

Biodiesel: A Potential Replacement Fuel for Compression Ignition Engines to Meet the Sustainability Criteria

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Abstract

Biodiesel has shown great potential as a replacement fuel for Compression Ignition engines to meet sustainability criteria. Biodiesel has been found to reduce greenhouse gas emissions, particulate matter, and other harmful pollutants. Furthermore, Biodiesel fits into conventional diesel engines without much modification, making it a viable option for the transportation sector. Global demand for fossil fuels has risen dramatically because of fast technological progress and population growth. The trend is anticipated to continue, with estimates from the US Energy Information Administration (EIA) predicting a 28 percent increase in energy consumption between 2015 and 2040. Biodiesel is one of the newest alternatives to fossil fuels that has attracted a lot of interest due to its similarities to diesel. World energy demand is increasing due to expanding economic activity, which in turn is driven by population growth and improving standards of living. Economic activity, in one way or another, requires mobility, and this is consuming most of the world's oil supply. In this regard, energy consumption in the transport sector is becoming the determining factor in sustaining ever-increasing economic activity. Meanwhile, the transport sector is responsible for about 29% of total energy-related CO₂ emissions. The possible solution suggested by many scholars, to avert the negative environmental effect of using conventional transport fuels, entails shifting to renewable forms of energy like liquid biofuels and electricity. Among the liquid biofuels, biodiesel is receiving due recognition for its environmental and fuel benefits. The use of biodiesel as a transport fuel has many advantages and disadvantages. These are associated with several factors including the characteristics of the raw materials used, and the type of processes applied for biodiesel production. This paper examines the research carried out with biodiesel as a transport fuel, emphasizing the technical and economic aspects of the advantages of using biodiesel as a transport fuel. The various biodiesel fuel properties are examined and the major factors affecting these properties are indicated.

Keywords: Biodiesel, Biodiesel Properties, feed stocks, Sustainable Alternative, Biodiesel Standards, Blending, Transesterification, Compound Annual Growth Rate.

Introduction

Biodiesel (America's first domestically produced, commercially available advanced biofuel and meets EPA requirements for inclusion and use under the new Renewable Fuel Standard (RFS-2)) has received much attention in the past decade due to its ability. It is one of the sources to replace fossil fuels, which are likely to run out within a century. Especially, the environmental issues concerned with the exhaust gas emissions by the usage of fossil fuels also encourage the use of biodiesel, which has proved to be eco-friendly more than fossil fuels. Biodiesel made from agricultural products (oxygenated by nature) reduces India's and most of the countries' dependence on oil imports, supports local agricultural industries and enhances farming incomes and offers benefits in terms of usually reduced emissions. Among those, vegetable oils, animal fats, their derived biodiesels (methyl or ethyl esters) and bio-alcohols are considered as very promising fuels. The advantages of biodiesels as diesel fuel are

minimal sulfur and aromatic content, and higher flash point, lubricity, cetane number, biodegradability and non-toxicity.

The global market for Biodiesel is estimated at US\$34.9 Billion in 2023 and is projected to reach US\$49.4 Billion by 2030, growing at a Compound Annual Growth Rate (CAGR) of 5.1% from 2023 to 2030. Growth in the biodiesel market is driven by several factors, including supportive government policies, technological advancements in production, and a growing collective environmental consciousness among consumers. Governments worldwide are offering tax incentives and subsidies to promote biodiesel as part of their efforts to reduce carbon emissions and boost renewable energy use. Technological improvements have also made biodiesel production more efficient and cost-effective, broadening its appeal and feasibility across various sectors. Additionally, the shift in consumer behavior towards more sustainable and eco-friendly products has increased demand for biodiesel[1]. Figure 1 illustrates the global market for Biodiesel estimates.

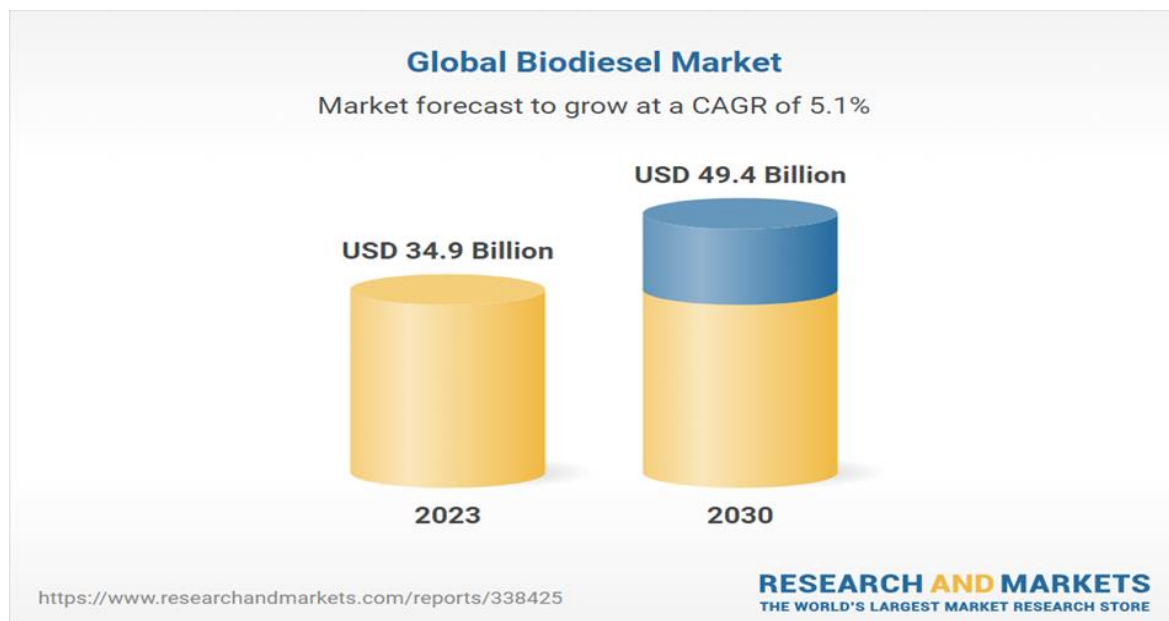


Figure 1 The global market for Biodiesel estimates [1].

The existing petroleum reserves are limited and are to be completely exhausted soon. World energy demand is increasing due to expanding economic activity, which in turn is driven by population growth and improving standards of living. The faster population growth rate has led to a massive hike in demand for energy consumption[2]. The fossil fuels derived from the existing petroleum reserves extend significant energy generation contributions to the present day. Hence, the day is not far enough when the global community will barely be left with any stock of petroleum products such as gasoline, diesel, and by-products [3]. Moreover, fossil fuels such as petrol (gasoline), diesel, and aviation fuels in internal combustion engines result in severe air pollution, which is highly detrimental to the sustenance of all life on earth [4,5]. Although compression ignition engines (diesel engines) are one of the most efficient energy conversion devices, their exhaust emissions pose a danger to the environment. Diesel engines, especially heavy-duty ones, form the backbone of the modern transport sector worldwide. Conventional diesel has been widely used in diesel engines. The fuel properties of diesel make it the most suitable for undergoing ignition due to compression in diesel engines[6]. However, certain drawbacks of conventional diesel have been a great concern. Diesel fuel has poor lubricating properties. The combustion of diesel results in severe exhaust emissions such as the NO_x emission causes lung cancer and SO_x concentration is the prime source of acid rain. The low flash point of diesel makes its transportation and storage very hazardous. Therefore, the need of the hour is to switch to some alternate source(s) of fuel or energy that can enhance the performance and control the exhaust emissions of modern-day diesel engines[7]. Many researchers, scientists, and environmentalists have been working to develop alternate fuel and energy sources for years[2]. Consequently, solar energy, biodiesel, lithium-ion and lithium-sulfur batteries, CNG, and hydrogen fuel have evolved as keys to cater

to the need for the rising fuel demand with simultaneous control of air pollution and degrading environment [8-14]. Among the various alternative fuels, biodiesel has proven to be very promising in improving the diesel engine's performance and mitigating its dangerous exhaust emissions[15].

