2010). <https://doi.org/10.1016/j.wasman.2010.01.007>
83. Meher, L.C.; Dharmagadda, V.S.S.; Naik, S.N.: Optimization of alkali-catalyzed transesterification of Pongamia pinnata oil for production of biodiesel. *Biores. Technol.* **97**(12), 1392–1397 (2006). <https://doi.org/10.1016/j.biortech.2005.07.003>
84. Özsezen A.N.: (2007) Atık palmiye yağından üretilen biyodizelin motor performans ve emisyon karakterleri üzerine etkisinin incelenmesi, (Doktora Tezi), Kocaeli Üniversitesi Makine Eğitimi ABD, Kocaeli
85. Bouaid, A.; Martínez, M.; Aracil, J.: Production of biodiesel from bioethanol and Brassica carinata oil: oxidation stability study. *Biores. Technol.* **100**, 2234–2239 (2009). <https://doi.org/10.1016/j.biortech.2008.10.045>
86. Alptekin, E.; Canakci, M.; Sanli, H.: Biodiesel production from vegetable oil and waste animal fats in a pilot plant. *Waste Manage.* **34**(11), 2146–2154 (2014). <https://doi.org/10.1016/j.wasman.2014.07.019>
87. Abdul-Majeed, W.S.; AAl-Thani, G.S.; Al-Sabahi, J.N.: Application of flying jet plasma for production of biodiesel fuel from wasted vegetable oil. *Plasma Chem. Plasma Process* **36**, 1517–1531 (2016). <https://doi.org/10.1007/s11090-016-9735-0>
88. Muley, P.D.; Wang, Y.; Hu, J.; Shekhawat, D.: Microwave-assisted heterogeneous catalysis. In: Spivey, J.; Han, Y.-F.S.; Dushyant, S. (Eds.) *Catalysis: Volume 33*. Royal Society of Chemistry (2021)
89. Khan, H.M.; Iqbal, T.; Mujtaba, M.A.; Soudagar, M.E.M.; Veza, I.; Fattah, I.M.R.: Microwave assisted biodiesel production using heterogeneous catalysts. *Energies* **14**, 8135 (2021). <https://doi.org/10.3390/en14238135>
90. Palm, M.O.; de Freitas, A.; Barbosa, S.L.; Gonçalves, M.W.; Duarte, D.A.; de Camargo Catapan, R.; de Carvalho Pinto, C.R.S.: Plasma-assisted catalytic route for transesterification reactions at room temperature. *Fuel* **307**, 121740 (2022). <https://doi.org/10.1016/j.fuel.2021.121740>
91. Li, J.; Ma, C.; Zhu, S.; Yu, F.; Dai, B.; Yang, D.: A review of recent advances of dielectric barrier discharge plasma in catalysis. *Nanomaterials* **9**(10), 1428 (2019)
92. Lu, X.; Laroussi, M.; Puech, V.: On atmospheric-pressure non-equilibrium plasma jets and plasma bullets. *Plasma Sour. Sci. Technol.* **21**, 777–788 (2012)
93. Hyun, Y.-J.; Mok, Y.-S.; Jang, D.-I.: Transesterification of vegetable oils in pulsed-corona plasma discharge process. *J. Korean Oil Chem. Soc.* **29**(1), 81–88 (2012)
94. Cubas, A.L.V., et al.: Biodiesel production using fatty acids from food industry waste using corona discharge plasma technology. *Waste Manage* **47**, 149–154 (2016). <https://doi.org/10.1016/j.wasman.2015.05.040>
95. Oliveira, P.A.; Baesso, R.M.; Moraes, G.C.; Alvarenga, A.; Costa-Félix, R.P.: Ultrasound methods for biodiesel production and analysis biofuels - state of development. IntechOpen (2018)
96. Costa-Felix, R.P.B.; Ferreira, J.R.L.: Comparing ultrasound and mechanical steering in a biodiesel production process. *Phys. Procedia* **70**, 1066–1069 (2015). <https://doi.org/10.1016/j.phpro.2015.08.227>



97. Shinde, K.; Kaliaguine, S.: A comparative study of ultrasound biodiesel production using different homogeneous catalysts. *ChemEngineering* **3**(1), 18 (2019). <https://doi.org/10.3390/chemengineering3010018>
98. Stavarache, C.; Vinatoru, M.; Maeda, Y.: Aspects of ultrasonically assisted transesterification of various vegetable oils with methanol. *Ultrason Sonochem.* **14**(3), 380–386 (2007). <https://doi.org/10.1016/j.ultsonch.2006.08.004>
99. Shinde, K.; Nohair, B.; Kaliaguine, S.: A parametric study of biodiesel production under ultrasounds. *Int. J. Chem. React. Eng.* **15**, 117–125 (2017)
