

Production of biodiesel from waste cooking oil and factors affecting its formation: A review

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Abstract: Growing concern regarding energy resources and the environment has increased interest in the study of alternative sources of energy. To meet increasing energy requirements, there has been growing interest in alternative fuels like biodiesel to provide a suitable diesel oil substitute for internal combustion engines. Biodiesels offer a very promising alternative to diesel oil since they are renewable and have similar properties. It is a promising substitute as an alternative fuel and has gained significant attention due to the predicted shortness of conventional fuels and environmental concern. The utilization of liquid fuels such as biodiesel produced from waste cooking oil by transesterification process represents one of the most promising options for the use of conventional fossil fuels. However, as the biodiesel is produced from vegetable oils and animal fats, there are concerns that biodiesel feedstock may compete with food supply in the long-term. Hence, the recent focus rely on using waste cooking oil as the substantial feed stocks for biodiesel production.

Keywords: Transesterification, Waste Cooking Oil, Micro-Emulsion Process, Pyrolysis

1. Introduction

Today it is very essential to use alternative fuel because of energy security, environmental concerns and socio-economic reasons. Escalating oil prices and depletion of oil reserves necessitate better alternatives of energy from fossil fuels. With the rise in concern for pollution caused by fossil fuels such as petroleum, coal and natural gas, alternative fuels and renewable sources of energy such as biodiesel are coming in vogue (Garlapati et al., 2013). Besides, the side effect of petroleum based fuels is that over the years there has been a steady increase in the amount of pollution produced by these fuels. The use of these energy sources over many years have resulted to the rise in global temperature levels also known as global warming (Ogunwole, 2012).

Over the last few years biodiesel has gained importance as an alternative fuel for diesel engines. Manufacturing biodiesel from used vegetable oil is relatively easy and possesses many environmental benefits. The use of vegetable oils as frying oils produces significant amounts of used oils which may present a disposal problem. Their use for biodiesel production has the advantage of their low

price. Used vegetable oil is described as a 'renewable fuel' as it does not add any extra carbon dioxide gas to the atmosphere, as opposed to fossil fuels, which cause changes in the atmosphere. Vegetable oil from plant sources is the best starting material to produce biodiesel because the conversion of pure triglyceride to fatty acid methyl ester is high and the reaction time is relatively short. The most common way to produce biodiesel is by transesterification, which refers to a catalyzed chemical reaction involving vegetable oil and an alcohol to yield fatty acid alky esters and glycerol (Thirumarimurugan *et al.*, 2012).

The use of edible vegetable oils and animal fats for biodiesel production has recently been of great concern because they compete with food materials. As the demand for vegetable oils for food has increased tremendously in recent years, it is impossible to justify the use of these oils for fuel use purposes such as biodiesel production. Moreover, these oils could be more expensive to use as fuel. Hence, the contribution of non-edible oils such as jatropha and soapnut will be significant as a non-edible plant oil source for biodiesel production (Arjun *et al.*, 2008).

The costs of raw materials for biodiesel production accounts for large percent of the direct biodiesel production

costs required. Thus, one way of reducing the biodiesel production costs is to use the less expensive raw material containing fatty acids such as animal fats, non edible oils, and waste cooking oils and by products of the refining vegetables oils (Ogunwole, 2012). Alnuami (2014) compares the cost of biodiesel production based on the materials used. It can be seen that amongst the four materials such as palm oil, jatropha oil, soya bean oil and waste cooking oil, waste cooking oil can be seen as the cheapest and most economical raw material for biodiesel production.

However, production of biodiesel from edible oils competes with the use of those oils as food resource for human being. Thus, finding cheaper and non edible oils for biodiesel production is an important target. Therefore, some non edible oils and frying oils have been gained more attention as feedstocks for biodiesel production. However, oils of higher free fatty acid (FFA) content cannot be transesterified in the presence of an alkaline base catalyst for it leads to catalyst deactivation and soap formation. As a result, the FFA content should be reduced. A dual step transesterification namely acid base transesterification (ABTE) was used to reduce the high FFA contents of oils or fats. The oil is pretreated with an acid dissolved in methanol, where as the second step is base catalyzed transesterification in which oil reacts with methanol in the presence of an alkaline catalyst to form ester and glycerol (Fadhil *et al.*, 2012).

