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Review Article

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A Review on Biodiesel Production as Alternative Fuel

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ABSTRACT

Biodiesel has become a key source as a substitution fuel and is making its place as a key future renewable energy source. As an alternative fuel for diesel engines, it is becoming increasingly important due to diminishing petroleum reserves and the environmental consequences of exhaust gases from petroleum-fuelled engines. To minimize the biofuel cost, in recent days waste cooking oil was used as feedstock. The used cooking oils are used as raw material, adaption of continuous transesterification process and recovery of high quality glycerol from biodiesel by-product (glycerol) are primary options to be considered to lower the cost of biodiesel. There are four primary ways to make biodiesel, direct use and blending, micro-emulsions, thermal cracking (pyrolysis) and transesterification. The utilization of liquid fuels such as biodiesel produced from used 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. Currently, the higher GHG emissions from fossil fuel has persuaded the policy makers, investors and researchers to think more of the substitution of fossil fuels to save the planet. In this review, the processes of biodiesel production by transesterification and factors affecting biodiesel production are also addressed.

Key words: *Biodiesel; Transesterification, Pyrolysis, Micro-emulsion, Direct Use and Blending*

INTRODUCTION

Fossil fuels are non-renewable energy resources. Although, these fuels are contributing largely to the world energy supply, their production and use have raised environmental concerns and political debates. It has been shown that 98% of carbon emissions are resulted from fossil fuel combustion[1]. The need of energy is increasing continuously due to rapid increase in the number of industries and vehicles owing to population explosion. The sources of this energy are petroleum, natural gas coal, hydrocarbon and nuclear. The major disadvantages of using petroleum based fuels are atmospheric pollution created by the use of petroleum diesel. The petroleum diesel combustion emits several greenhouse gases. Apart from these emissions, petroleum diesel is also major source of these air containments including NOX, SOX, CO, particulate matter and volatile organic compounds[2].

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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[3]. The concept of bio-fuel is not new. Rudolph Diesel was the first to use a vegetable oil (peanut oil) in a diesel engine in 1911. The use of bio-fuels in place of conventional fuels would slow the progression of global warming by reducing sulfur and carbon oxides and hydrocarbon emissions. Because of economic benefits and more power output, biodiesel is often blended with diesel fuel in ratios of 2, 5 and 20%. The higher the ratio of biodiesel to diesel, the lower the carbon dioxide emission. Using a mixture containing 20% biodiesel reduces carbon dioxide net emissions by 15.66% while using pure biodiesel makes the net emission of carbon dioxide zero[4].

Biodiesel is defined as monoalkyl esters of long chain fatty acids originated from natural oils and fats of plants and animals, is a kind of alternative for fossil fuels. Biodiesel has attracted wide attention in the world due to its renewablity, biodegradablity, nontoxicity and environmentally friendly benefits[5]. 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. 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[6].

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[7] and[8] 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. 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, leaning and transesterification. Among these techniques, transesterification is the hot favorite[9].

Biodiesel is an alternative diesel fuel derived from vegetable oils or animal fats. The main components of vegetable oils and animal fats are triglycerides or also known as ester of fatty acid attached to glycerol[10,11].

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[12].

This paper reviews 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 and different production processes.

II. BIODIESEL AND ITS RAW MATERIALS

Biodiesel is an alternative liquid fuel that can substantially replace conventional diesel and reduce exhaust pollution and engine maintenance costs. This renewable fuel can be produced from different feedstock containing fatty acids such as animal fats, non edible oils

(Jatropha oil, Karanji or Pongamia oil, Neem oil, Jojoba oil, Cottonseed oil, Linseed oil, Mahua oil, Deccan hemp oil, Kusum oil, Orange oil, and Rubber seed oil), and waste cooking oils and by products of the refining vegetables oils and algae[12,13].

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[14].

III. PRODUCTION OF 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. 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[9].

IV. 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[15].

V. 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[4]. A micro emulsion is defined as the colloidal equilibrium dispersion of optically isotropic fluid microstructures with dimensions generally in the range of 1–150 nm formed spontaneously from two normally immiscible liquids and one or more ionic or non-ionic[15,17].

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 vaporization 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[16].

VI. THERMAL CRACKING (PYROLYSIS)

Pyrolysis is defined as the conversion of one substance into another by means of heat or heating with the aid of a catalyst. Pyrolysis involves heating in the absence of air or oxygen and cleavage of chemical bonds to yield 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[16]. 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[15].

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 (biodiesel) and glycerol. The reaction requires a catalyst, usually a strong base, such as sodium and potassium hydroxide or sodium methylate[18] and[19]. and / or sulfuric acid based transesterification processes. Acid catalysts are too slow to be practical for converting triglycerides to biodiesel; however, acid catalysts are quite effective at converting FFAs to biodiesel. Therefore, an acid-catalyzed pretreatment step to convert the FFAs to esters, followed by an alkali-catalyzed step to convert the triglycerides should provide an efficient method to convert high FFAs to biodiesel[20]. Transesterification process helps reduce the viscosity of the oil[19]. 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 [18] and[21]. The stoichiometric reaction requires 1 mol of a triglyceride and 3 mol of the alcohol. However, an excess of the alcohol is used to increase the yields of the alkyl esters and to allow its phase separation from the glycerol formed[22].