Conversion technologies for biodiesel production

Biodiesel derived from domestic renewable sources such as animal fats, vegetable oils, and algal oil has considerably similar properties and characteristics to petroleum-based diesel, making it a promising alternative fuel. Edible oils are commonly produced from edible feedstocks such as coconut oil, soybean oil, palm oil, rapeseed oil, olive oil, corn oil, etc. Different non-edible oils including jatropha oil, petroleum nut oil, and castor oil can also be used for biodiesel production. In the case of waste oils, the possible feedstocks are waste cooking oil, fish oil, animal tallow oil, and pyrolysis oil while algal oil is usually sourced from *Chlorella vulgaris* algae. Generally, the process flow for biodiesel production includes feedstock production and harvesting, oil extraction, oil refining, transesterification, and distillation.

Biodiesel Production

The production process, known as transesterification, involves reacting the raw material with alcohol in the presence of a catalyst to produce biodiesel and glycerine, a valuable byproduct.

Biodiesel origin lies in nature, specifically in the agricultural farm fields, as biodiesel is derived from many edible and non edible oilseeds. The biodiesel is extracted from edible vegetable oil sources such as soybean, sunflower, safflower, coconut, palm, rapeseed, olive, linseed, cashew nut, corn, neem, and rice bran. On the other hand, the sources of non-edible oilseeds are mahua, karanja and jatropha. Waste cooking oil and meat tallow are also sources of biodiesel. Biodiesel is mainly the mono-alkyl ester of long-chain fatty acids obtained from various oilseeds. Biodiesel is produced by many processes such as hydro-treating of crop oils, Fischer- Tropsch process, rapid pyrolysis, micro-emulsion, dilution, and transesterification. It then is subjected to purification by various methods such as ion-exchange resins. The general way of production of biodiesel is through trans-esterification, in which the primary process is the conversion of the triglycerides into diglycerides. The secondary process involves the conversion of diglycerides into mono-glycerides. Also tertiary step involves the conversion of mono-glycerides into glycerol and biodiesel or Fatty Acid Methyl Ester (FAME). In this method, the vegetable oil is made to react with alcohol by including a catalyst, preferably hydroxides of metal, and producing methyl and ethyl ester. Moreover, alcohol usage with alkali as a catalyst in the trans-esterification process has proven promising for biodiesel production.

Biodiesel production from vegetable oils

Transesterification of vegetable oils with simple alcohol has long been the preferred method for producing biodiesel. In general, there are two methods of transesterification. One method simply uses a catalyst, and the other is without a catalyst. The former method has a long history of development, and the biodiesel produced by this method is now available in North America, Japan and some Western European countries [16].

The process of production of biodiesel from vegetable oils is depicted in Figure 2. The energetics have indicated that about 50 kW of electricity per ton of biodiesel is required, of which 60–70% is consumed for the production of glycerin. The process requires mixing of vegetable oil with a mixture prepared by dissolving the KOH catalyst in methanol and heating at 70°C while stirring for 1 h. The mixture is allowed to settle under gravity. The glycerin, being heavier, settles down in the bottom layer and the upper layer constitutes the biodiesel (esters). The glycerin is separated and the esters are washed with water for catalyst recovery. The biodiesel layer is finally dried using silica gel and it is now ready for blending with diesel in various proportions for engine operation[16]. The blend, for convenience, is referred to as Bxx, where XX indicates the amount of biodiesel in percentage in the blend (i.e. B-20 blend is 20% biodiesel and 80% diesel).

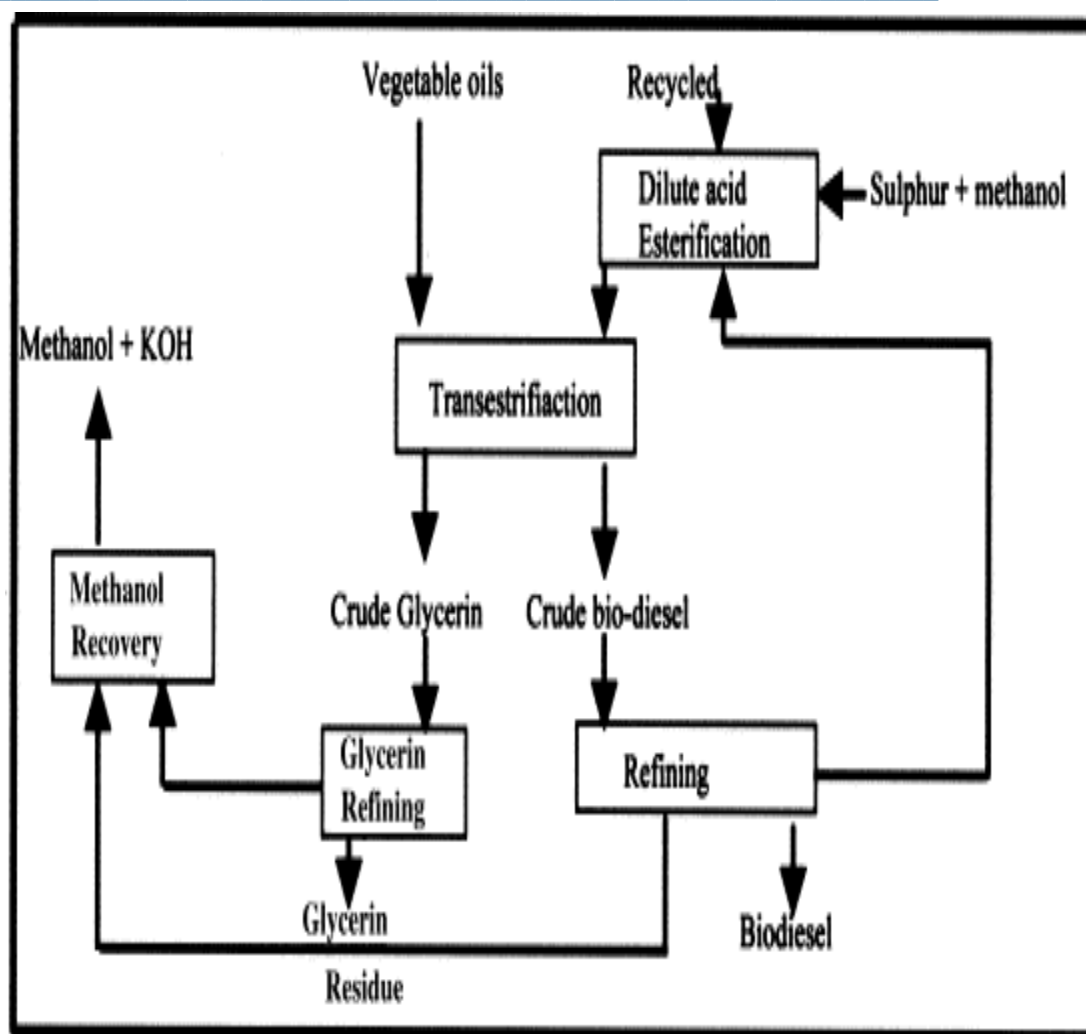


Figure 2 Biodiesel production from vegetable oils [16].