Biodiesel can be defined as the alkyl monoesters of fatty acids from vegetable or animal fats. It can be used as an alternative for petro diesel for it is renewable, non toxic and biodegradable fuel (Fadhil *et al.*, 2012). As an alternative fuel, it has many advantages as it is derived from a renewable, domestic resource, thereby relieving dependence on petroleum fuel trade in. It is biodegradable and nontoxic when compared to petroleum based diesel, biodiesel has a more favorable combustion emission profile, such as low emissions of carbon monoxide, particulate matter and unburned hydrocarbons. Carbon dioxide produced by combustion of biodiesel can be recycled by photosynthesis, thus minimizing the impact of biodiesel combustion on the greenhouse effect. Biodiesel has a relatively high flash point, which makes it less volatile and safer to transport or handle than petroleum diesel. Engine wear and long engine life are advantages that can be provided by biodiesel as it does have lubricating properties. Therefore, use of biodiesel is being grown vividly during the last years (Ogunwole, 2012).

Diesel engines are widely used for different application in industrial power plants, transportation, agriculture etc. Despite these advantages, the environmental pollution caused by diesel engines becomes a major concern throughout the world. Diesel engines produce smoke, particulate matter, oxides of nitrogen (NO_x), oxides of carbon (CO & CO₂) and unburnt hydrocarbon. Several alternative fuels have been studied to either substitute diesel fuel partially or completely. Vegetable oils are

proposed to be promising alternatives to diesel, as they are produced in rural areas. The oil produced from seeds can provide self employment opportunities (Mulimani *et al.*, 2012).

This paper reviews the technologies vital for production of biodiesel starting with the direct use or blending of oils, continuing with micro emulsion and pyrolysis and finishing with an emphasis on the current process of choice, transesterification. Besides, it deals with the factors affecting biodiesel production process such as temperature, reaction time, methanol to oil molar ratio, type and amount of catalyst, stirring rate and free fatty acid and moisture content.

2. Waste/Used Cooking Oil

The feedstock coming from waste vegetable oils or commonly known as waste cooking oils is one of the alternative sources among other higher grade or refined oils. Waste cooking oil is easy to collect from other industries such as domestic usage and restaurant and also cheaper than other oils (refined oils). Hence, by using these oils as the raw material, we can reduce the cost in biodiesel production. The advantages of using waste cooking oils to produce biodiesel are the low cost and prevention of environment pollution. These oils need to be treated before disposal to the environment to prevent pollution. Due to the high cost of disposal, many individuals dispose waste cooking oils directly to the environment especially in rural area. So that, the use of waste cooking oils is an effective way to reduce the cost of biodiesel production (Arifin, 2009).

Used cooking oil has sufficient potential to fuel the compression ignition engines. The kinematic viscosity of used cooking oil (UCO) is about 10 times greater, and its density is about 10% higher than that of mineral diesel. These properties play vital role in the combustion; therefore these must be modified prior to the use of UCO in the engine. Many techniques have been developed to reduce the kinematic viscosity and specific gravity of vegetable oils, which include pyrolysis, emulsification, leaching and transesterification. Among these techniques, transesterification is the hot favorite. This is because of the fact that this method is relatively easy, carried out at normal conditions, and gives the best conversion efficiency and quality of the converted fuel (Shahid *et al.*, 2012).

3. Biodiesel

Biodiesel is increased attention as an alternative, non-toxic, biodegradable, and renewable diesel fuel. Biodiesel is usually produced by the transesterification of vegetable oil or animal fat with short chain alcohol such as methanol or ethanol. It has higher oxygen content than petroleum diesel and its use in diesel engines have shown great reductions in emission of particulate matter, carbon monoxide, sulfur, polyaromatics, hydrocarbons, smoke and

noise. In addition, burning of vegetable oil based fuel does not contribute to net atmospheric CO₂ levels because such fuel is made from agricultural materials which are produced via photosynthetic carbon fixation (Sukjit and Punsuvon, 2013).

4. Process of Synthesizing Biodiesel

There are different processes which can be applied to synthesize biodiesel such as direct use and blending, micro emulsion process, thermal cracking process and the most conventional way is transesterification process.

4.1. Direct Use and Blending

The direct use of vegetable oils in diesel engine is not favorable and problematic because it has many inherent failings. Even though the vegetable oils have familiar properties as biodiesel fuel, it required some chemical modification before can be used into the engine. It has only been researched extensively for the past couple of decades, but has been experimented with for almost hundred years. Although some diesel engine can run pure vegetable oils, turbocharged direct injection engine such as trucks are prone to many problems. Energy consumption with the use of pure vegetable oils was found to be similar to that of diesel fuel. For short term use, ratio of 1:10 to 2:10 oil to diesel has been found to be successful (Arifin, 2009).

