

Do Biofuels really a need of the day: Approaches, Mechanisms, Applications and Challenges

Azka Ali and Ayesha Mushtaq*

Department of Chemistry, University of Agriculture Faisalabad, Pakistan.

Abstract

The rising world population, declining fossil fuel reserves, and the growing environmental concerns have made biofuels an exceptionally attractive alternative energy source for the future. Biofuels include any energy-enriched chemicals generated directly through the biological processes or derived from the chemical conversion from biomass of prior living organisms. They can be primary or secondary. Biofuels like bio-alcohols, biodiesel, green-diesel, and bio-ATF are developed in response to the increasing demand for liquid fuel and predicted decrease in fossil fuels. As a highly promising alternative to fossil fuels, biofuels have excellent usage without any modifications to diesel engines. The properties of alternative oils are compared favorably with the characteristics required for internal combustion engine fuels. The approaches of biofuel production from multiple feedstocks using different mechanisms and their applications in transportation, enzymatic biofuel cells, electricity generation, and aviation are studied. For this purpose, mechanisms like fermentation, direct use and blending, micro-emulsions, transesterification, anaerobic digestion and catalytic deoxygenation are reviewed. Despite the benefits, several issues in biofuel production and challenges including high feedstock cost, high viscosity, and high nitrogen oxides emission are faced.

Keywords: Bio-ATF; Biodiesel; Transesterification; Dimethyl ether, fossil fuels

Full length review article

*Corresponding Author, e-mail: azkaaliwaraich99@gmail.com

1. Introduction

Energy has played a significant role in upholding the stability of our community. Wood and straw were typical fuels used to obtain energy thousands of years ago. Then fossil fuels were used to replace these natural fuels. As per the 2014 World Energy Outlook (WEO) report, worldwide energy requirements are expected to rise by approximately 40% from now until 2040, but the proportion of fossil fuels in the total quantity of energy produced by all sources is expected to decline. As the demand for energy in both the transportation and power generation sectors is increasing at an ever-increasing rate, with the resulting increase in harmful emissions and expected decline in fossil fuel reserves, scientists, analysts, and researchers are finding alternative renewable resources that can meet the demand while also being ecologically and cost-effective [1].

These renewable resources are competitive alternative fuels that are available, accepted by the environment, and used entirely or substantially in diesel engines. Numerous alternative fuels like bio-alcohols, biodiesel, biogas, etc. are applied in conventional diesel engines [2]. Biofuels are solid, liquid, and gaseous fuels that have been generated in the last few years using innovative regenerative processes and technology for the reuse of fresh biotic sources [3]. These are durable fuels generated from abundant organic materials known as biomass. It contains a

wide range of plants and wastes, including decomposable waste, agroforestry, farming leftovers, waste and sewage from the paper manufacturing industry, and waste from construction sites. Some unique crops that are grown for the production of energy and the extraction of fuels are used to make biofuels. These plants include algae, microalgae, and seaweed. They are referred to as energy crops [4]

2. Biodiesel

One of the most frequent approaches to biofuels is biodiesel. Biodiesel is thought to be an alternative fuel that is prepared from a variety of feedstock, including edible, non-edible, animal fats, and other resources [5]. Biodiesel is a clean-burning fuel extracted from natural sources under mild operating conditions [6]. Animal fats, non-edible and edible vegetable oils, and used frying oils are utilized to generate biodiesel, which is assumed to be a renewable and carbon-neutral substitute for petroleum fuels. Biodiesel is a mixture of long-chain monoalkyl esters of fatty acids. Biodiesel is a monoalkyl ester prepared from fatty acid esters of edible, non-edible, and waste oils [7-8].

Biodiesel has been divided into the first, second, and third generations based primarily on its natural origin, whereas the fourth generation is derived from artificial biological instruments and is still in the early stages of basic research. Edible feedstock's are used to prepare first-generation biodiesel, e.g., rapeseed oil, rice oil, coconut oil,

corn oil, palm oil, mustard oil, olive oil, rice oil, etc. Due to their preference for biodiesel generation over food production, deforestation, soil damage, and the high price of edible oils have prevented their use. Straw, bagasse, forest byproducts, and specifically cultivated energy crops grown in marginal areas are examples of non-food materials used as feedstock for the production of second-generation biofuels.