2.2 Biodiesel Production from Waste Animal Fat

All the chemicals used are of analytical grade. To increase biodiesel production, the acquired fat must be pre-processed before being exposed to the transesterification procedure. This involves eliminating nonfatty macro residues and water content in fats, adjusting the pH, and liquefying them. Fatty acids that separate from glycerol during hydrolysis are known as free fatty acids [FFA]. Any fat with less than 15% FFA is referred to as yellow grease because of its yellowish hue. Brown grease has a brownish-black color and is composed of highly oxidized fats with FFA levels above 15%. Fat is extracted using a thermal method, which includes melting the fat into liquid and pushing it out of the matrix using heat.

Figure 3 illustrates a schematic diagram of the Biodiesel Production from Waste Animal Fat. In the reaction chamber, acid (H_2SO_4) and base (KOH) catalysts are employed separately to react with alcohol and fat molecules. The chamber heat was increased gradually to maintain the constant temperature. It runs with the best process parameters and a stopwatch to keep track of reaction time. The molar ratio (1: 1 to 1: 6), catalyst concentrations of 0.1 to 2.0 wt%, temperatures (30–60°C), and time durations of 1 to 4 hrs were used. Following transesterification, the reaction mixture must be purified to meet biodiesel quality requirements. Gravity decantation was used to separate the reaction products into biodiesel and glycerol, and the biodiesel was then water-washed and dried. The water washing was done with 5% (v/v) hot water at 60°C for 15 min. To ensure that all residues were removed, the washing operation was repeated four times. After water wash, the biodiesel is dried at 110°C.

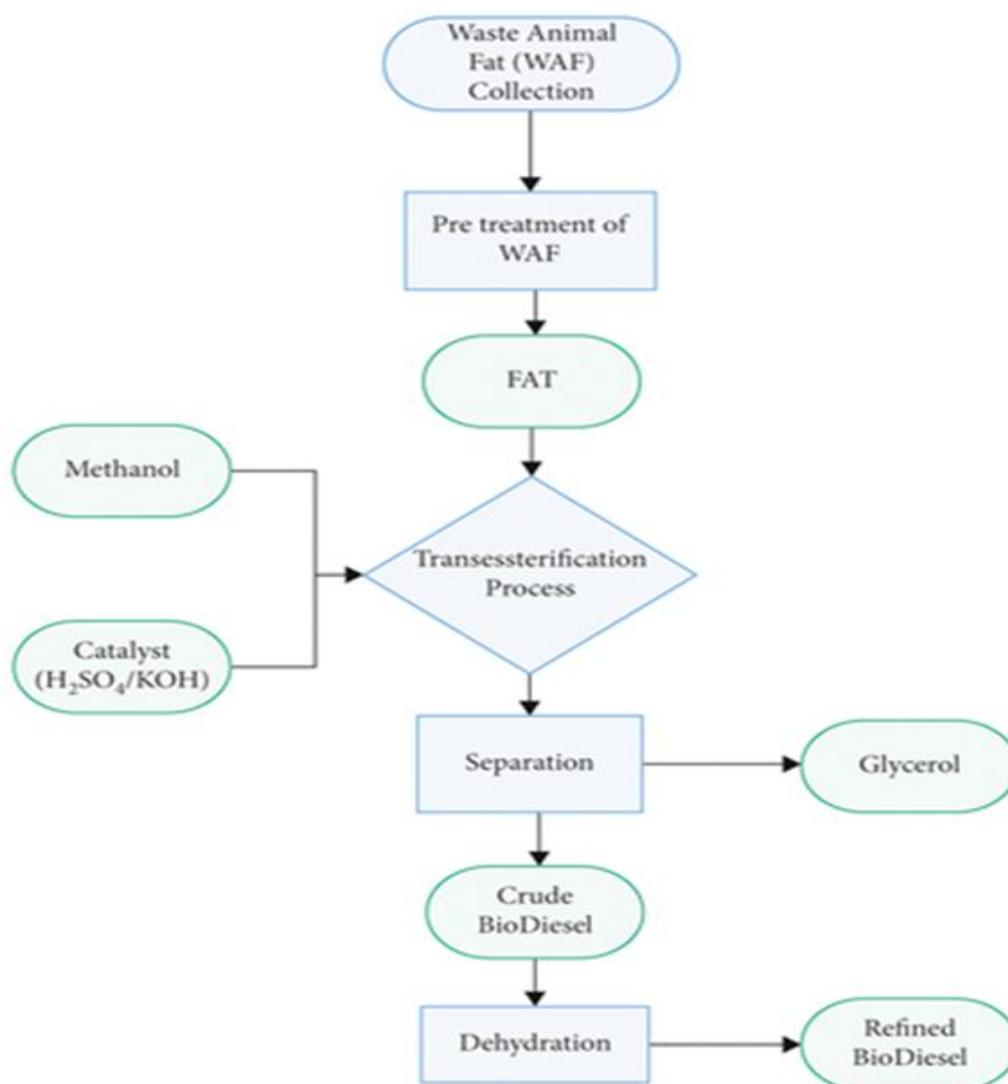


Figure 3: Schematic diagram of the Biodiesel Production from Waste Animal Fat

Feedstocks

The main step for biodiesel production is the selection of feedstock. Each type of feedstock has a different composition of fatty acids, which defines the properties of biodiesel, and finally it affects the life cycle of biodiesel. The physical and chemical properties of oils obtained from different feedstocks are described by many authors [2-10,16-17]. Depending on the raw feedstock, biodiesel can be classified as one of four biofuel generations: (1) produced from edible oil, (2) produced from oils of nonedible plants, (3) produced from microalgae lipids, used cooking oil, or waste animal fats, and (4) produced from genetically modified microorganisms (12). Given classification includes only the origin of biodiesel but does not consider the quality and properties of the final product obtained from diverse feedstocks. The section below briefly describes the current state, development, application, advantages, and limitations for each generation of biofuel.

Biodiesel fuel standards

As far as the quality of biodiesel is concerned, there are no universally accepted fuel standards that can be applied worldwide. Different markets use their specific fuel quality standards.

Table 1. The most important biodiesel quality standards in the world.

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Country / region	Specifications	Description
EU	EN 14213	Heating fuels – Fatty acid methyl esters (FAME) – Requirements and test methods
EU	EN 14214	EN 14214 Automotive fuels – Fatty acid methyl esters (FAME) for diesel engines – Requirements and test methods
USA	ASTM D 6751	ASTM D6751 – 11a Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels
Australia		Fuel Standard (Biodiesel) Determination 2003
Brazil	ANP 42	Brazilian Biodiesel Standard (Agência Nacional do Petróleo)
India	IS15607	Biodiesel (B 100) blend stock for diesel fuel – Specification
Japan	JASO M360	Automotive fuel – Fatty acid methyl ester (FAME) as blend stock
South Africa	SANS 1935	Automotive biodiesel fuel

This variation in fuel quality standards is mainly due to reasons such as the variation in the types of diesel engines used, government regulations associated with emissions, the country's stage of development, the purpose of the fuel use, as well as the climatic conditions of the country or region where the biodiesel is used. Table 1 describes the most common diesel quality standards in the world [41].