4.2. Micro-Emulsion Process

The problem of the high viscosity of vegetable oils was solved by micro-emulsions with solvents such as methanol, ethanol, and 1-butanol. Micro-emulsion is defined as a colloidal equilibrium dispersion of optically isotropic fluid microstructures with dimensions generally in the 1-150 nm range formed spontaneously from two normally immiscible liquids and one or more ionic or non-ionic amphiphiles (Arifin, 2009; Parawira, 2010).

The components of a biodiesel micro-emulsion include diesel fuel, vegetable oil, alcohol, and surfactant and cetane improver in suitable proportions. Alcohols such as methanol and ethanol are used as viscosity lowering additives, higher alcohols are used as surfactants and alkyl nitrates are used as cetane improvers. Microemulsions can improve spray properties by explosive vaporisation of the low boiling constituents in the micelles. Micro-emulsion results in reduction in viscosity increase in cetane number and good spray characters in the biodiesel. However, continuous use of micro-emulsified diesel in engines causes problems like injector needle sticking, carbon deposit formation and incomplete combustion (Parawira, 2010).

4.3. Thermal Cracking (Pyrolysis)

Pyrolysis can be defined as the conversion of one substance into another by means of heat in the absence of air (or oxygen) or by heat in the presence of a catalyst which result in cleavage of bonds and formation of a

variety of small molecules. The pyrolysis of vegetable oil to produce biofuels has been studied and found to produce alkanes, alkenes, alkadienes, aromatics and carboxylic acids in various proportions. The equipment for thermal cracking and pyrolysis is expensive for modest biodiesel production particularly in developing countries. Furthermore, the removal of oxygen during the thermal processing also removes any environmental benefits of using an oxygenated fuel. Another disadvantage of pyrolysis is the need for separate distillation equipment for separation of the various fractions. Also the product obtained is similar to gasoline containing sulphur which makes it less ecofriendly (Parawira, 2010). Pyrolytic chemistry is difficult to characterize because of the variety of reaction path and the variety of reaction products that may be obtained from the reaction occur. The pyrolyzed material can be vegetable oils, animal fats, natural fatty acids and methyl esters of fatty acids. The first pyrolysis of vegetable oil was conducted in an attempt to synthesize petroleum from vegetable (Arifin, 2009).

4.4. Transesterification

The most common way to produce biodiesel is the transesterification method, which refers to a catalyzed chemical reaction involving vegetable oil and alcohol to yield fatty acid alkyl esters (i.e., biodiesel) and glycerol. The reaction requires a catalyst, usually a strong base, such as sodium and potassium hydroxide or sodium methylate. A catalyst is usually used to improve the reaction rate and the yield. Since the reaction is reversible, excess alcohol is used to shift the equilibrium to the product side. Especially methanol is used as alcohol because of its low cost and its physical and chemical advantages. Methanol can quickly react with vegetable oil and NaOH can easily dissolve in it. To complete a transesterification reaction stoichiometrically, a 3:1 molar ratio of alcohol to triglycerides is necessary. In practice, the ratio needs to be higher to drive the equilibrium to a maximum ester yield (Saribiyik *et al.*, 2012; Antony Raja *et al.*, 2011).

The triglycerides are reacted with a suitable alcohol (Methyl, Ethyl, or others) in the presence of a catalyst under a controlled temperature for a given length of time. The final products are Alkyl esters and Glycerin. The Alkyl esters, having favorable properties as fuels for use in CI engines, are the main product and the Glycerin, is a by-product. The chemical reaction of the tri-glyceride with methyl alcohol is shown below. With higher alcohols the chemical equation would change correspondingly (Jaichandar and Annamalai, 2011).

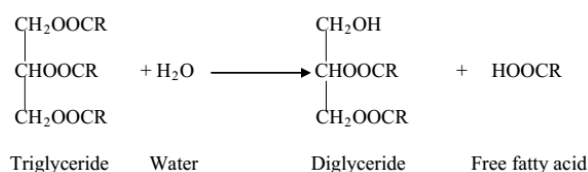


Figure 1. General equation for transesterification of triglycerides.