Animal fats are also considered to be second generation, due to saturated fatty acids they cannot be used in cold climates. Third-generation biodiesel is made from waste oils and microalgae. Third-generation biodiesel has a lower greenhouse effect, more growth and production, and a lesser influence on the food supply [7]. A chemical process called transesterification transforms triglycerides into diglycerides, which are then transformed into monoglycerides, or methyl- or ethyl-esters known as biodiesel. The illustrative representation for the production of biodiesel is discussed in Fig 1.

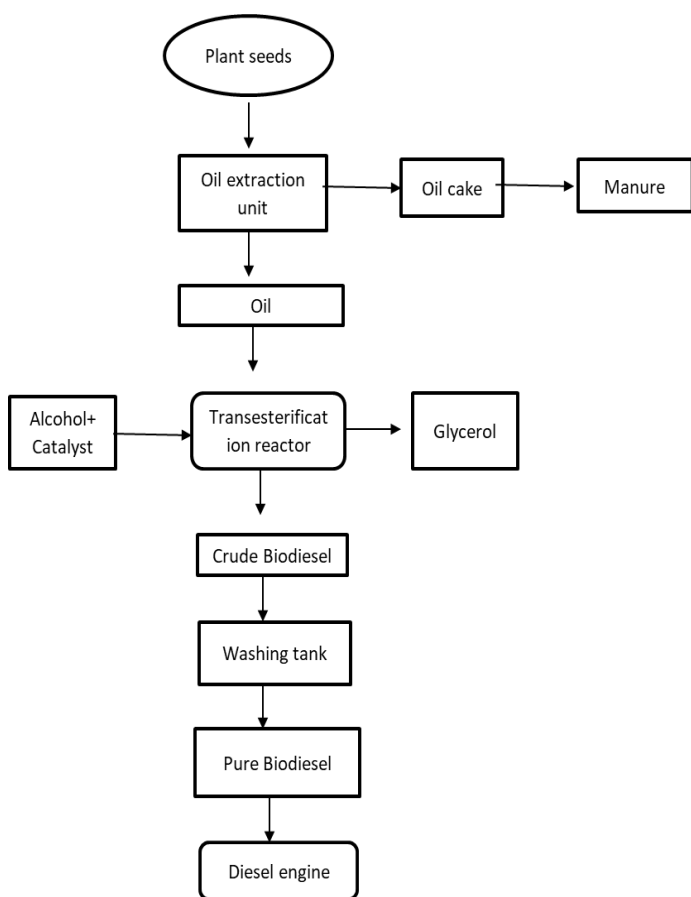


Figure 1: Flow chart diagram for biodiesel production.

Production cost and production scale are two key factors for generating biodiesel. The presence of feedstock constitutes 80.4% of the whole production cost [9]. Due to various issues created by using oils without any modification, numerous efforts are being made to improve and modify the quality of oils so they are functional as alternative fuels in conventional engines. Dilution, pyrolysis, micro-emulsion, and transesterification are the four processes used to produce biodiesel [10]. A thermal decomposition method using a catalyst in the absence of

oxygen is called pyrolysis. Pyrolysis is a quick and efficient process. High cetane and mild viscosity characterize the pyrolysis product. No dilution is required, and the final product can have better combustion properties [11].

A solvent like methanol or ethanol is used in an attempt to make micro-emulsion, which results in biodiesel with a suitable viscosity. The process that produces biodiesel most effectively is transesterification, which involves using a catalyst and an alcohol such as methanol or ethanol. Triglycerides are converted to monoglycerides, which are then converted to glycerol, which stays at the bottom as the biodiesel rises to the top. To speed up the reaction, acid or basic catalysts are used. To generate biodiesel that complies with standard criteria, a number of variables affect the transesterification process. These variables include alcohol and catalyst type, amount of water in free fatty acids, the reaction's temperature as well as time, a particular mixing method, and specific gravity [12].