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 chemical reaction of the tri-glyceride with alcohol is shown below. With higher alcohols the chemical equation would change correspondingly[23].

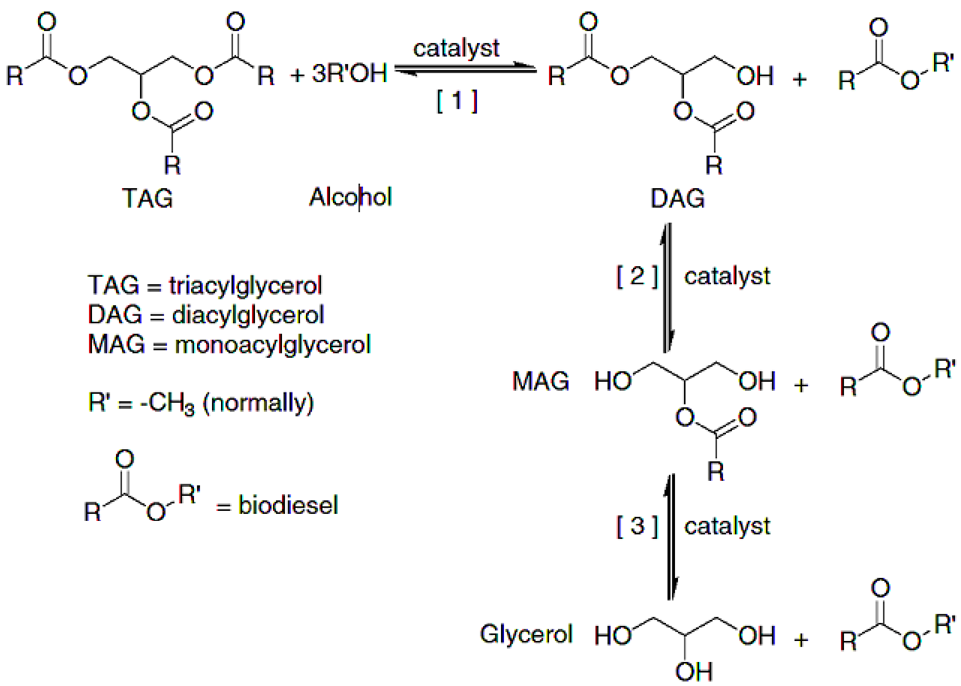

Fig. 1: Biodiesel Production by Transesterification[13]

VII. 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[16,24].

Temperature

Reaction temperature is the important factor that will affect the yield of biodiesel. For example, higher reaction temperature increases the reaction rate and shortened 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[25] and causes methanol to vaporize resulting in decreased yield[26].

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[25]. 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[27].

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[25] and[28].

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. In order to shift the reaction to the right, it is necessary to either use excess alcohol or remove one of the products from the reaction mixture. The second option is usually preferred for the reaction to proceed to completion. The reaction rate is found to be highest when 100% excess methanol is used[29,26].

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 increaseswith the raise of methanol molar ratio[30].

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)[25]. 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 ofthe 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[31] and[28].

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[28 ,31]. Most literatures indicate that during the transesterification reaction, the reactants initially form a two-phase liquid system. The mixing effect has been found to play a significant role in the slow rate of the reaction. As phase separation ceases, mixing becomes insignificant. The effect of mixing on the kinetics of the transesterification process forms the basis for process scale-up and design[32].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[28,31].

Free fatty acid and water content

The FFA and moisture contents have significant effects on the transesterification of glycerides with alcohol using catalyst. The high FFA content (>1% w/w) will happen soap formation and the separation of products will be exceedingly difficult, and as a result, it has low yield of biodiesel product[33]. In addition formation of gels and foams hinders the separation of glycerol from biodiesel[25]. For instance, Water content in waste cooking oil will accelerate the hydrolysis reaction and simultaneously reduce the amount of ester formation[34].

To overcome this problem, supercritical methanol method was proposed. It may be noted that water has less influence in supercritical methanol method[25].Therefore, water content should not always exceed 0.5% to obtain 90% yield of biodiesel and it is more critical for an acid-catalyzed reaction than base catalyzed reaction[35].

Stated the moisture levels of the collected waste chicken fats vary widely, being as high as 18%[28]. 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.

CONCLUSION

Biodiesel has attracted wide attention in the world due to its renewablity, biodegradablity, non toxicity and environmentally friendly benefits. It is an important new alternative transportation fuel. It can be produced from different feedstock containing fatty acids such as animal fats, non edible oils, and waste cooking oils and by products of the refining vegetables oils and algae. Transesterification is a commonly employed method for its production. 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 is strongly affected by parameters such as molar ratio of alcohol, reaction temperature, reaction time and catalyst concentration. Hence, this paper concentrates on the development of economically viable as well as ecofriendly substrates for biodiesel production and briefly discusses the factors that affect the biodiesel production.

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