
Biodiesel Production for C.I. Engine from Various Non- Edible Oils: A Review

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Abstract: *Energy is an essential input for economic growth, human welfare, social development and improving the quality of life. Since their exploration, the fossil fuels continued as the major conventional energy source. With increasing trend of modernization and industrialization, the world energy demand is also growing at a faster rate. Apart from their indigenous production, majority of developing countries import crude oil to cope up with their increasing energy demand. Thus, a major chunk of their hard earned export earning is spent for purchase of petroleum products. India is also a net energy importer and almost 82 of the country's export earnings are directly spent for purchase of petroleum products. There had been sharp increase in the consumption pattern of petroleum products in India. The transport and agriculture sectors are the major users of the conventional liquid fuels.*

Biodiesel has become an alternative fuel because of its environmental benefits and it is obtained from renewable resources. There are four primary methods to make biodiesel: blending, pyrolysis, microemulsion and transesterification. The most commonly used method is the transesterification of triglycerides with alcohol in the presence of a catalyst. There is a growing interest in using non-edible oils as the feedstock for biodiesel production because it does not compromise the edible oils, which are mainly used for food consumption. Non-edible oils are not suitable for human consumption because of the presence of toxic components.

In this paper, an attempt has been made to review the different approaches and techniques used to generate biodiesel from non-edible oils. The main factors affecting the biodiesel yield, for example the molar ratio of alcohol to oil, reaction temperature, catalyst concentration and reaction time are discussed. Lastly, the environmental considerations and economic aspects of biodiesel are also addressed.

Keywords: *Biodiesel, Transesterification, Non- edible oils.*

1. INTRODUCTION

The scarcity of fossil fuels, it is essential to look for energy sources which are more secure and produce less greenhouse gas emissions. Bio-diesel, an earth friendly choice of consumers and renewable sources of alternative fuel occupies a great volume of the world's fuel sector. Due to its clean emission characteristics, availability of continued and increasing use of petroleum and its limited resources enhances the production of bio-diesel. Considering all economic and environmental benefits, production of bio-diesel is growing quickly as an alternative fuel of petroleum diesel around the world. Bio-diesel is generally defined as fatty esters made from vegetable oils through a simple transesterification process. The concept of using vegetable fuel as an engine fuel came from Rudolf Diesel (1858–1913) who developed the first engine and ran it with peanut oil vegetable fuel. Vegetable oils are vital energy sources though sometimes vegetable oils create various problems in engine components. This problem may be occurred due to their different volatility and molecular structure from diesel fuel as well as high viscosity compared to diesel fuel [3–4]. This problem can be eliminated from bio-diesel by applying different chemical process such as transesterification, supercritical and catalyst-free process on vegetable oils. Through this process molecular structure and properties of vegetable oil is changed and fatty acid methyl esters is formed which is commercially known as Bio-diesel fuel. Bio-diesel can produce 4.5 units of energy against every unit of fossil energy needed to produce biodiesel [6,7]. Beside this, bio-diesel is nontoxic, biodegradable and safer to breathe [8].

Modern compression ignition (CI) or diesel engines require clean burning, stable fuel that operates and performs well under numerous conditions. Bio-diesel satisfies all these objectives and is the only

alternative fuel that can be used in any unmodified compression ignition engine [8]. Physicochemical properties of bio-diesel from different sources, such as oxygen content, cetane number, viscosity, density and heat value greatly influence the engine performance and emissions characteristics. Properties of bio-diesel are dependent on the sources of bio-diesel [4,5]. When using bio-diesel or bio-diesel blends it is recommended [8,9] that the B100 meets the specific standards for blending with petroleum diesel, be aware of bio-diesel's freezing properties, wipe painted surfaces immediately after contact with bio-diesel, store bio-diesel or bio-diesel blended soaked rags in a safe place to avoid spontaneous combustion and use the bio-diesel within 1 year. Diesel engines are a major source of air pollutions that are now widely known to have an impact on human health and overall greenhouse gases. The National Environment Protection Council, the Australian State and Territory Governments have all agreed on a National Environment Protection Measure for Ambient Air Quality [10].