In comparison to diesel fuel, biodiesel has lower heating values, and more surface tension, viscosity, and density. Because saturated fatty acids are present, biodiesel has higher pouring points than diesel fuel. By using biodiesel in diesel engines, carbon monoxide, traces of hazardous chemicals, nitrogen oxides, soot, and particulate matter are emitted. Low CO and UHC are produced while using high biodiesel concentrations and diesel fuel in conventional engines. However, because biodiesel is oxygenated in nature, it combusts completely and the NOx emissions are enhanced [13].

3. Bio-alcohols

3.1. Methanol

There are three different types of alcohol: methanol, a simple form of alcohol; ethanol for commercial use; and DME, a potential material fuel for burning. A blend of these three types of alcohol is utilized in internal combustion engines in combustion [14]. Due to methanol's liquid state, it can be handled and distributed easily at room temperature. Methanol is produced by gasifying coal or catalyzing the reaction between hydrogen and carbon monoxide [15]. Because of its poisonous and corrosive nature and an energy density that is only half that of fuels for automobiles and ships, methanol faces a number of challenges in its use. As it is unstable by nature, it requires constant recharging or large fuel tanks for longer trips. Methanol blend combustion can lower NOx emissions while raising brake thermal efficiency [16-17].

3.2. Ethanol

Fermentation is a method for producing ethanol. It has been blended with conventional fuels and used in compression ignition engines. Because it has a lower heat efficiency than diesel fuels, large capacity tanks are required when using it in compression ignition engines. Blends of combined ethanol lead to incomplete combustion in CI engines. As a result, emissions are produced equally efficiently as when using only traditional fuels [18].

3.3. Dimethyl ether

Dimethyl ether has been prepared by the dehydration of methanol. Recently, it has been observed that ignition compression engines combustion and performance can be improved by blending dimethyl ether with

conventional fuels. It is an excellent fuel to replace conventional fuels because it is non-toxic and non-carcinogenic [19]. It burns with a blue flame and a pleasant aroma. Compared to alcoholic fuels, it has a greater heating value and approximately the same cetane number as diesel fuel [20]. On the other hand, dimethyl ether combustion emits a very small amount of greenhouse gases. DME is an extremely effective diesel fuel substitute for compression ignition engines. The primary barrier to using dimethyl ether is its reduced heat capacity, which necessitates the use of large storage tanks [21].

4. Green diesel

Second-generation biofuel is the term used to describe green diesel. It was designed in reaction to the growing demands for liquid fuel as well as the predicted decline in fossil fuel availability, particularly conventional diesel, which is the primary fluid fuel employed in vehicles used for transportation. Deoxygenation can produce green diesel from a variety of feedstock's, including used cooking oils, fatty acids, animal fats, and vegetable oils. Typically, a multiphase system is used to conduct the deoxygenation reaction during the manufacture of green diesel. Liquid alkane hydrocarbons, also referred to as green diesel, can be developed through three major routes in the fluid state of the processes, which include hydrodeoxygenation, decarbonylation, and decarboxylation [22].

In order to replace petroleum-based diesel, green diesel has been developed using waste vegetable oil, crops for energy, sanitary waste, organic sludge, and other non-edible oils as feedstock [10-23]. The diesel generated from a non-edible source and conventional fuel has identical chemical compositions and fluid fuel characteristics. Green diesel production has drawn interest due to its increased heating value and cetane number, its less corrosive nature, and its excellent oxidative stability. The molecular structure of bio-hydrogenated or green diesel is similar to that of conventional fuel. Deoxygenation of triglycerides, fatty acids, and their derivatives can produce it. which involves removing oxygen from the reactant. Alkane hydrocarbons are created by removing oxygen from oxygenating molecules [24].

Green diesel is generated from triolein, nonedible oils, utilized cooking oil, animal fats, and various kinds of triglycerides. In contrast to using triglyceride as a feedstock, the synthesis of green diesel made from the distillation of fatty acids such as stearic, palmitic, oleic, and palm fatty acids use less hydrogen because deoxygenation occurs in an early step in the absence of hydrogenolysis [25]. The catalyst's metal active sites determine how effectively deoxygenation produces green diesel. They are highly reactive; therefore, noble metals like palladium, platinum, and rhodium are preferred for the manufacturing of green diesel as the first group of metal catalysts. Instead of the excellent activity of noble metal catalysts for the manufacture of hydrogen- and non-hydrogenated green diesel, there are economical limits due to the high expenses associated with high production costs [26].