Advantages of biodiesel fuel

Among the many important advantages of biodiesel fuel, some can be pointed out when comparing it with petroleum diesel for transportation. They are listed below:

- Biodiesel is non-aromatic, almost sulfurless, produced from renewable sources, presently vegetable oils or animal fats. On the other hand, the lubricity property of biodiesel is much better than that of low-sulfur diesel fuel. Little biodiesel additive (about 1%) is enough to significantly improve the conventional diesel fuel's lubricity.
- Full life cycle analysis indicates that, on average, biodiesel emits less CO₂ than conventional fossil fuels. The use of biomass energy has the potential to greatly reduce GHG emissions and thus biodiesel has a significantly smaller contribution to global warming when compared to fossil fuels. Although fossil fuels release carbon dioxide captured by photosynthesis millions of years ago, biomass releases carbon dioxide

that is largely balanced by the carbon dioxide captured in its growth, depending on how much energy was used to grow, harvest, and process the fuel.

- Biodiesel tailpipe CO₂ emissions per mass unit of biodiesel burnt are lower than for petroleum diesel. It has reduced visible smoke, noxious fumes and odors, and emits 40–50% less particulate matter (PM), 30–70% less HC, 20–50% less CO, and less 50% in soot emissions, although the NO_x may be about 10–15% higher this problem can be overcome by retarding the injection timing.
- Raw materials can be produced in marginal land or in such a way that increases soil productivity due to the utilization of crops that allow the fixation of nitrogen in the soil.
- Many different types of crops can be used depending on the local soil and climatic conditions. Also, wastes that are hard to deal with, such as animal fats, can be used as well. The broad variety of raw materials makes it possible to produce biodiesel at the local scale, to be used in a farm or at industrial production, for example, to supply transportation fuels at a regional or even at national scale.
- When compared to other biofuels, such as bioethanol from corn, biodiesel has higher energy content and requires less energy, water and materials per unit of energy produced.
- The technologies associated with the production of biodiesel and preprocessing of raw materials are simple and easy to implement based on currently available process units.
- It is safe for use in all conventional diesel engines and offers similar performance and engine durability as petroleum diesel fuel. Therefore, no new types of engines are necessary, or significant changes to existing ones, making the adoption of biofuel simpler and reducing the resistance to change.
- Biodiesel has 10–20% higher oxygen content than pure diesel, it is eco-friendly, inexhaustible, and readily available from agricultural sources and biomass.

Monitoring the quality of biodiesel

Biodiesel quality can be provided efficiently if its entire manufacturing process is monitored: from monitoring feedstock acidity to assuring complete separation of biodiesel

from glycerin to removing the excess of alcohol and contaminants before its marketing.

Quality assurance and monitoring should include storage, testing, blending and distribution. Fuel quality monitoring is conducted by independent laboratories that can

accredit manufacturers, distributors and quality analysis laboratories. One example is the

BQ-9000® program in the United States of America, a program based on voluntary cooperation, which accredits manufacturers, marketers and biodiesel quality analysis

laboratories. Monitoring the quality of biodiesel contributes to its promotion and public

acceptance [1,18].

Biodiesel fuel properties

The properties of biodiesel can be grouped by multiple criteria. The most important are those that influence the processes taking place in the engine (ignition qualities, ease of starting, formation and burning of the fuel-air mixture, exhaust gas formation and quality [17,18].

Stringent quality assurance criteria are required for the successful commercialization and market acceptance of biodiesel. The properties of biodiesel indicate if it is appropriate for the engine's performance, longevity,

emissions, sulfated ash, carbon residue, and copper-strip corrosion. Acid number, calorific value, viscosity, cetane number, density, flash point, fire point, cloud point, pour point, Content of metals (Ca, Na, Mg, K and P) and other characteristics distinguish biodiesel [1,17,18].

Cetane number

Cetane number (CN) is a dimensionless indicator that characterizes the ignition quality of fuels for compression ignition engines (CIE). Since in the CIE burning of the fuel-air mixture is initiated by compression ignition of the fuel, the cetane number is a primary indicator of fuel quality as it describes the ease of its self-ignition. Theoretically, the cetane number is defined in the range of 15-100; the limits are given by the two reference fuels used in the experimental determination of the cetane number:

a linear-chain hydrocarbon, hexadecane ($C_{16}H_{34}$, also called n-cetane), very sensitive to ignition, having a cetane number of 100, and a strongly branched-chain hydrocarbon, 2,2,4,4,6,8,8-heptamethylnonane (HMN, also called isocetane), having the same chemical formula $C_{16}H_{34}$, with high resistance to ignition, having a cetane number of 15. The cetane number is the percentage by volume of normal cetane in a mixture of normal cetane and HMN, which has the same ignition characteristics as the test fuel. Thus the cetane number is given by the formula: $CN = n\text{-cetane } [\%, v/v] + 0.15 \times HMN [\%, v/v]$. Determination of the cetane number on the mono-cylinder engine specially designed for this purpose (EN ISO 5165, ASTM D613) is an expensive and lengthy operation. A cheaper and faster alternative is to determine the derived cetane number through ignition delay in a constant-volume combustion chamber (ignition quality tester – IQT), a widely accepted method described in ASTM D6890 and ASTM D7170, accepted by the biodiesel quality standard ASTM D6751. The cetane number indicates ignition delay, i.e. the time elapsed since the injection of fuel into the combustion chamber and self-ignition of the fuel-air mixture. Thus, ignition time lag means a low cetane number and vice versa. The upper and lower limits of the cetane number ensure the proper functioning of the engine. If the cetane number is too low, starting the engine will be difficult, especially at low temperatures and the engine will function unevenly and noisily, with cycles without combustion, it will warm more slowly, combustion will be incomplete and engine pollution will increase, especially hydrocarbon emissions. In the case of a fuel with a very high cetane number, ignition will be carried out before a proper mix with air, resulting in incomplete combustion and an increase in the amount of exhaust smoke. Also, if the cetane number is too high the fuel will ignite close to the injector causing it to overheat, and unburned fuel particles can plug the injector nozzles. The optimal range of the CN is between 41 and 56 but must not be higher than 65 [19]. The minimum cetane number of biodiesel is 51 in the European Union, 47 in the United States and 45 in Brazil. The minimum CN for diesel oil is 40 in the USA (ASTM D 975) and 51 in Europe (EN 590). The cetane numbers of the main pure methyl and ethyl esters [20,21].

The cetane number of a substance depends on its molecular structure. The cetane number decreases with the number of double bonds, nd , in fatty acid ester molecules (degree of unsaturation, characterized by the iodine number) and increases with the number of carbon atoms, nc . Generally, the cetane number of ethyl esters is higher than that of methyl esters. Methyl- and ethyl palmitate as well as methyl- and ethyl stearate have a high cetane number, but methyl- and ethyl linoleate have a low cetane number. The cetane number of biodiesel depends on the cetane number and the concentration of the esters it is made up of. The cetane number of biodiesels is higher than that of the vegetable oils from which they are produced ($34.6 < CN < 42$) and is between 39 and 67. The cetane number values of biodiesel produced from various feedstocks are presented [21-25].