This paper reviews the production of biodiesel using vegetable oils such as Karanja and Jatropha as potential feedstock, the technologies implemented, the process variables, economic aspects and environmental consideration of biodiesel production.

1.1. Modification of Non-Edible Vegetable Oils

It is well-known that vegetable oils are treated as alternative fuels for diesel engines as they have high heat content. However, the direct use of these vegetable oils leads to various problems. The high viscosities of vegetable oils which are about 10 times higher than of Grade No. 2D diesel fuel leads to poor atomization of the fuel, incomplete combustion, coking of the fuel injectors and so on. These disadvantages together with the usage of unsaturated vegetable oils that may result in engine damage can be solved by chemically modifying the biodiesel, which has similar characteristics to diesel [10,11].

1.2. Impact of Free Fatty Acids

The free fatty acids (FFAs) and moisture content have negative impacts on the transesterification of glycerides with alcohol when an alkali catalyst is used. High FFA content is unfavourable in an alkali-catalysed transesterification reaction because the FFA will react with the catalyst to form soap and the separation of products will be extremely difficult, resulting in a lower yield of biodiesel. The Jatropha curcas oil quality will deteriorate due to improper handling and storage. Improper handling and exposure of the oil to atmospheric air and sunlight contributes to a rise in FFA concentration [22].

2. BIODIESEL AND ITS PROPERTIES

Biodiesel stands for a variety of ester based oxygenated fuels derived from renewable biological sources. In other words, biodiesel refers to a vegetable oil or animal fat-based diesel fuel consisting of long-chain alkyl (methyl, ethyl or propyl) esters or alkyl esters of fatty acids. It is a non-toxic, biodegradable and renewable fuel which can be used in compression ignition engines with little or no chemical modifications with significantly lower emissions than petroleum-based diesel when it is burned. In addition it does not contribute to the increase in carbon dioxide levels in the atmosphere and thus minimizes the intensity of the greenhouse effect. In addition, biodiesel is better than diesel fuel in terms of its properties such as sulphur content, flash point, aromatic content and biodegradability [3,8]. Table 1 represents the fuel properties of methyl esters (biodiesel) from various plant based oils. Although at present biodiesel cannot entirely replace petroleum-based diesel fuel, this alternative fuel is becoming increasingly important due to diminishing petroleum reserves that leads to a rise in petroleum prices and the environmental consequences of exhaust gases from the petroleum-fuelled engines [7,22].

Table1. Fuel properties of methyl ester from different oils [8]

Properties	Jatropha methyl ester	Karanja methyl ester	Canola methyl ester	Corn methyl ester	Biodiesel standard ASTM D 6751-02
Specific gravity	0.86-0.88	0.88-0.89	0.88-0.90	0.88-0.89	0.87-0.90
Viscosity (mm ² /s)	2.35-2.47	5.52-5.79	2.56-2.84	2.45-2.56	1.9-6.0
Calorific value (MJ/kg)	39.65-41.63	37.8-39.69	44.65-44.93	44.92-45.06	-
Acid value (mg/KOH/g)	0.61-0.66	0.72-0.76	-	-	0.8 max
Cetane number	60.74-63.27	59.68-60.90	55.90-56.10	58.37-59.00	47 min
Pour point (°C)	-6 to 2	-3 to -1	-4 to -1	-5 to -2	-15 to 10

2.1. Methods of Biodiesel Production

A number of methods are currently available that have been well established for the production of biodiesel fuel. Crude oils are worthwhile to be modified in order to reduce their viscosities so that the product obtained has suitable properties to be used as engine fuels. There are many procedures available for this modification to produce a better quality of biodiesel. This can be accomplished in four primary ways; blending of crude oils, micro emulsions, thermal cracking and transesterification [7,15].

