A Review on Production of Biodiesel Using Catalyzed Transesterification

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Abstract. Biodiesel is arguably an important fuel for compression ignition engine as far as sustainability and environmental issues are concerned. It can be produced from both edible and non-edible vegetable oils and animal fats. Owing to higher viscosity, the utilization of crude vegetable oil is not advisable as it results engine failure. For reducing the viscosity and improving the other fuel characteristics comparable to that of diesel fuel, different approaches have been developed. However, transesterification process is very reliable, less costly and easy method compared to other methods. Due to more free fatty acids content in most of the non-edible vegetable oils, a pretreatment is employed to convert the acids to ester, then transesterified with suitable alcohol. Primarily yield of biodiesel depends upon the molar ratio of oil/alcohol, reaction temperature, reaction time, amount of catalyst, type of catalyst, stirring speed. Both homogeneous and heterogeneous catalysts are used for synthesis purposes. Heterogeneous catalysts are less costly, environmental benign and can be derived from natural resources. Enzymatic catalysts are more environmental benign than heterogeneous catalysts but are costly, which hinders its widespread research and utilization. This article reviews the results of prominent works and researches in the field of production of biodiesel via catalyzed transesterification process.

Keywords: *transesterification, acid-catalyzed, base-catalyzed, homogeneous catalysts, heterogeneous catalysts*

INTRODUCTION

The scarcity of fossil diesel, ever increasing population and their demand for energy, increasing cost of petroleum fuel, strict emission norms, climate change and global environmental problem has renewed interest among scientific community and researchers to search for an alternative source of energy. Climate change is real and it is happening in an unprecedented rate and decades ahead of what the scientific community projected. The fossil based liquid fuel is majorly used in transportation and agricultural sectors in any developing or developed countries. People and their ever increasing thirst for energy have brought devastating consequences of global warming, climate change and other environmental problems. Presently energy, environment and sustainability are the hot topics to discuss about across the globe [1]. Petroleum based fuels are finite and distributed across certain regions of the world. Transportation and agricultural sector are the two main consumers of finite reserved petro-diesel [1-4,40]. The concept of using vegetable oil in diesel engine is not new. In 1911 Dr. Rudolf Diesel used peanut oil to energize one of his diesel engines. He encouraged using various vegetable oils in diesel engines. Not only Dr. Diesel but Henry Ford has similar kind of vision. In 1925 he hailed biofuel as the “fuel of the future” after he had successfully ran his model T ford with bio-ethanol [5]. India like other energy independent countries has also set the target to replace or supplement petro-diesel. Biodiesel prepared from vegetable oils as a sustainable liquid fuel has gained a lot of attention for several reasons. Now the time has come to add feathers to the ideas of legends and save the prospects of every future generation.

Since then many more investigations would have been tried, if cheap crude oil had not come to dominate the market. Again from last two decades bio-origin oil has gained a lot of attention from all over the world, due to alarming trends in global energy demand and other global-environmental issues [2]. Biofuels, in particular biodiesel has proved promising among other renewable sources. It provides a lot of advantages such as foreign exchange savings, security reasons, reduction of greenhouse gas emissions, regional development etc. [2]. As per TERI and energy policy 70% of high speed diesel is consumed in transportation sector and the demand is expected to grow 6-8% in coming years [6]. India is world's fourth largest consumer of crude and petroleum products after USA, China and Japan. As per "The energy statistics report, Gov. of India", the net import is very large compared to net production of petroleum diesel [6]. To deal with the present crisis a lot of awareness programme, seminars, and conferences has been promoted in India and other countries as well. Biodiesel has emerged as a suitable option, especially for the transportation sector.

Biodiesel is an alternative fuel derived from vegetable oils or animal fats by reacting it with some suitable alcohol. The alternative fuel derived from oils and fats has properties similar to diesel fuel. Some important advantages of biodiesel are; it is derivation from a renewable feedstock, biodegradability, very low sulphur content, lower exhaust emission, nearly carbon neutral fuel and important disadvantages such as high feedstock cost, inferior storage stability, poor low temperature operability and more NOx exhaust emissions [7].

The choice of particular feedstock for biodiesel production depends on three things.

a. Availability
b. Price
c. Policy

As per biofuel policy (Gov. of India), it has been suggested to investigate only on non-food oil for the production of biodiesel and bio-ethanol from sugar cane molasses. Production of biofuel in India mainly depends on feedstock like Jatropha, Karanj, mahua etc. Planning commission proposed a target of 20% blending biodiesel with high speed diesel. The report estimated that 13.4 million hector of land can be used to cultivate jatropha, where 11.2 million ha is required to meet the popular 20% blending target [6]. This paper reviews some prominent work regarding the production of biodiesel by using catalysed transesterification.