Heat of combustion

The heat of combustion (heating value) at constant volume of a fuel containing only the elements carbon, hydrogen, oxygen, nitrogen, and sulfur is the quantity of heat liberated when a unit quantity of the fuel is burned in oxygen in an enclosure of constant volume, the products of combustion being gaseous carbon dioxide, nitrogen, sulfur dioxide, and water, with the initial temperature of the fuel and the oxygen and the final temperature of the products at $25^{\circ}C$. The unit quantity can be mol, kilogram or normal square meter. Thus the units of measurement of the heating value are $\ln \text{ kJ/kmol}$ or kJ/kg . The volumetric heat of combustion, i.e. the heat of combustion per unit volume of fuel, can be calculated by multiplying the mass heat of combustion by the density of the fuel (mass

per unit volume). The volumetric heat of combustion rather than the mass heat of combustion is important to volume-dosed fueling systems, such as diesel engines. The gross (or high, upper) heating value (Q_g) is obtained when all products of the combustion are cooled down to the temperature before the combustion and the water vapor formed during combustion is condensed. The net or lower heating value (Q_n) is obtained by subtracting the latent heat of vaporization of the water vapor formed by the combustion from the gross or higher heating value. The net heat of combustion is related to the gross heat of combustion: $Q_n = Q_g - 0.2122 \cdot H$, where H is the mass percentage of hydrogen in the fuel. As in internal combustion engines, the temperature of exhaust gases is higher than the boiling temperature of water (water vapor is discharged), for assessing the heating value of the fuel, the lower heating value of the biodiesel is more relevant. The heating value of fatty acid esters increases with molecular chain length (with the number of carbon atoms, n_c) and decreases with their degree of unsaturation (the number of double bonds, n_d) [18]. The mass heating value of unsaturated esters is lower than that of saturated esters, however, due to their higher density, the volume heating value of unsaturated esters is higher than that of saturated esters. For example, methyl stearate ($n_d=0$) has a mass heating value of 40099 kJ/kg, and methyl oleate ($n_d=1$) has 40092 kJ/kg. As reported to the volume unit, the heating value of methyl stearate is 34070 kJ/L, while the volume heating value of methyl oleate is 34320 kJ/L. The presence of oxygen in the ester molecules decreases the heating value of biodiesel by 10...13% compared to the heating value of diesel fuel [18]. Since fuel dispensing in CIE is volumetric, the energy content of the injected dose will be reduced in the case of biodiesel, therefore, the specific fuel consumption for biodiesel will be higher. This is partially compensated by the fact that the density of biodiesel is higher than that of diesel fuel.

Density of biodiesel

Fuel density (ρ) is the mass of unit volume, measured in a vacuum. Since density is strongly influenced by temperature, the quality standards state the determination of density at 15 °C. Fuel density directly affects fuel performance, as some of the engine properties, such as cetane number, heating value and viscosity are strongly connected to density. The density of the fuel also affects the quality of atomization and combustion. As diesel engine fuel systems (the pump and the injectors) meter the fuel by volume, modification of the density affects the fuel mass that reaches the combustion chamber, and thus the energy content of the fuel dose, altering the fuel/air ratio and the engine's power. Knowing the density is also necessary in the manufacturing, storage, transportation and distribution process of biodiesel as it is an important parameter to be taken into account in the design of these processes. The density of esters depends on the molar mass, the free fatty acid content, the water content and the temperature. Density values determined for pure esters are presented [18] and for different biodiesel feedstock are listed [18]. The density of biodiesel is typically higher than that of diesel fuel and is dependent on fatty acid composition and purity. As biodiesel is made up of a small number of methyl or ethyl esters that have very similar densities, the density of biodiesel varies between tight limits. Contamination of the biodiesel significantly affects its density; therefore density can also be an indicator of contamination.

Viscosity of biodiesel

The viscosity of liquid fuels is their property to resist the relative movement tendency of their composing layers due to intermolecular attraction forces (viscosity is the reverse of fluidity). Viscosity is one of the most important properties of biodiesel. Viscosity influences the ease of starting the engine, the spray quality, the size of the particles (drops), the penetration of the injected jet and the quality of the fuel-air mixture combustion [26]. Fuel viscosity has both an upper and a lower limit. The fuel with a too-low viscosity provides a very fine spray, the drops having a very low mass and speed. This leads to insufficient penetration and the formation of black smoke specific to combustion in the absence of oxygen (near the injector) [19].

Too viscous biodiesel leads to the formation of too big drops, which will penetrate the wall opposite the injector. The cylinder surface being cold, will interrupt the combustion reaction and blue smoke will form (an intermediate combustion product consisting of aldehydes and acids with a pungent Odor) [19]. Incomplete combustion results in lower engine power. Too high viscosity leads to the increase of combustion chamber deposits and the increase of the needed fuel pumping energy, as well as the increased wear of the pump and the injector elements due to higher mechanical effort. Too high viscosity also causes operational problems at low temperatures because the

viscosity increases with decreasing temperature (for temperatures at or below $-20\text{ }^{\circ}\text{C}$ viscosity should be at or below $48\text{ mm}^2/\text{s}$). Viscosity also influences the lubricity of the fuel as some elements of the fuel system can only be lubricated by the fuel (pumps and injectors). Due to the presence of electronegative oxygen, biodiesel is more polar than diesel fuel; as a result, the viscosity of biodiesel is higher than that of diesel fuel. The viscosity of pure ethyl esters is higher than the viscosity of methyl esters [18]. The viscosities of biodiesels from different feedstocks are presented [18].

Cold flow properties

Generally, all fuels for CIE may cause starting problems at low temperatures, due to worsening of the fuel's flow properties at those temperatures. The cause of these problems is the formation of small crystals suspended in the liquid phase, which can clog fuel filters partially or totally. Because of the sedimentation of these crystals on the inner walls of the fuel system's pipes, the flow section through the pipes is reduced, causing poor engine fueling. In extreme situations, when low temperatures persist longer (e.g. overnight), the fuel system can be completely blocked by the solidified fuel. The cold flow performances of the fuels can be characterized by the cloud point (CP), the pour point (PP), the cold filter plugging point (CFPP) and viscosity (ν). An alternative to CFPP is the low-temperature flow test (LTFT). Recently, the U.S. introduced a new method for assessing the cold flow properties of biodiesel, called the cold soak filtration test (CSFT).

Cloud point (CP)

The cloud point (CP) is the temperature at which crystals first start to form in the fuel. The cloud point is reached when the temperature of the biodiesel is low enough to cause wax crystals to precipitate. Initially, cooling temperatures cause the formation of solid wax crystal nuclei that are submicron in scale and invisible to the human eye. Further decrease of temperature causes these crystals to grow. The temperature at which crystals become visible (the crystal's diameter $\geq 0.5\text{ }\mu\text{m}$) is defined as the cloud point because the crystals form a cloudy suspension. Below the CP these crystals might plug filters or drop to the bottom of a storage tank. The CP is the most commonly used measure of low-temperature operability of the fuel. The biodiesel cloud point is typically higher than the cloud point of conventional diesel. The cloud point of biodiesel depending on the nature of the feedstock is between $-5\text{ }^{\circ}\text{C}$ (ALME) and $17\text{ }^{\circ}\text{C}$ (TME)[21, 25].