100. Oliveira, P.A.; Baesso, R.M.; Morais, G.C.; Alvarenga, A.V.; Costa-Félix, R.P.B.: Ultrasound-assisted transesterification of soybean oil using low power and high frequency and no external heating source. *Ultrasonics Sonochem.* **78**, 105709 (2021). <https://doi.org/10.1016/j.ultsonch.2021.105709>
101. Mohamad Aziz, N.A.; Yunus, R.; Kania, D.; Abd Hamid, H.: Prospects and challenges of microwave-combined technology for biodiesel and biolubricant production through a transesterification: a review. *Molecules* **26**, 788 (2021)
102. Nayak, S.N.; Bhasin, C.P.; Nayak, M.G.: A review on microwave-assisted transesterification processes using various catalytic and non-catalytic systems. *Renew. Energy* **143**, 1366–1387 (2019)
103. Soltani, S.; Rashid, U.; Yunus, R.; Taufiq-Yap, Y.H.: Synthesis of biodiesel through catalytic transesterification of various feedstocks using fast solvothermal technology: a critical review. *Catal. Rev.* **57**(4), 407–435 (2015). <https://doi.org/10.1080/01614940.2015.1066640>
104. Li, H.; Zhang, C.; Pang, C.; Li, X.; Gao, X.: The advances in the special microwave effects of the heterogeneous catalytic reactions. *Front. Chem.* **8**, 355 (2020). <https://doi.org/10.3389/fchem.2020.00355>
105. Khedri, B.; Mostafaei, M.; Safieddin Ardebili, S.M.: A review on microwave-assisted biodiesel production. *Energy Sourc., Part A: Recov., Utilization, Environ. Effects* (2018). <https://doi.org/10.1080/15567036.2018.1563246>
106. Baghurst, D.R.; Mingos, D.M.P.: Superheating effects associated with microwave dielectric heating. *J. Chem. Soc. Chem. Commun.* **20**, 674–677 (1992). <https://doi.org/10.1039/c39920000674>
107. Berlan, J.; Giboreau, P.; Lefevre, S.; Marchand, C.: Synthèse organique sous champ microondes : premier exemple d'activation spécifique en phase homogène. *Tetrahedron Lett.* **32**, 2363–2366 (1991). [https://doi.org/10.1016/S0040-4039\(00\)79924-2](https://doi.org/10.1016/S0040-4039(00)79924-2)
108. de la Hoz, A.; Diaz-Ortiz, A.; Moreno, A.: Microwaves in organic synthesis. thermal and non-thermal microwave effects. *Chem. Soc. Rev.* **3**, 164 (2005)
109. Azcan, N.; Danisman, A.: Microwave assisted transesterification of rapeseed oil. *Fuel* **87**(10–11), 1781–1788 (2008). <https://doi.org/10.1016/j.fuel.2007.12.004>
110. Duz, M.Z.; Saydut, A.; Ozturk, G.: Alkali catalyzed transesterification of safflower seed oil assisted by microwave irradiation. *Fuel Process. Technol.* **92**, 308–313 (2011). <https://doi.org/10.1016/j.fuproc.2010.09.020>
111. Sherbiny, S.A.; Refaat, A.A.; Sheltawy, S.T.: Production of biodiesel using the microwave technique. *J. Adv. Res.* **1**, 309–314 (2010)
112. Kumar, R.; Ravi, K.G.; Chandrashekar, N.: Microwave assisted alkali-catalyzed transesterification of Pongamia pinnata seed oil for biodiesel production. *Bioresour. Technol.* **102**, 6617–6620 (2011). <https://doi.org/10.1016/j.biortech.2011.03.024>
113. Encinar, J.M.; González, J.F.; Martínez, G.; Sánchez, N.; Pardal, A.: Soybean oil transesterification by the use of a microwave flow system. *Fuel* **95**, 386–393 (2012). <https://doi.org/10.1016/j.fuel.2011.11.010>
114. Venkatesh, K.H.; Regupathi, I.; Saidutta, M.B.: Optimization of two step karanja biodiesel synthesis under microwave irradiation. *Fuel Process. Technol.* **92**, 100–105 (2011). <https://doi.org/10.1016/j.fuproc.2010.09.003>
115. Chen, H.-Y.; Cui, Z.-W.: A microwave-sensitive solid acid catalyst prepared from sweet potato via a simple method. *Catalysts* **6**, 211 (2016). <https://doi.org/10.3390/catal6120211>