2.1.1. Blending of Crude Oils

Crude vegetable oils can be mixed directly with diesel fuel to improve the viscosity so as to solve the problems associated with the use of pure vegetable oils with high viscosities in compression ignition engines. Caterpillar Brazil, in 1980, used a 10% mixture of vegetable oil to maintain total power without any alteration or adjustment to engines. A blend of 20% vegetable oil and 80% diesel fuel was also successfully reported [23]. Dilution with 25 parts of sunflower oils with 75 parts of diesel with a viscosity of 4.88 cSt at 40 °C has been studied by Ziejewski et al. [24]. Further, it was also reported that the viscosity of 25/75 high oleic sunflower oil/diesel fuel blend was 4.92 cSt at 40 °C and has passed the 200 h Engine Manufacturers' Association (EMA) test.

2.1.2. Micro-Emulsification

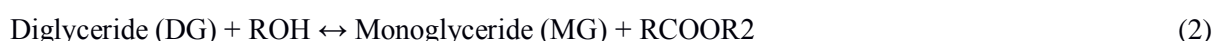
Another approach to reduce the viscosity of vegetable oils is by microemulsion. Microemulsions are clear, stable isotropic fluids with three components: an oil phase, an aqueous phase and a surfactant. The aqueous phase may contain salts or other ingredients, and the oil may consist of a complex mixture of different hydrocarbons and olefins. This ternary phase can improve spray characteristics by explosive vaporization of the low boiling constituents in the micelles. All micro-emulsions with butanol, hexanol and octanol can meet the maximum viscosity limitation for diesel engines [15]. A microemulsion prepared by blending soybean oil, methanol, 2-octanol and cetane improver in the ratio of 52.7:13.3:33.3:1.0 has passed the 200 h EMA test [25].

2.1.3. Pyrolysis

Pyrolysis is the process of conversion of one substance into another by means of heat or with the aid of catalyst in the absence of air or oxygen. The material used for pyrolysis can be vegetable oils, animal fats, natural fatty acids and methyl ester of fatty acids [15]. Soybean oil has been thermally decomposed in air using the standard ASTM method for distillation. The viscosity of the pyrolysed soybean oil distillate is 10.2 cSt at 37.8 °C, which is higher than the ASTM specified range for No. 2 diesel fuel but acceptable as still well below the viscosity of soybean oil [10].

2.1.4. Transesterification

Transesterification (alcoholysis) is the chemical reaction that involves triglycerides and alcohol in the presence of a catalyst to form esters and glycerol. This transesterification involving three consecutive reversible reactions, they are the conversion of triglycerides to diglycerides, followed by the conversion of diglycerides to monoglycerides. Glycerides are then converted into glycerol, giving one ester in each step. A catalyst is usually used to improve and enhance the reaction rate so that the reaction can be completed in a shorter reaction time. Several catalysts have been investigated for the purpose of transesterification by many researchers. Examples are magnesium, calcium oxides and carbonates of basic and acidic macro-reticular organic resins, alkane alumina, phase transfer catalysts, sulphuric acids, p-toluene sulphonic acid and dehydrating agents as a co-catalyst [26]. However, basic catalysts are usually favoured over acid catalysts because of the higher reactivity and the milder process conditions such as the lower temperature required [27]. Due to this transesterification being reversible, excess alcohol is used to shift the equilibrium towards the product. A successful transesterification reaction produces ester and crude glycerol. Though esters are the desired products of transesterification reactions, glycerin recovery is also important due to its numerous applications in daily products [28]. The transesterification reaction can be catalysed by alkalis, acids or enzymes [3]. The overall transesterification reaction is given by three consecutive and reversible equations as shown below. Triglyceride.





Alkali Catalysed Transesterification.