5. Bio-ATF

In recent years, because of environmental concerns and policy implications, the generation of alternative renewable aircraft turbine fuel (ATF) has received *Ali and Mushtaq, 2023*

considerable interest in both industry and academia. The atmospheric distillation column or hydrocracker units are used to obtain ATF directly. Small amounts of ATF are obtained as a coker product after hydrotreatment. Aviation fuels must fulfil the international standards set forth by ASTM and be able to replace existing petroleum aviation fuel with 100 percent renewable aviation fuel. Aviation fuel contains ricinoleic acid, palmitic acid, stearic acid, and linoleic acid in different percentages. Fig. 2 shows a pie chart indication of the different concentrations of palmitic acid, stearic acid, linoleic acid, and ricinoleic acid in bio-ATF.

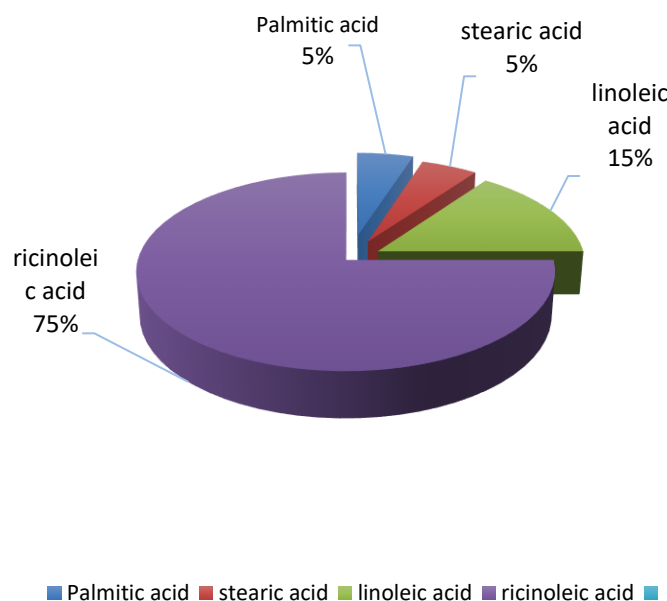


Figure 2. Different components of bio-ATF in different proportions

Numerous processes turn waste cooking oil, non-edible oils, and biomass-derived materials into aviation fuel. Some technologies are available commercially, while others are still in the research and development stage. The bio-oil-based feedstock is converted into bio-aviation fuels by hydroprocessing techniques such as hydrotreating, deoxygenation, isomerization, and hydrocracking. These technologies have a wide range of aviation fuel qualities that are strongly impacted by the type of feedstock, working process variables, and catalyst design. The production of biofuel from triglyceride-based oils has also been developed using methods such as catalytic hydro thermolysis [27].

Several methods used to convert solid-based feedstock into biofuels include the gasification of biomass-derived intermediates, pyrolysis of bio-oils, and biochemical processing of sugars and alcohols. Byproducts from these processes, such as syngas, alcohols, sugars, and bio-oils, can be transformed into bio jet fuel by a variety of techniques, including fermentative and catalytic approaches. Industries are now concentrating on developing the best processes that use eco-friendly catalysts with the right metal loading and inexpensive feedstock's to produce bio jet fuels [28].

6. Mechanisms

6.1. Direct use and blending

Vegetable oil or animal fat are both acceptable fuels for direct injection engines. It can provide sufficient power with a high heating value. Due to its undesirable properties, it cannot be employed directly in engines without modification. To overcome these problems, traditional fossil fuels and alternative fuels are blended together. This kind of mixing will improve fuel quality as well as conventional diesel consumption. Therefore, the most practicable approach is to use an alternative fuel, such as biofuels. Multiple ratios will be used for the bio-oil and diesel blends.

6.2. Catalytic cracking

Vegetable oils can be converted into liquid biodiesel through a method called catalytic cracking. It includes olefins, aldehydes, ketones, and carboxylic acids, as well as linear and cyclic paraffin. From various edible or non-edible oils using various types of catalysts, the catalytic cracking method is employed to generate biofuels with a broad range of fractions, such as gasoline, kerosene, and diesel. Catalytic cracking has a reaction temperature of roughly 450, which is less than that of most biomass pyrolysis processes [29].