5. Biodiesel Production Processes

Biodiesel derived from biological resources is a renewable fuel, which has drawn more and more attention recently. A fatty acid methyl ester is the chemical composition of biodiesel. Transesterification is widely used for the transformation of triglyceride into fatty acid methyl ester. The manufacturing process is based on the transesterification of triglycerides by alcohols to fatty acid methyl esters, with glycerol as a byproduct. The base catalyzed production of biodiesel generally has the following processes.

5.1. Mixing of Alcohol and Catalyst

This typical process is mainly done by mixing alkali hydroxide (commonly potassium hydroxide and sodium hydroxide) with common alcohols (methanol and ethanol) in the mixer with standard agitator to facilitate the mixing. Alkali hydroxide is dissolved in the alcohol to produce alkoxide solution (Garlapati *et al.*, 2013).

5.2. Chemical Reaction

The alcohol and catalyst mixture is then charged into a closed reaction vessel and the oil is added. The reaction system is totally closed to the atmosphere to prevent the loss of alcohol, since it easily vaporizable. The reaction mixture is kept just near the boiling point of the alcohol to speed up the reaction. Excess alcohol is normally used to ensure total conversion of the oil to its esters as there is no problem of recovering of the alcohol for later use after recycling.

5.3. Separation

After the reaction is completed, there exists glycerol and biodiesel formation. Both have a significant amount of the excess alcohol that was used in the reaction which is in need of being recovered. The reacted mixture is sometimes neutralized at this step if the basic media that is caused by alkali hydroxide is occurred. The glycerol phase is much denser than biodiesel phase, making biodiesel to be floated. The two products can be separated by gravity using settling vessel. The glycerol is drawn off at the bottom of the settling vessel and biodiesel is drawn off at the top. In some cases, a centrifuge is used to separate the two materials faster by screening both phases (Garlapati *et al.*, 2013).

5.4. Alcohol Removal

After the glycerol and biodiesel phases have been separated, the excess alcohol in each phase is removed with a flash evaporation process or by distillation commonly. But currently extractive distillation can instead be used to fasten the process and to be more economical. On the other hand, the alcohol is removed and the mixture neutralized before the glycerol and esters have been separated to prevent the effect of basic media inside the reactor. After the alcohol is being recovered it is used as main raw

material (Garlapati *et al.*, 2013).

5.5. Biodiesel Washing

After transesterification the upper ester layer may contain traces of NaOH, methanol and glycerol. Since the remaining unreacted methanol in the biodiesel has safety risks and can corrode engine components, the residual catalyst (NaOH) can damage engine components, and glycerol in the biodiesel can reduce fuel lubricity and cause injector coking and other deposits. These being water soluble is removed by washing (4 -6 times) the biodiesel with water maintained at 40-50°C. Washing is carried out by spraying hot water over the biodiesel; precautions were taken to avoid soap formation (Mulimani, *et al.*, 2012). The washed biodiesel needs drying in order to remove trace impurities. In some processes washing step is not necessary depending on the quality of biodiesel produced (Garlapati *et al.*, 2013).

After the completion of washing process the biodiesel may contain some traces of water. Biodiesel is heated to 110 °C to remove the trapped traces of water (for drying) (Mulimani, *et al.*, 2012).

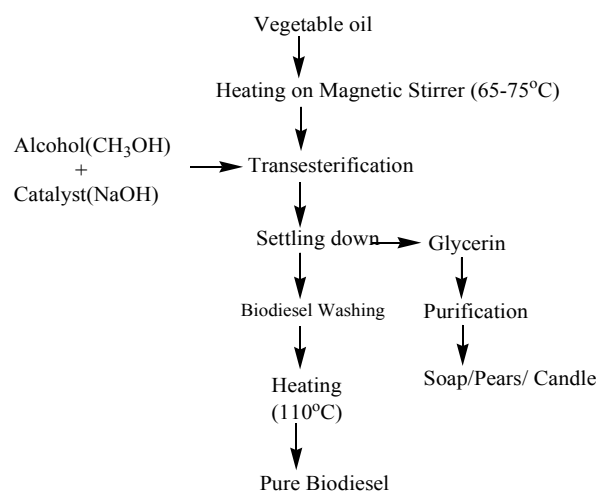


Figure 2. Flow chart of Biodiesel production process (Mulimani, *et al.*, 2012).