PRODUCTION OF BIODIESEL

Vegetable oils are mainly composed of triglyceride contains 3 moles of fatty acids with 1 mole of glycerol. The chemical structure is

$$\begin{array}{c} CH_2\text{—}COOR^x \\ | \\ CH\text{—}COOR^y \\ | \\ CH_2\text{—}COOR^z \end{array}$$

Where R^x, R^y, R^z represents hydrocarbon chain of fatty acids. Depending up on the length of carbon chain and no of double bond fatty acids varies. Direct use of vegetable oil is not recommended due to several reasons, such as incomplete combustion, high viscosity, poor cold flow properties, ignition delay, high carbon deposit, injector coking, piston ring sticking, lubrication oil dilution and oil contamination etc. [4].

Hence fuel modification found a promising and potential solution to use tree borne oils in compression ignition engine. Major fuel modification processes are;

1. Dilution
2. Preheating
3. Micro-emulsion
4. Pyrolysis
5. Transesterification

From all the processes transesterification process proves to be the best process for fuel modification and the biodiesel is the product of this process.

Transesterification

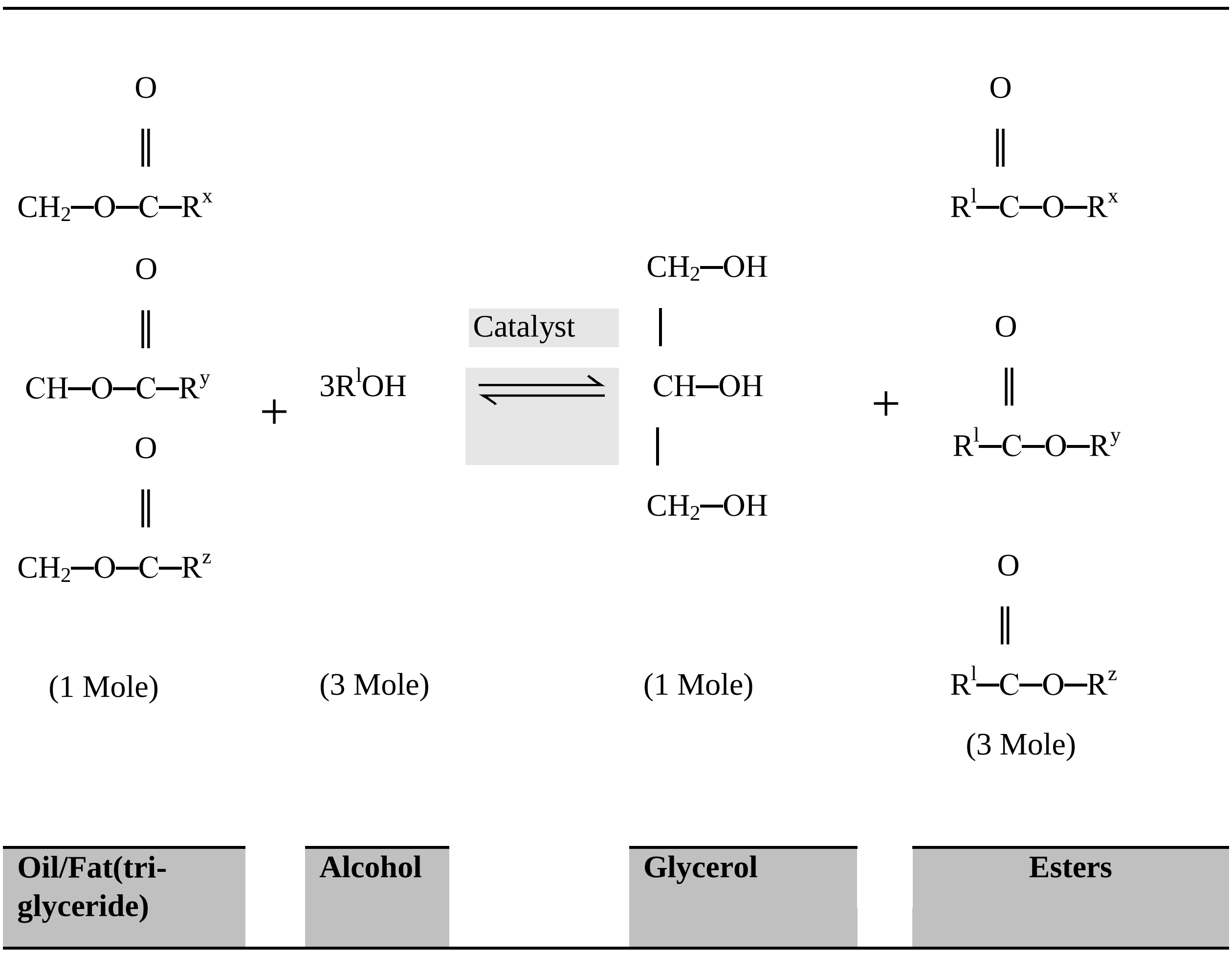

FIGURE 1. Transesterification reaction

It is the reaction of a vegetable oil or animal fat with alcohol to obtain esters and glycerine as shown in Fig.1. The ester is known as biodiesel. Transesterification means to transfer one form of ester to another form. It may require some kind of catalyst to speed up the reaction and facilitates maximum yield of esters. The alcohol is generally methanol, ethanol, butanol, propanol etc. The oils and fats are pre-treated to remove impurities and water. If, FFA level is