6.3. Micro-emulsions

Microemulsions do not undergo any reactions. Compared to other alternative fuels, such as biodiesel, hydrotreated vegetable oil, and Fischer-Tropsch diesel, they are preferred. The existing engine and infrastructure are unaffected by this fuel alteration, which is simple and has a minimal production cost. The type of diesel used greatly affects how the micro emulsion forms. Synthetic gas-based Fischer Tropsch diesel emits fewer pollutants than petro diesel [30]. To create micro-emulsions, oils are combined with suitable emulsifiers such as alcohol, primary methanol, ethanol, propanol, or butanol. The biggest drawback of using micro-emulsion as engine fuel is the formation of carbon deposits in engines and incomplete combustion [31]. Fig. 3 represents micro emulsion-based biofuels.

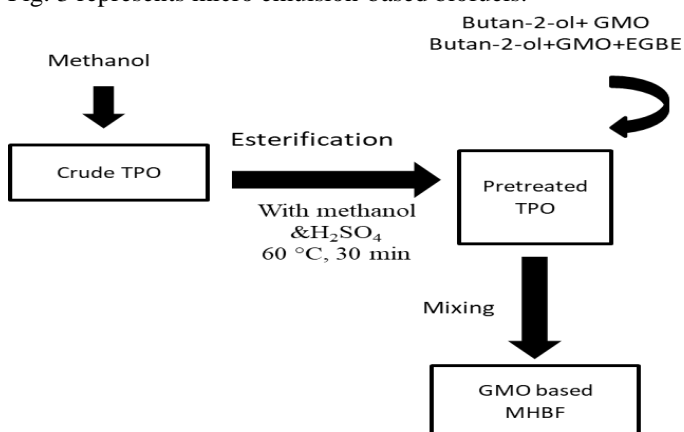


Figure 3. Micro emulsion-based hybrid Biofuels

7. Transesterification

In the presence of a catalyst, transesterification is the reaction of an oil feedstock with an alcohol like methanol. Various kinds of catalysts, for example, homogenous, heterogeneous, and enzyme catalysts, can be used in the transesterification process. The transesterification reaction faces two major challenges. Firstly, the heterogeneous nature poses challenges in mass transfer limitations, and secondly, due to the reversible nature of transesterification, a higher alcohol to oil ratio is required [29-32].

8. Fermentation

Sugars are converted into ethanol and carbon dioxide during microbial fermentation, which is the primary stage in the manufacture of bioethanol. According to the particular carbohydrate content of the biomass, microorganisms were selected for the fermentation process. Microorganisms that cause pentose fermentation may be utilized alone in their pure form or in conjunction with hexose-fermenting microorganisms in co-culture. In batch, fed batch, or continuous fermentation operations, pure and co-cultures may be utilized. When compared to batch or fed-batch operations, continuous processes can produce better results since ethanol and other byproducts are continuously eliminated, allowing high concentrations to produce significant yields of bioethanol [33].

It is obviously important to find suitable microbes for the fermentation of hexose and pentose carbohydrates, considered a technological challenge in the conversion of lignocellulose to ethanol [34]. The solid-state fermentation performs the hydrolysis and fermentation in a single unit, allowing for significant equipment, investment, and operation cost reductions. With the solid state fermentation method, the ethanol produced from the sugars created from biomass is quickly fermented, preventing the accumulation of inhibiting sugars and allowing for better ethanol yields with less enzyme.

9. Anaerobic digestion

The stability and treatment of waste organic substances can be achieved by the anaerobic digestion process, which is generally known as an interesting alternative. The properties of organic material that was subjected to reactions to check for significant levels of soluble sugars or lipids led to the observation of a number of technical limits. Various stages characterised the technology of anaerobic digestion as an applicable solution for the control of variables, optimising the environment of the major microorganisms associated with the process. In addition to increasing methane production and solid removal, it also enables a larger energy output by producing hydrogen fuel molecules.