Pour point (PP)

The pour point is the temperature at which the fuel contains so many agglomerated crystals that it is essentially a gel and will no longer flow. This occurs if the temperature of the biodiesel drops below CP when the microcrystals merge and form large clusters, which may disrupt the flow of the biodiesel through the pipes of the engine's fuel system. Similarly to the cloud point, the pour point values also depend on the feedstock the biodiesel produced [18]. Pour point values are between $-15\text{ }^{\circ}\text{C}$ (REE and YMEE) and $16\text{ }^{\circ}\text{C}$ (PME). Although CP and PP are relatively easily determined, they only provide indicative values for the minimum temperature at which the fuel can be used. While at cloud point the fuel can still be used in acceptable conditions, at pour point this is no longer possible. In other words, the cloud point overestimates the minimum operating temperature, and the pour point underestimates it.

Cold filter plugging point (CFPP)

The cold filter plugging point is the lowest temperature at which 20 mL of fuel passes through a filter within 60 s by applying a vacuum of 2 kPa. The CFPP test employs rapid cooling conditions. For this reason, CFPP does not reflect the actual limit of the fuel's operability temperature. The test does not take into account the fuel systems specially designed to operate at low temperatures (heavy-duty vehicles and some light-duty vehicles). Nevertheless, most standards require the determination of this parameter and its value is regulated depending on the climatic conditions of each region or country. The values of the CFPP of biodiesel produced from various feedstocks are listed [18]. CME has the lowest value, while TME has the highest. Biodiesel produced from the most common feedstocks has inferior cold flow properties compared to conventional diesel fuel (has a higher cloud point and pour point compared to petroleum diesel), which can lead to operational issues in cold climates,

such as filter plugging due to wax buildup or reduced fuel flow. Conventional diesel blends with 10 % (v/v) biodiesels typically have significantly higher CP, PP and CFPP than petroleum diesel fuel.

Low-temperature flow test (LTFT)

Although CFPP is accepted almost worldwide as the minimum temperature at which fuel can be exploited, mainly because of the rapid cooling of the sample, the test does not entirely reflect the real cooling conditions of the fuel. The Low-Temperature Flow Test (LTFT) is a similar attempt to the test determining the CFPP, the major difference being the cooling speed of the fuel sample, which in this case is 1 °C/h, reflecting more accurately the real conditions, when for example the fuel in the fuel system of a vehicle is cooled over a frosty night. In determining the low-temperature flow temperature the sample volume is 180 mL, the filter is finer, and the vacuum filtration pressure is higher. Like CFPP, LTFT is defined as the lowest temperature at which 180 mL of fuel safely passes through the filter within 60 s. Since the LTFT is not included in biodiesel quality standards, currently there is very limited information about its values for biodiesel [18].

Cold soak filtration test (CSFT)

This test is the newest requirement under ASTM D6751, added in 2008 in response to data indicating that in blends with petroleum diesel of up to 20% some biodiesels could form precipitates above the cloud point. Some substances that are or seem to be soluble at ambient temperature come out of the solution if temperature decreases or biodiesel is stored at ambient temperature for a longer period. This phenomenon was observed both in the case of pure biodiesel and its blends with diesel fuel. Solid or semi-liquid substances can, in turn, cause filter clogging. The CSFT allows highlighting this danger and improving biodiesel due to this phenomenon. Cold soak consists of chilling a 300 ml sample for 16 hours at 4 °C, then warming it up to ambient temperature (68-72 °F, 20-22 °C) and filtering with a 0.7-micron glass Fiber filter with a stainless-steel filter support. The result of this test is filtering time. There are two time limits for filtration: in the case of net biodiesel for use throughout the year, the filtration time is 360 seconds or less; if the seller claims the post-blended biodiesel is fit for use in temperatures below 10 °F (-12 °C) the filtration time is 200 seconds or less. The test result depends mainly on the type and quality of the used feedstock, the purity of biodiesel, the soap value, the total glycerin, etc. The higher the soap value, the higher the cold soak filtration results. In addition, it was found that total glycerin can also negatively influence the cold soak filtration results. When the total glycerin is within the ASTM D 6751 standard's limits (Less or equal to 0.24%), it will show no negative effect on the cold soak filtration results [25]. Because CSFT has only recently been included in biodiesel quality standards, at present there is very little reported data on this parameter [18].

Biodiesel lubricity

Lubricity describes the ability of the fuel to reduce the friction between surfaces that are under load. This ability reduces the damage that can be caused by friction in fuel pumps and injectors [27]. Lubricity is an important property consideration when using low and ultra-low sulfur fuels (ULSD). The fuel lubricity can be measured with High Frequency Reciprocating Rig (HFRR) test methods as described in ISO 12156-1. The maximum corrected wear scar diameter (WS 1.4) for diesel fuels is 460 μm (EN 590). Reformulated diesel fuel has a lower lubricity and requires lubricity-improving additives (which must be compatible with the fuel and with any additives already found in the fuel) to prevent excessive engine wear. The lubricity of biodiesel is excellent. Biodiesel may be used as a lubricity improver. The lubricity of some biodiesels and the influence of biodiesel concentration on this parameter in blends with diesel fuel are shown [21,27]. The lubricity of biodiesel depends on the feedstock it is produced from. Biodiesel from jatropha oil has the highest and biodiesel sunflower oil has the lowest lubricity. Generally, it can be stated that 1% (v/v) biodiesel mixed with ultra-low sulfur diesel fuel (ULSD) already provides lubricity that meets the requirements of the commercial diesel fuel's lubricity quality standards.

Flash Point (FP)

The flash point is the minimum temperature calculated to a barometric pressure of 101.3 kPa at which the fuel will ignite (flash) on application of an ignition source under specified conditions. It is used to classify fuels for

transport, storage and distribution according to hazard level. The flash point does not affect the combustion directly; higher values make fuel safer concerning storage, fuel handling and transportation. FP varies inversely with the fuel's volatility. The minimum flash point for biodiesel is 93 °C in the United States, 100 °C in Brazil, and 120 °C in Europe. Biodiesel's flash point decreases rapidly as the amount of residual (un-reacted) alcohol increases (methanol's flash point is 11–12 °C, and ethanol's is 13–14 °C). Thus, measuring the biodiesel flash point helps indicate the presence of methanol or ethanol. For example, the presence of 0.5% methanol in biodiesel reduces biodiesel flash point from 170 °C to 50 °C. If the flash point is used to determine the methanol content, the ASTM standard imposes for it a minimum value of 130 °C. This limit may be considered too severe because at the maximum permissible concentration of methanol of 0.2% w/w biodiesel flash point drops below 130 °C. The flash point of biodiesel produced from various feedstocks is available [21, 22, 23, 24, 25, 28, 29].

Acid value

The acid value (AV), also called neutralization number or acid number is the mass in milligrams, of potassium hydroxide (KOH) required to neutralize the acidic constituents in one gram of the sample. The acid value determination is used to quantify the presence of acid moieties in a biodiesel sample. In a typical procedure, a known amount of sample dissolved in an organic solvent is titrated with a solution of potassium hydroxide with known concentration and with phenolphthalein as a color indicator. The acidic compounds that could be found in biodiesel are 1) residual mineral acids from the production process, 2) residual free fatty acid from the hydrolysis process or the post-hydrolysis process of the esters and 3) oxidation byproducts in the form of other organic acids [30]. This parameter is a direct measure of the content of free fatty acids, thus the corrosiveness of the fuel, of filter clogging and the presence of water in the biodiesel. A too-high amount of free glycerin can cause functioning problems at reduced temperatures and fuel filter clogging. This parameter can also be used to measure the freshness of the biodiesel. Fuel that has oxidized after long-term storage will probably have a higher acid value.