more than 3, then single step alkali catalysed transesterification is not possible. However, it needs a pre-treatment to reduce the FFA level to the limit, which can be easily converted to biodiesel by alkali catalysed transesterification [8]. The pre-treatment step is generally known as esterification as shown in Fig.2. Acid catalyst such as sulphuric acid is used for the esterification process. For chemical balance, it requires 3:1 molar ratio of alcohol to triglycerides to complete transesterification process as shown in Fig.1. However higher molar ratio is used normally to get more ester yield. The alkali catalysts used are KOH, NaOH, sodium methoxide etc. The acid catalysts used are sulphuric acids, sulfonic acids, hydrochloric acids etc. The alkali catalysed transesterification is very faster than acid catalysed transesterification process. So in industrial sector, alkali- catalysed transesterification process is followed [9, 10, 11].

Generally, all the non-edible seeds contain very large amount of free fatty acids [12]. Hence need a pre-treatment to obtain biodiesel. In the pre-treatment process the fatty acid (carboxylic acids) reacts with alcohol to yield ester.

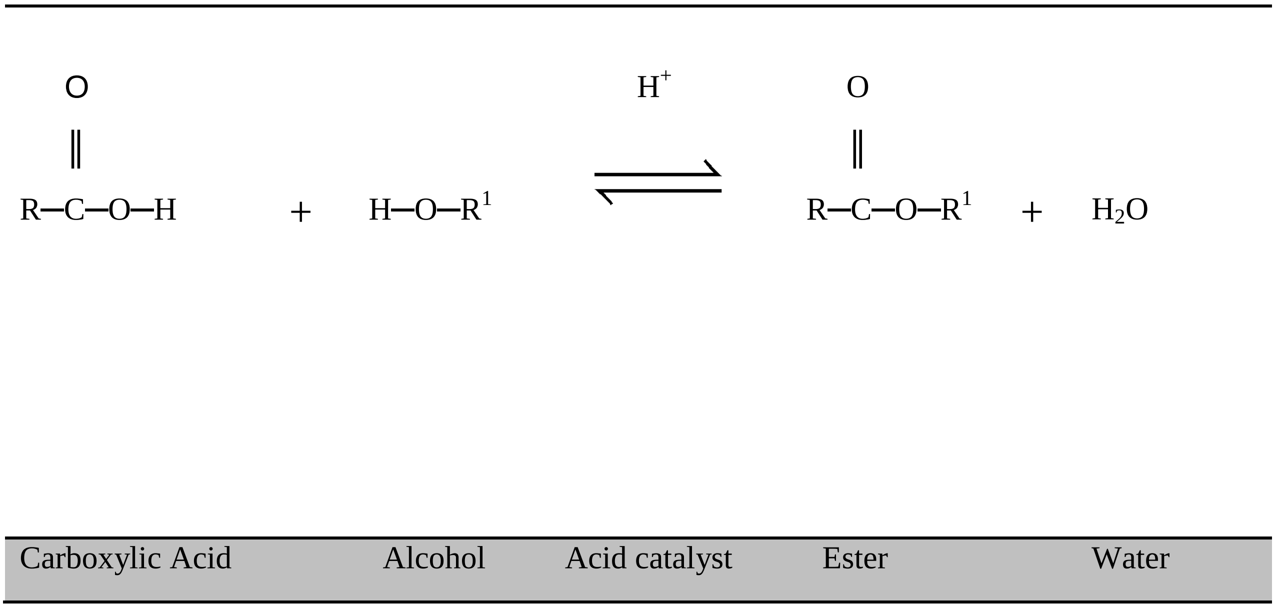

FIGURE 2. Esterification reaction

SOURCES OF BIODIESEL

Several researchers reported from the last two decades 300 oil bearing seeds has been identified and the researches on it is still going on. However, some feedstock proved promising and after transesterification their chemical properties brought to a level that can be comparable with high speed diesel fuel. The feedstocks available can be grouped into four major categories.