Anaerobic digestion is a method for converting organic matter into biogas and stable organic effluent through microorganisms set metabolic activities that take place in a non-toxic environment. Naturally, this process occurs in wetlands and swamps, as well as in the gastrointestinal tracts of many animals. The study of this biochemical process has increased in recent years because of the growing energy crisis and rising environmental concerns, which allowed the utilization of effluents and waste substances by various manufacturing processes to

make it a viable choice. Examples include farming, domesticating animals, organic sludge, and sewage waste. Hydrolysis, acidogenesis, acetogenesis, and methanogenesis are the four phases that generally make up the biochemical process. A biochemical process is done by a group of microbes [35].

10. Catalytic deoxygenation

Catalytic deoxygenation is a technique for improving biofuel that removes oxygen content that can cause corrosion, instability, and a poor heating value. The high oxygen level of biofuel degrades the fuel quality. Consequently, it is essential to upgrade biofuels through catalytic deoxygenation [36]. Many researchers have focused on noble metal-based catalytic deoxygenation in the past. Noble catalysts had been shown to be superior at deoxygenating feed, but they were unattractive due to their high cost and limited availability [24].

Sulphide catalysts, meanwhile, were also problematic because they may produce Sulphur leaching, which would contaminate the final product. Therefore, the development of low-cost, sulfide-free catalysts is required. Interestingly, transition metal oxides like nickel, cobalt, manganese, zinc, and cerium are considered excellent catalyst promoters since they can achieve results that are equivalent to those of noble metal-promoted catalysts [37]. The nickel-promoted catalyst was found to have the maximum deoxygenation activity of these at inert conditions with an 80% diesel selectivity [38].

11. Applications

11.1. Enzymatic biofuel cells

The range of applications for enzyme-based biofuel cells is exceptionally broad. Using enzymatic biofuel cells with low current density in biosensors is one of the first and foremost applications that comes to mind. biosensors. Enzymatic biofuel cells have undergone incredible development in recent years to progress from the laboratory setting to practical applications in implantable configurations. It led to the development of a range of enzymatic biofuel cell prototype designs, including microfluidic prototypes, bio-batteries, and paper-based biofuel cells. As opposed to traditional H cell systems, several of these proto-types were designed to reduce the amount of internal resistance. It helps improve the device's overall performance by increasing the current or power density of the cell. Implantation of enzymatic biofuel cells in human blood has also been performed because of the tremendous advancement in this field [39].

11.2. Transportation fuel

Renewability, biodegradability, sustainability, and carbon neutrality are just a few of the priorities that biofuels offer. Therefore, it has a high probability of resolving environmental issues including the greenhouse effect and air pollution. The two most popular liquid biofuel approaches are biodiesel and bioethanol, which are widely utilized substitutes for fuels for transportation that contain hydrocarbons, such as gasoline and diesel. Available forms of biofuel are solid fuel, for example, bio-char, and gaseous fuel, e.g., hydrogen and methane.

As long as there are vehicles on the road, biofuels as an alternative fuel will not be a new concept. Samuel

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Morely created an ethanol-fueled engine in 1826, and Henry Ford created an ethanol-powered Model T engine in 1908. As a major alternative energy source and substitute for petroleum-based fuel in transportation, biodiesel is gaining prominence. The most researched and promising alternative to fossil fuels is biofuels. They also reduce greenhouse gas emissions [40].

11.3. Electricity generation

The last few decades have experienced a lot of interest in biofuel-derived electricity as a sustainable energy source that is also environmentally friendly. It should be noted that as the world's population has grown, more intensive agricultural and animal farming techniques have been required to generate more food and feed commodities [41]. Large amounts of agricultural waste are generally produced by these activities. These agricultural waste is utilized to generate electricity [42].

For the purpose of producing energy from butanol, a customised generator can be used. For the purpose of producing energy from butanol, a customized generator can be used. Concentric ferromagnetic steel is used in the generator. Using the heat from exhaust gas, a contra-flow heat exchange took place at the outer shell to evaporate the liquid.