The alkali-catalysed transesterification of vegetable oils proceeds faster than the acid-catalysed reaction and the mechanism of this alkali-catalysed transesterification has been shown in Fig. 1. The reaction mechanism is formulated in three steps. The first step is the reaction of the carbonyl carbon atom with the anion of the alcohol, forming a tetrahedral intermediate, from which the alkyl ester and corresponding anion of the diglycerides are formed. Another catalytic cycle is started when the catalyst reacts with a second molecule of alcohol. From there, diglycerides and monoglycerides are converted into alkyl esters and glycerol [3]. Tapanes et al. [5] have studied the reaction mechanism of the catalyst-based transesterification of *Jatropha* oil and have proven the three step reaction mechanism. They reported that the reaction rate for *Jatropha* transesterification with ethanol is slightly lower than that with methanol as the stronger inductive effect of the ethyl group causes the breaking of the ethanol molecule to form an ethoxide anion which becomes more difficult than for the methoxide anion.

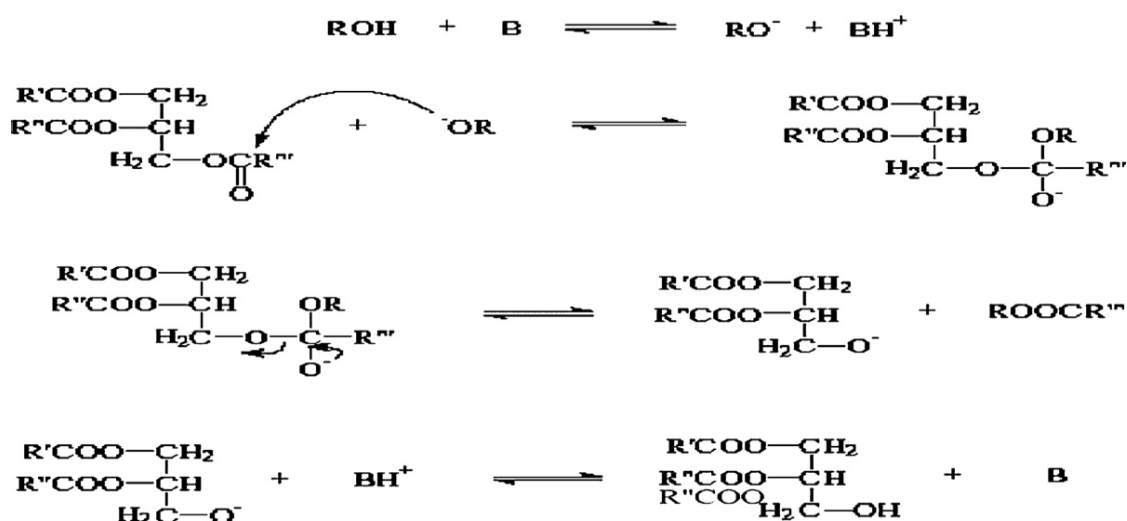


Fig1. Mechanism of alkali-catalysed transesterification [3]

A transesterification reaction starts when the oil, alcohol and the catalyst are mixed and stirred in a reaction vessel either in a lab scale small flask or larger scale and a high yield of biodiesel can be obtained as long as the ratio of oil, alcohol and the catalyst are in the optimum ratio. Many researchers have investigated and studied the operating parameters that affecting transesterification reactions. The optimum variables for effective transesterification of *Jatropha* oil are 20% methanol (by weight of oil), a molar ratio of methanol to oil of 5:1, and 1.0% of NaOH as a catalyst (by weight of oil). A maximum methyl ester yield of 98% was obtained after 90 min with a 60 °C reaction temperature and this biodiesel was found to be within the specified limits. It was also found that when the concentration of methanol and NaOH were above or below their optimum, there was no significant increase in the yield of biodiesel [29]. Due to the high FFA of *Jatropha* oil, as high as 15% has been reported, a two-stage transesterification process was selected to improve the methyl ester yield. After acid pretreatment or acid catalyst esterification to reduce the FFA content in *Jatropha* oil, subsequent transesterification give an optimum methyl ester yield of 90% in 2 h. The optimum methanol to oil ratio was 24% w/w and 1.4% w/w NaOH to oil as the alkaline catalyst at a reaction temperature of 65 °C [22].