Iodine value

The iodine value (IV) or iodine number was introduced in biodiesel quality standards for

evaluating their stability to oxidation. The IV is a measurement of the total unsaturation of fatty acids measured in g iodine/100 g of biodiesel sample when formally adding iodine to the double bonds. Biodiesel with high IV is easily oxidized in contact with air. The iodine value highly depends on the nature and ester composition of the feedstocks used in biodiesel production. Therefore the IV is limited in various regions of the world depending on the specific conditions: 120 in Europe and Japan, 130 in Europe for biodiesel as heating oil, 140 in South Africa, in Brazil it is not limited and in the U.S., Australia and India it is not included in the quality standard (it would exclude feedstocks like sunflower and soybean oil). Biodiesel with high IV tends to polymerize and form deposits on injector nozzles, piston rings and piston ring grooves. The tendency of polymerization increases with the degree of unsaturation of the fatty acids.

Biodiesel stability

Biodiesel quality can be affected by oxidation during storage (in contact with air) and

hydrolytic degradation (in contact with water). The two processes can be characterized by the oxidative stability and hydrolytic stability of the biodiesel. Biodiesel oxidation can occur during storage while awaiting distribution or within the vehicle fuel system itself.

The stability of biodiesel can refer to two issues: *long-term storage stability or aging* and

stability at elevated temperatures or pressures as the fuel is recirculated through an engine's fuel system [31]. For biodiesel, storage stability is highly important. Storage stability refers to the ability of the fuel to resist chemical changes during long-term storage. These changes usually consist of oxidation due to contact with oxygen from the air [32]. Biodiesel composition greatly affects its stability in contact with air. Unsaturated fatty acids, especially the polyunsaturated ones (e.g. C18:2 and C18:3) have a high tendency to oxidation. After oxidation, hydroperoxides (one hydrogen atom and 2 oxygen atoms) are attached to the fatty acid chain. Oxidation reactions can be catalyzed by some of the materials present (the material the reservoir is produced from) and light. After the

chemical oxidation reactions, hydroperoxides are produced that can, in turn, produce short-chain fatty acids, aldehydes, and ketones. Hydroperoxides can polymerize forming large molecules. Thus, oxidation increases the viscosity of biodiesel. In addition, oxidation increases acid value, the color changes from yellow to brown, solid deposits can form in the engine fuel system (pipes and filters), the lubricity and heating value of the biodiesel is reduced. When water is present, the esters can hydrolyze to long-chain free fatty acids, which also causes the acid value to increase [32]. These acids can catalyze other degradation reactions such as reverse trans-esterification and oxidation. The water required for hydrolysis can be present as a contaminant [33]. For determining the oxidation stability of biodiesel two types of tests are currently used: the Rancimat test, contained in EN 14214 and the oxidative stability index (OSI) included in ASTM D6751.

The Rancimat test method (EN 14112, EN 15751) is an accelerated oxidation test in which the biodiesel to be tested is run at elevated temperatures (110 °C) whilst exposing the sample to a stream of purified air (10 L/hour) accelerating the oxidation process of the oil. After passing through the biodiesel, the air is fed into a collection flask containing distilled water and a probe to measure conductivity. As the biodiesel sample degrades, the volatile organic acids produced are carried to the collection flask, and the conductivity of the solution is recorded by the probe. Oxidation stability will be given by the induction period, defined as the time between the start of the test and the sudden conductivity increase of the solution in the collection flask. This results in auto-oxidation in a few hours, instead of months.

The oxidative stability index (OSI) is another measurement method of the conductivity

increase caused by the formation of secondary products in the oxidation process. The OSI is defined as the time until the conductivity of a biodiesel sample rises most rapidly during an accelerated oxidation test. The oxidation of biodiesel is influenced by its composition (increases with the level of unsaturation of fatty acids in its composition), i.e. the feedstock used to manufacture the biodiesel. For example, the content of oleic acid methyl ester in the case of biodiesel produced from sunflower oil may vary between 48 and 74%. In addition, the induction period of biodiesel made from rapeseed oil is 12 times greater than those obtained from soybean oil and 25 times higher than those produced from linseed oil. The presence of metals (the tank walls and metals contained in the biodiesel) can accelerate the oxidation process, whereas sulfur is an antioxidant [30]. Oxidation stability can be improved by using the appropriate additives. Additives such as tert-butylhydroquinone (TBHQ), butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), propyl gallate (PrG) and alpha-tocopherol (vitamin E) have been found to enhance the storage stability of biodiesel. Biodiesels produced from some feedstocks (e.g. soybean oil) naturally contain some antioxidants. Any fuel that will be stored for more than 6 months, whether it is diesel fuel or biodiesel, should be treated with an antioxidant additive [32].

Water and sediments

Water content is a purity indicator for the biodiesel. Biodiesel should be dried after water

washing to get the water specification below 500 ppm (0.050 %). Even when biodiesel is dried properly by the producer, water can accumulate during storage and transportation.

The moisture accumulated in biodiesel leads to the increase of free fatty acid concentration, which can corrode metal parts of the engine's fuel system. Biodiesel is much more hygroscopic (it attracts water) than diesel oil. The biodiesel absorbs water during storage when the temperature is higher and the water absorbed is precipitated at lower temperatures. Following these repeated processes, the accumulated water is deposited on the bottom of the tank. Water in biodiesel facilitates microbial growth and the formation of sediments. To measure the water and sediment content, a 100 mL sample of undiluted fuel is centrifuged at a relative centrifugal force of 800 for 10 minutes at 21 to 32°C (70 to 90°F).

After centrifugation, the volume of water and sediment that has settled into the tip of the centrifuge tube is read to the nearest 0.005 mL and reported as the volumetric percent of water and sediment.

Sulfated ash

Sulfated ash is a measure of ash formed from inorganic metallic compounds. After the

burning of biodiesel, in addition to CO₂ and H₂O a quantity of ash is formed consisting of unburned hydrocarbons and inorganic impurities (e.g. metal impurities). Metallic ash is very abrasive and may cause excessive wear of the cylinder walls and the piston ring.

Carbon residue

Carbon residue indicates the presence of impurities and deposits in the engine combustion chamber and is also an indicator of the quantity of glycerides, free fatty acids, soaps and transesterification reaction catalyst residues.

Copper-strip corrosion

Copper-strip corrosion is an indicator of the corrosiveness of biodiesel, of the presence of fatty acids derived from materials that did not enter a reaction during the production process.

Content of metals

The content of metals (Ca, Na, Mg, K and P) can lead to combustion chamber deposits, filter- and fuel injection pump clogging, and can harm the catalyst.

Tables of selected Biodiesel properties

The selected properties of the biodiesel are given in Table 1.

Table 1 Properties of different biodiesels [34,35,36, 37].