11.4. Aviation

Commercial airlines are now using bio-jet fuel, which is manufactured from vegetable oil and can be blended with conventional jet fuel up to 50%, according to ASTM certification. Recent research trends reveal that the majority of sustainable aviation fuel is generated by complex fluid biomass via hydroprocessing technology in order to lessen dependence on conventional jet fuel. The production technology, which is often the hydroprocessing technology, must therefore be understood. The hydroprocessing technology involved multiple steps, such as cracking, deoxygenation, and isomerization, for fluid biomass conversion into sustainable jet fuel. This traditional procedure is improved and made even simpler into a single-step reaction. It lowers the production cost by minimizing the post-treatment work required after each reaction step. The cost of producing hydrogen, the price of catalysts, and the size of the plant are other economic aspects that will be taken into account as having a significant effect on the scale and cost of the production of biofuels [43].

12. Challenges

12.1. Feedstock cost

Primarily, biofuel was generated from vegetable oils, e.g., palm oil. High feedstock prices increased the price of biodiesel. Despite the fact that vegetable oil production could meet the demand for fuel, due to the very high cost of feedstock, it could not compete with petroleum diesel [44]. In other words, the average palm oil cost was considerably higher than the cost of crude, which led to the high price of biodiesel. Because of the high feedstock prices in Asian countries, it had become a concern as palm oil was a fuel source. That was mainly the reason why biodiesel in these countries could not fully replace petroleum-based fuel.

In the future, the researchers will explore cost-effective feedstock's as an alternative solution [45]. Vegetable oil prices are likely to rise along with the

development of biodiesel production as a result of the competition that will inevitably emerge in the food market. Non-edible sources can serve as substitutes in this situation for the manufacture of biodiesel since, in addition to not competing with food, they also offer a highly practical means of reducing the cost of biodiesel production.

12.2. Impacts of biodiesel

In 2017, crops made up over 78% of the world's biodiesel production. Biofuels, including biodiesel, have resulted in deforestation in Indonesia and Malaysia in order to meet 20% of Europe's need for biofuels. This demonstrated the possibility of adverse environmental effects from first- and second-generation biodiesel. Despite the fact that a lot of crops had grown, their capacity to store carbon may not be as great as that of the forest, which could lead to a rise in carbon dioxide levels and may cause a worsening of global warming. Therefore, first- and second-generation biodiesels may have both positive and negative effects on the environment [45].

12.3. Viscosity

It is commonly known that the viscosity of biodiesel is higher than petroleum diesel, which has a bad impact on engine performance. High viscosity causes a number of biodiesel disadvantages, including reduced quality of atomization and low heat atomization quality, which release less heat, which compares to its low energy density with fossil fuel diesel. A higher volume of biodiesel is required for a given amount of energy as compared to petroleum diesel. Hence, the cost-performance ratio of biodiesel is lowered [46-47]. Biodiesel is already considered expensive publicly, so the low cost-to-performance ratio will make the situation worse. Additionally, due to incomplete combustion, in cold temperatures, high-viscosity biodiesel can cause issues with engine bearings. Thus, high-viscosity biodiesel has become a technical challenge that should be overcome in the future.

12.4. Nitrogen oxides emission

Fuel viscosity affects the emission of NO_x. Increased NO_x emissions could be caused by increased viscosity. Biodiesel can release more nitrogen oxides than petroleum diesel because it has a higher viscosity compared to petroleum diesel. Fuel density and cetane number were also identified as additional factors that could affect nitrogen oxide emissions. Increased fuel density and a lowered cetane number cause the emission of nitrogen oxides [48].

13. Conclusions

Biofuels are the sustainable replacement of fossil fuels. This review article covers approaches for biofuel generation in terms of feedstock's used for biofuel production, various production mechanisms, applications of biofuels in different fields of life and challenges faced. Each approach has its own benefits and limitations based on feedstock generation. Methanol, ethanol, dimethyl ethers emerges as bio-alcohol fuels. The evolution of generations of feedstock primarily focused on biofuel quality enhancement with less deterioration to environment. However, there are challenges and limitations that can still be further improved in the biofuel generation process, such as high cost of feedstock, impacts of biodiesel, higher

viscosity and emission of nitrogen oxides. Despite of challenges biofuels bring a lot of advantages to the transportation systems in terms of environmental, technology, economy and social aspects.

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