Acid Catalyzed Transesterification

The acid-catalysed transesterification process is not very popular as a base-catalysed process due to the slower reaction rate and the high methanol to oil molar ratio requirement. In addition, an acid-catalyst has a lower activity and the transesterification reaction occurs at a higher process temperature than for the base-catalysed reaction [27]. The use of solid acid catalysts still requires a higher temperature and pressure in order to be more effective. Moreover, a long reaction time makes the process impractical and uneconomical [35]. On the other hand, the advantage of using an acid-catalysed transesterification is the tolerance towards the presence of high FFAs in the feedstock. In fact, acid catalysts can directly produce biodiesel from low-cost lipid feedstock with an FFA greater

than 6% [34]. Liquid acid catalysts such as sulphuric acid have a tolerance and less sensitive to FFA and can simultaneously conduct esterification and transesterification by giving a high yield in esters [35]. Other acid catalysts included sulphonic acid, phosphoric acid, hydrochloric acid, Lewis acids ($AlCl_3$ or $ZnCl_2$), etc. [27].

3. MAIN FACTORS AFFECTING THE YIELD OF BIODIESEL

There are few important variables that influence the transesterification reaction. In order to obtain maximum yield of biodiesel, these variables must be at their optimum.

3.1. Reaction Temperature

The rate of reaction is strongly affected by the reaction temperature. A higher reaction temperature can decrease the viscosities of oils and result in an increase in reaction rate as more energy is being supplied for the reaction to occur. Thus the yield of the biodiesel product is improved. However, the reaction temperature must be less than the boiling point of alcohol (boiling point of methanol is at 60–70 °C at atmospheric pressure) to ensure the alcohol will not be lost through vaporization. Also, the yield of biodiesel decreases if the reaction temperature goes beyond its optimum level because a higher reaction temperature will accelerate the saponification reaction which results in a lower yield. Depending on the types of oil, the maximum yield is obtained at temperatures ranging from 60 to 80 °C [7,11].

3.2. Molar Ratio of Alcohol to Oil

The stoichiometric ratio for the transesterification reaction involves 3mol of alcohol and 1mol of triglyceride to produce 3 mol of fatty acid ester and 1mol of glycerol. Excess alcohol is used during transesterification to ensure that the oils will be completely converted to ester due to the forward reaction being more favourable. Furthermore, a higher alcohol to triglyceride ratio can result in a greater ester conversion in a shorter time. The molar ratio is associated closely with the type of catalyst used. For base-catalysed transesterification where the free fatty acids are less than 1% after pretreatment, a molar ratio of methanol to oil of 5:1 or 6:1 is sufficient to convert *Jatropha* oil to biodiesel [16,17,29]. However, where the percentage of free fatty acids in oils is high, a molar ratio as high as 20:1 or 24:1 is needed when using acid-catalysed transesterification [35,38].

3.3. Concentration of Catalyst

Catalyst concentration can affect the yield of the biodiesel produced. As mentioned earlier, basic catalysts are usually preferred to acid catalysts because of the higher reactivity and the lower process temperature required [27]. Freedman et al. [48] found that sodium methoxide was more effective than sodium hydroxide because of the reduced amount of water produced upon mixing sodium hydroxide with methanol. As the catalyst concentration increases, the conversion of triglycerides and the yield of biodiesel also increased. A concentration of NaOH in the range of 1.0–1.4% (w/w) has been found to produce 90–98% conversion from *Jatropha* oil to methyl ester [20,27]. As for the concentration of KOH ranging from 0.55 to 2.0% (w/w), 95–99% of *Jatropha* biodiesel has been obtained [8,16,17,30]. However, the yield of biodiesel was reduced if the alkali catalysts were added above their optimum concentration as this causes more soap formation [7].