Sl No.	Biodiesel	Density [kg/m ³]	Kinematic Viscosity [mm ² /s]	Specific Heat Capacity [kJ/kg K]	Boiling Point/Smoke Point [° Celsius]	LCV [MJ/Kg]	Cetane No.
1	Jatropha	873	4.23	0.082	219	38.2–42.15	33.7–51
2	Karanja	880–890	4.37–9.6	–	316	34–38.8	45–67
3	Mahua	880–916	3.98–5.72	–	–	35.6–38.9	43.5
4	Diesel	850	2.44–2.6	2.05	–	43	50
5	JOME	862–886	–	–	–	37.2–43	43–59
6	KOME	865–898	–	–	–	36–42.1	36–61
7	MOME	828–865	–	–	–	36.8–43	47–51
8	Linseed	920	–	1.88	–	37.7–39.8	28–35
9	LOME	874–920	–	–	–	37.5–42.2	48–59
10	Rubber seed	910–930	34–76.4	–	–	37.5	37
11	RSOME	858–900	–	–	–	36.5–42.1	49–57
12	Cotton seed oil	850–885	6–9.6	–	223/185	36.8	41.8
13	COME	872–885	–	–	–	40.1–40.8	45–60
14	Neem	820	8.8	–	–	33.7–39.5	51
15	NOME	820–942	–	–	–	39.6–40.2	51–53
16	Cashew nut shell oil	958	–	–	–	–	33
17	Rapeseed	872–885	4.585–11	1.83	220–230	39.71	37.6
18	ROME	873	–	–	–	39.8	53
19	Palm oil	870–878.4	4.5–5.11	1.86	230	36.55	42
20	POME	878	–	–	–	40	64
21	Marine gas oil & diethylene glycol dimethyl ether blend	864	–	–	–	40.97	54.9
22	Marine gas oil & jatropha oil methyl ester blend	857	–	–	–	42.23	48.8
23	Sunflower	880–885.6	4.381–4.4	2.244	227	39.58	37.1
24	Soybean	885–914	4.057–39.5	1.97	300	39.62	37.9
25	Sesame	910	–	2.117	177	39.35	40.2
26	Coconut	877	3.18	–	350	–	–
27	Corn	885.8	4.363	2.039	227	39.5	37.6
28	Peanut	886.4	5.251	2.045	–	39.782	41.8
29	Cramble	900	–	–	–	40.482	44
30	Safflower	920	26.64	2.076	–	39.52	41.3
31	Rice bran	890	4.03	–	254	38.85	–
32	Honne	910	–	–	90.9	39.1	51
33	Polanga	869	3.99	–	–	–	–
34	Canola	872	4.22	–	204	–	54.3
35	Tung	–	–	–	–	–	37.1
36	Thevetia Peruviana	929	20.13	–	–	–	61.5
37	Pongamia	866	4.8	–	316	36.5	51
38	Camelina	918	24	–	–	–	–
39	Jatropha + Tyre Pyrolysis oil	887	5.2	–	–	38.8	–
40	Orange skin powder (B 30)	851.5	4.1	–	176	40.99	–
41	Calophyllum inophyllum	870	5.4	–	–	37.9	59.5

Table 2 illustrates the Cold flow properties of biodiesels.

Table 2 Cold flow properties of biodiesels [38, 39, 40].

Sl No.	Biodiesel	Flash Point [°C]	Flame Point [°C]	Cloud Point [°C]	Pour Point [°C]	Iodine Value [g/100 g]
1	Jatropha	148	178-197	10.2	4.2	93-121
2	Karanja	170-205	-	-2-14.6	-6-5.1	86.5-87
3	Mahua	129-208	141	-	6	55-70
4	Diesel	68-75	80	-2	-20	112.69
5	JOME	-	-	-	-	-
6	KOME	-	-	-	-	-
7	MOME	-	-	-	-	-
8	Linseed	241	-	1.7	-15	136-178
9	LOME	-	-	-	-	-
10	Rubber seed	37	-	14	-1	-
11	RSOME	-	-	-	-	-
12	Cotton seed oil	24	-	-1.7	-15	103-0115
13	COME	-	-	-	-	-
14	Neem	180	222	-	-	67-76
15	NOME	-	-	-	-	-
16	Cashew nut shell oil	-	-	-	-	240
17	Rapeseed	177-275	-	-3.9	-31.7	94-120
18	ROME	-	-	-	-	-
19	Palm oil	267	182	31	8	50-55
20	Sunflower	183	-	7.2	-15	118-145
21	Soybean	69-163	-	-3.9	-12.2	120-136
22	Sesame	260	-	-3.9	-9.4	104-120
23	Coconut	-	-	1	-	100-117
24	Corn	167	-	-1.1	-40	109-133
25	Peanut	193	-	12.8	-6.7	84-106
26	Crambe	274	-	10	-12.2	93
27	Safflower	174	-	-4	-7	120-135
28	Rice bran	169	-	-	-	95-108
29	Honne	228	-	-2.5	-0.8	79-98
30	Polanga	140	-	13.2	4.3	-
31	Canola	153	-	-4	-6	110-126
32	Tung	-	-	-	-	163-173
33	Thevetia Peruviana	-	-	-	-	78-82
34	Pongamia	172	230	-	-	86.5-87
35	Camelina	>220	-	3	-7	127-155
36	Jatropha + Tyre Pyrolysis oil	132	-	-	-	-
37	Orange skin powder (B 30)	70	83	-	-	-
38	CalophyllumInophyllum	170	253	-	-	-

CONCLUSIONS

This paper provides a comprehensive analysis of biodiesel, examining factors such as feedstock, fuel standards, production methods, as well as Biofuel properties. It further discusses potential solutions and advancements that could help overcome these obstacles, including technological innovations, and diversification of feedstocks. The analysis underscores the importance of a multifaceted approach to tackling the challenges in biodiesel production and highlights the potential of biodiesel as a significant contributor to a sustainable energy future.

The world's growing economy would necessitate more energy use. Rapid technological development and population growth are driving global demand for fossil fuels. Although fossil fuels remain the main source of energy, the volume of renewable sources of energy is constantly increasing. Biodiesel is one of the newest alternatives to fossil fuels that has attracted a lot of interest due to its similarities to diesel. Biodiesel is a promising alternative fuel due to the number of advantages compared to fossil fuel. Biodiesel has shown great potential as a replacement fuel for Compression Ignition engines to meet sustainability criteria. Biodiesel has been found to reduce greenhouse gas emissions, particulate matter, and other harmful pollutants. Furthermore, Biodiesel fits into conventional diesel engines without much modification, making it a viable option for the transportation sector.

The growing energy demand and non-renewable nature of conventional diesel have shifted the focus of researchers on the search for alternate fuels. Intensive research works, experiments and tests have been conducted on alternate fuels by keeping in view their non-polluting, environment-friendly, sustainable and renewable nature at the core. Consequently, biodiesel and alcohols have emerged as promising oxygenated fuel additives blended with conventional diesel and can be employed in modern-day diesel engines with the least modifications.

Based on the extensive review analysis, the following conclusions can be drawn: The outcomes from the various research studies held in the past revealed that biodiesel and alcohol proved to be the key alternate fuels.

Adequate and constant quality of biodiesel can only be assured by respecting the biodiesel quality standards. To achieve this goal, it is necessary to monitor the quality throughout the biodiesel manufacturing process, from the feedstock to the distribution stations. The physicochemical properties of biodiesels are strongly influenced by the nature and composition of the feedstocks used in their production. Therefore, quality requirements for the marketing of biodiesel vary from region to region.

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