6. Factors Affecting Biodiesel Production

The process of transesterification brings about drastic change in viscosity of the vegetable oil. The high viscosity component, glycerol, is removed and hence the product has low viscosity like the fossil fuels. The biodiesel produced is totally miscible with mineral diesel in any proportion. Flash point of the biodiesel is lowered after transesterification and the cetane number is improved. The yield of biodiesel in the process of transesterification is affected by several process parameters which include; presence of moisture and free fatty acids (FFA), reaction time, reaction temperature, catalyst and molar ratio of alcohol and oil (Parawira, 2010).

The main factors affecting the transesterification are molar ratio of alcohol to oil, amount and catalyst type, reaction time, reaction temperature, stirring rate, presence of free fatty acids and moisture (Mulimani *et al.*, 2012; Highina, *et al.*, 2012).

6.1. Temperature

Reaction temperature is the important factor that will affect the yield of biodiesel. For example, higher reaction temperature increases the reaction rate and shortens the reaction time due to the reduction in viscosity of oils. However, the increase in reaction temperature beyond the optimal level leads to decrease of biodiesel yield, because higher reaction temperature accelerates the saponification of triglycerides (Mathiyazhagan and Ganapathi, 2011) and causes methanol to vaporize resulting in decreased yield (Anitha and Dawn, 2010).

Usually the transesterification reaction temperature should be below the boiling point of alcohol in order to prevent the alcohol evaporation. The range of optimal reaction temperature may vary from 50°C to 60°C depends upon the oils or fats used (Mathiyazhagan and Ganapathi, 2011). Therefore, the reaction temperature near the boiling point of the alcohol is recommended for faster conversion by various literatures. At room temperature, there is up to 78% conversion after 60 minutes, and this indicated that the methyl esterification of the FFAs could be carried out appreciably at room temperature but might require a longer reaction time. In butyl esterification, however, temperature had stronger influence. Temperature increases the energy of the reacting molecules and also improves the miscibility of the alcoholic polar media into a non-polar oily phase, resulting in much faster reactions (Ogbu and Ajiwe, 2013).

6.2. Reaction Time

The increase in fatty acid esters conversion observed when there is an increase in reaction time. The reaction is slow at the beginning due to mixing and dispersion of alcohol and oil. After that the reaction proceeds very fast. However the maximum ester conversion was achieved within < 90 min. Further increase in reaction time does not increase the yield product i.e. biodiesel/mono alkyl ester. Besides, longer reaction time leads to the reduction of end product (biodiesel) due to the reversible reaction of transesterification resulting in loss of esters as well as soap formation (Mathiyazhagan and Ganapathi, 2011; Jagadale and Jugulkar, 2012).

6.3. Methanol to Oil Molar Ratio

One of the most important parameters affecting the yield of biodiesel is the molar ratio of alcohol to triglyceride. Stoichiometrically 3 moles of alcohol and 1 mole of triglyceride are required for transesterification to yield 3 moles of fatty acid methyl/ethyl esters and 1 mole of glycerol is used. It is varied from 5.6 – 7.8:1 for both the catalyst systems. Biodiesel yield could be elevated by

introducing an excess amount of methanol to shift the equilibrium to the right hand side (Anitha and Dawn, 2010).

Methanol, ethanol, propanol, butanol and amyl alcohol can be used in the transesterification reaction, amongst these alcohols methanol is applied more frequently as its cost is low and it is physically and chemically advantageous (polar and shortest chain alcohol) over the other alcohols. In contrast, ethanol is also preferred alcohol for using in the transesterification process compared to methanol since it is derived from agricultural products and is renewable and biologically less offensive in the environment. The effect of volumetric ratio of methanol and ethanol to oil was studied. Results exhibit that highest biodiesel yield is nearly 99.5% at 1:6 oil/methanol. In comparison, biodiesel yield using methanol continuously increases with the raise of methanol molar ratio (Hossain and Boyce, 2009).

6.4. Type and Amount of Catalyst

Biodiesel formation is also affected by the concentration of catalyst. Most commonly used catalyst for biodiesel production is sodium hydroxide (NaOH) or Potassium hydroxide (KOH) (Mathiyazhagan and Ganapathi, 2011). The type and amount of catalyst required in the transesterification process usually depend on the quality of the feedstock and method applied for the transesterification process. For a purified feedstock, any type of catalyst could be used for the transesterification process. However, for feedstock with high moisture and free fatty acids contents, homogenous transesterification process is unsuitable due to high possibility of saponification process instead of transesterification process to occur.