3.4. Reaction Time

The conversion rate increases with reaction time. Initially the reaction was slow due to the mixing and dispersion of alcohol into the oil as reported by Freedman et al. After some time, the reaction proceeds faster until maximum yield is reached [48]. For base-catalysed transesterification, the yield of biodiesel reaches maximum at a reaction time of 120 min or less [22,30,32]. Acidcatalysed transesterification requires an even longer reaction time than the base-catalysed reaction because base catalysts are usually exhibit a higher reactivity than acid catalysts [27]. The reaction time needed during the conversion of triglycerides to biodiesel may range from 18 to 24 h as investigated in previous work [13,38]. However, an excess reaction time will lead to a reduction in the product yield due to the backward reaction of transesterification, causing more fatty acids to form soaps [7].

4. ECONOMIC ASPECTS OF BIODIESEL

Biodiesel has become more attractive recently due to its environmental benefits and the fact that it is sustainable because it is made from renewable sources. It has several outstanding advantages as an

effective alternative fuel with a lower level of pollution. However, the cost of biodiesel is the major challenge as it varies depending on the feedstock, processing, transporting, the price of crude petroleum and others [3,23].

Vegetable oils are renewable and a potential source of energy content close to petroleum diesel fuel. However, the relatively high cost of vegetable oils (about four times the cost of diesel in India) has made biodiesel not economically feasible as the methyl ester produced from these edible oils is much more expensive and cannot compete economically with diesel fuels. The cost of raw materials accounts for 60–75% of the total cost of biodiesel fuel [3,23]. Leduc et al. [49] also reported a rise of 40% in biodiesel cost associated with an increase in the feedstock cost. Lim and Teong [50] also determined that the price of the feedstock alone accounts for more than 75% of the overall cost of biodiesel production which is shown in Fig. 3. With the recent increase in the petroleum prices and the uncertainties of petroleum availability due to depletion, biodiesel is still gaining interest. Therefore there is a need to explore alternative feedstocks to lower the cost of biodiesel production.

5. ENVIRONMENTAL CONSIDERATIONS

Biodiesel is considered to be carbon neutral because the carbon dioxide released into the atmosphere during its consumption as a fuel is been recycled and reused for the growth of vegetable oil crops [11]. Biodiesel has a higher cetane number than diesel because of its long chain fatty acids with 2–3 double bonds, it is without aromatics and contains 10–11% oxygen by weight. These characteristics of biodiesel reduce the emission of carbon dioxide (CO), hydrocarbon (HC) and particulate in the exhaust gas compared to diesel fuel [51]. Biodiesel has a lower energy content than petrodiesel, and so it will require more fuel to produce the same energy compared to petrodiesel fuel. The burning rate of biodiesel is reduced by about 11% compared to diesel [52]. However, in view of the environmental impact through emissions, biodiesel has been reported to emit lesser pollutants compared to diesel.

6. CONCLUSIONS

The problem of diminishing petroleum reserves and the increasing awareness of environmental pollution from petroleum fuel emissions have led to the urge to find renewable alternative fuels as a substitute for petroleum based fuel. Biodiesel, which has environmental benefits and is produced from renewable resources, has become more attractive recently. Non-edible oils are becoming a potential feedstock for biodiesel production due to its suitable characteristics.

There are several methods proposed for biodiesel production, of which the transesterification of vegetable oils is the most preferable because of its renewability and sustainability. The factors that affect transesterification are the molar ratio of alcohol to glyceride, the amount of catalyst required, the reaction temperature, the reaction time and the amount of free fatty acids in the feedstock.

The cost of biodiesel is the major challenge and obstacle facing the commercialization of the products. This is due to the relatively high cost of vegetable oils as raw materials in biodiesel production and has made biodiesel not economically feasible. A continuous transesterification process can be one of the choices to lower the production cost. Also, the recovery of high quality by products such as glycerol for other useful applications is a possible way to offset the high cost of vegetable oils as feedstock. Further development and effort is required with more advanced techniques or methods for effective biodiesel production to have comparable characteristics to diesel, and which are sustainable and economically feasible. The emission compositions of biodiesel have contributed much in reducing environmental pollution where they are used, which has gained much attention and concern nowadays and eventually should be the majority point of view. Therefore, continuous development and improvement of biodiesel is needed in producing cleaner emissions with less impact on the environment and at a much lower cost compared to fossil fuels.

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