116. Hernando, J.; Leton, P.; Matia, M.P.; Novella, J.L.; Alvarez, Builla J.: Biodiesel and FAME synthesis assisted by microwaves: homogeneous batch and flow processes. *Fuel* **86**, 1641–1644 (2007)
117. Boldor D., Kanitkar A., Muley P., Balasubramanian S., Lima M., Sabliov C.M.: (2010) Microwave-assisted Transesterification of Soybean and Rice Bran Oil to Biodiesel, Pittsburgh, Pennsylvania, June 20 - June 23, ASABE Paper No. 1009067. doi:<https://doi.org/10.13031/2013.29799>
118. Mostafaei, M.; Ghobadian, B.; Barzegar, M.; Banakar, A.: Optimization of ultrasonic assisted continuous production of biodiesel using response surface methodology. *Ultrason. Sonochem.* **27**, 54–61 (2015). <https://doi.org/10.1016/j.ultsonch.2015.04.036>
119. Pandit, P.R.; Fulekar, M.H.: Egg shell waste as heterogeneous nanocatalyst for biodiesel production: optimized by response surface methodology. *J. Environ. Manage.* **198**, 319–329 (2017). <https://doi.org/10.1016/j.jenvman.2017.04.100>
120. Sabzimalaki, M.; Ghobadian, B.; Farsibaf, M.M.; Najafi, G.; Soufi, M.D.; Ardebili, S.M.S.: Optimization of biodiesel ultrasound-assisted synthesis from castor oil using response surface methodology (RSM). *Chem. Prod. Process. Model.* **10**(2), 123–133 (2015). <https://doi.org/10.1515/cppm-2014-0013>
121. Gole, V.L.; Gogate, P.R.: Intensification of synthesis of biodiesel from non-edible oil using sequential combination of microwave and ultrasound. *Fuel Process. Technol.* **106**, 62–69 (2013). <https://doi.org/10.1016/j.fuproc.2012.06.021>
122. Martinez-Guerra, E.; Gude, V.G.: Synergistic effect of simultaneous microwave and ultrasound irradiations on transesterification of waste vegetable oil. *Fuel* **137**, 100–108 (2014). <https://doi.org/10.1016/j.fuel.2014.07.087>
123. Chipurici, P.; Vlaicu, A.; Calinescu, I.; Vinatoru, M.; Vasilescu, M.; Ignat, N.D.; Mason, T.J.: Ultrasonic, hydrodynamic and microwave biodiesel synthesis – a comparative study for continuous process. *Ultrason. Sonochem.* **57**, 38–47 (2019). <https://doi.org/10.1016/j.ultsonch.2019.05.011>
124. Deshpande, S.R.; Sunol, A.K.; Philippidis, G.: Status and prospects of supercritical alcohol transesterification for biodiesel production. *Wiley Interdiscipl. Rev.: Energy Environ.* **6**(5), e252 (2017). <https://doi.org/10.1002/wene.252>
125. Saka, S.; Kusdiana, D.: Biodiesel fuel from rapeseed oil as prepared in supercritical methanol. *Fuel* **80**, 225 (2001)
126. Madras, G.; Kolluru, C.; Kumar, R.: Synthesis of biodiesel in supercritical fluids. *Fuel* **83**, 2029–2033 (2004)
127. Hawash, S.; Kamal, N.; Zaher, F.; Kenawi, O.; Diwani, E.: Biodiesel fuel from jatropha oil via noncatalytic supercritical methanol. *Fuel* **88**, 579–582 (2009)
128. Demirbas, A.: Biodiesel from waste cooking oil via base-catalyzed and supercritical methanol transesterification. *Energy Convers. Manage.* **50**, 923–927 (2009)

129. Micic, R.D.; Tomic, M.D.; Kiss, F.E.; Nikolic-Djoric, E.B.; Simikic, M.D.: Influence of reaction conditions and type of alcohol on biodiesel yields and process economics of supercritical transesterification. *Energy Convers. Manage* **86**, 717–726 (2014)
130. Singh, C.S.; Kumar, N.; Gautam, R.: Supercritical transesterification route for biodiesel production: effect of parameters on yield and future perspectives. *Environ Prog. Sustain. Energy*. **40**(6), e13685 (2021). <https://doi.org/10.1002/ep.13685>
131. Patil, P.D.; Reddy, H.; Muppaneni, T.; Ponnusamy, S.; Cooke, P.; Schuab, T.; Deng, S.: Microwave-mediated non-catalytic transesterification of algal biomass under supercritical ethanol conditions. *J Supercrit Fluids*. **79**, 67–72 (2013)

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