The yield of fatty acid alkyl esters generally increases with increasing amount of catalyst. This is due to availability of more active sites by additions of larger amount of catalyst in the transesterification process. However, on economic perspective, larger amount of catalyst may not be profitable due to cost of the catalyst itself. Therefore, similar to the ratio of oil to alcohol, optimization process is necessary to determine the optimum amount of catalyst required in the transesterification process (Kansedo, 2009; Jagadale and Jugulkar, 2012).

6.5. Mixing Intensity

Oils and alcohols are not totally miscible, thus reaction can only occur in the interfacial region between the liquids and transesterification reaction is a moderately slow process. So, Mixing is very important in the transesterification process, adequate mixing between these two types of feedstock is necessary to promote contact between these two feed stocks, therefore enhance the transesterification reactions to occur. Mechanical mixing is commonly used in the transesterification process. The intensity of the mixing could be varied depending on its necessity in the transesterification process. In general, the mixing intensity must be increased to ensure good and

uniform mixing of the feedstock. When vegetable oils with high kinematic viscosity are used as the feedstock, intensive mechanical mixing is required to overcome the negative effect of viscosity to the mass transfer between oil, alcohol and catalyst (Jagadale and Jugulkar, 2012; Kansedo, 2009).

Agitation speed plays an important role in the formation of end product (mono alkyl ester or biodiesel), because agitation of oil and catalyst mixture enhances the reaction. For example the mixing intensities chosen were 200 rpm, 400 rpm, 600 rpm and 800 rpm for 60 min while other parameters were kept constant. At 400 rpm higher conversion of end product were obtained. Because, lower stirring speed shows lower product formation. On the other hand higher stirring speed favors formation of soap. This is due to the reverse behavior of transesterification reaction (Mathiyazhagan and Ganapathi, 2011).

6.6. Free Fatty Acid and Moisture Content

The free fatty acid and moisture content are the key parameters for determining the viability of vegetable oils to be used in transesterification process. Presence of moisture content in the oil increases the amount of free fatty acids. To carry out this reaction to completion, less than 3% free fatty acid content in oils is needed.

Base-catalyzed transesterification reaction requires water free and low acid value (< 1) raw materials for biodiesel production. If the oil samples have high FFA content (more than 1%) then the reaction requires more alkali catalyst to neutralize the FFA. Presence of water gives greater negative effect than that of FFAs because water can cause soap formation and frothing which can cause increase in viscosity. In addition formation of gels and foams hinders the separation of glycerol from biodiesel. Free fatty acid and water always produce negative result during transesterification and causes soap formation and consumes the catalyst which leads to reduction of catalyst effect. They also lead to the reduction of methyl ester. To overcome this problem, supercritical methanol method was proposed. It may be noted that water has less influence in supercritical methanol method (Mathiyazhagan and Ganapathi, 2011).

As Jagadale and Jugulkar (2012) stated the moisture levels of the collected waste chicken fats vary widely, being as high as 18%. Therefore, it is not possible to convert these oils to biodiesel by using a single process. One drawback of biodiesel is that there is an inverse relationship between biodiesel's oxidative stability and its cold flow properties. Saturated compounds are less prone to oxidation than unsaturated compounds but they raise the cloud point of the fuel. The reaction of FFAs with alcohol produces ester, but also water that inhibits the of the transesterification glycerides. This is due to the effect of the water produced when the FFAs react with the alcohol to form esters. The coincidence of the lines indicates that water formation is the primary mechanism limiting the completion of the acid catalyzed esterification reaction with FFAs.

7. Conclusion

With exception of hydropower and nuclear energy, the major part of all energy consumed worldwide comes from petroleum, charcoal and natural gas. However, these sources are limited, and will be exhausted in the near future. Thus, Biodiesel is an alternative and renewable fuel for diesel engines and has become more attractive in recent times. The catalysts used in the production of biodiesel are acids, bases and enzymes. Transesterification is a commonly employed method to reduce the viscosity during the production of biodiesel. The purpose of this method is to reduce the viscosity of oil or fat using acid or base catalyst in the presence of methanol or ethanol. However, the biodiesel production by transesterification is strongly affected by molar ratio of alcohol, reaction temperature, reaction time and catalyst concentration. The main advantage in biodiesel usage is attributed to lesser exhaust emissions in terms of carbon monoxide, hydrocarbons and particulate matter. Hence, the paper concentrates on the development of economically viable as well as ecofriendly substrates such as waste cooking oil for biodiesel production and briefly discusses the factors that will affect the biodiesel production.

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