1. Edible vegetable oils: coconut, mustard, soybean, sunflower, Rice bran, Pumpkin, Palm etc.
2. Non-edible vegetable oil: Mahua, Jatropha, Karanja, Rubber seed, Neem, Castor, Tobbaco, Jojoba etc.
3. Waste or used vegetable oil.
4. Animal Fats: Poultry fat, Pork lard, beef tallow, Fish oil etc.

After feedstock, the next requirement for the production of biodiesel is suitable alcohol. The various alcohol used are methanol, ethanol, propanol, Iso-propanol, Butanol etc.
Several catalysts are identified and experimented by several scientists and researchers across the world for biodiesel production.
Broadly there are two types of catalysts

1. Homogeneous
2. Heterogeneous

CATALIZED TRANSESTERIFICATION PROCESS

Both acid and base type homogeneous catalysts are used for the production of biodiesel. Depending on the chemical composition of fuel and fatty acid content, the steps required for the production process is decided. The principle factor is protonation of the carbonyl group in triglyceride [13]. Some important homogeneous catalysts are sodium hydroxide, potassium hydroxide, Sodium methoxide and potassium methoxide.

Sinha et al. produced rice bran biodiesel by utilizing sodium hydroxide (NaOH) as catalyst. They optimized the methanol/oil molar ratio, reaction time, reaction temperature and amount of catalyst. The maximum yield of biodiesel was observed with molar ratio of 9, 0.75% NaOH, 1hr. reaction time and 55^{0}C reaction temperature [14]. Lubes et al. used both single and double step transesterification process for producing palm biodiesel. They optimized the process parameter and reported 1% by wt. NaOH, molar ratio of 6:1, reaction temperature 60 ^{0}C and reaction time of 1 hour [15]. Hoda used sodium hydroxide (NaOH) for the production of biodiesel from cotton seed oil and optimized the process parameter. He found by using methanol/oil molar ratio as 6, at reaction temperature 60 ^{0}C, 0.3% by wt. of catalyst with 1 hour of reaction time would result maximum yield of biodiesel [16]. Shashikant et al. prepared biodiesel from more acid value content mahua oil. They used a two-step transestrification process. The optimized process for first step i.e. esterification process was 0.3 methanol/oil molar ratio, 1% H_2SO_4 at 60 ^{0}C for 1 hour [17]. Zhang et al. produced biodiesel from waste cooking oil. They found acid catalyzed process was better than alkali catalyzed process [18]. Nabi et al. prepared biodiesel from more free fatty acid content Karanja oil. Due to high FFA, they pretreated the oil with H_2SO_4, and then used alkali catalysed transesterification process. From FT-IR, GC studies they found 97% methyl ester conversion and the B100 mainly contained ester compared to alkanes and alkenes in diesel fuel [19,20]. Ramadhas et al. produced biodiesel from rubber seed oil. They used a double-stage transesterification process for biodiesel production [21]. Freedman et al. used sodium methoxide for preparing biodiesel from soybean oil. They found 0.5% by wt. of sodium methoxide yield similar result as 1 % by wt. of sodium hydroxide. Meher et al. used potassium hydroxide for transestrification of Karanja oil. They found 1% KOH, molar ratio of 6, reaction temperature of 65 ^{0}C and reaction time 2 hour are the optimum parameter for maximum conversion [22]. Rashid et al. used various catalysts for the transesterification of cotton seed oil and made a comparative analysis [23]. Rushang et al. transesterified fish oil with ethyl alcohol. They found the viscosity of biodiesel increases with decrease in temperature. They also developed an equation to obtain viscosity from temperature and volume fraction of ethyl ester [24]. Victor et al. studied the biodiesel production from animal fats. They found the properties of different methyl esters of lard, chicken fat and beef tallow meet ASTM specifications. They found the oxidative stability of fat based alkyl ester were better than vegetable based alkyl ester [25].

Several heterogeneous catalysts have gained considerable attention for production of biodiesel by catalytic transesterification process. The major advantages of heterogeneous catalysts are its reusability, environment friendly non-toxic constituents [26]. Like homogeneous catalyst, it is also both acid and base type. Prominent solid base heterogeneous catalysts are metal oxides, KNO_3, BaO, Al_2O_3, CaO, MgO etc. Demirbas used CaO to produce methyl ester. Liu et al. used CrO as a solid heterogeneous catalyst to prepare soybean biodiesel [27]. Liu et al. also studied biodiesel production using calcium ethoxide as catalyst. The optimum parameter for production of soybean biodiesel were molar ratio of 12, calcium ethoxide by wt. 3%, reaction temperature 65 ^{0}C, reaction time 1.5 hour to yield 95% conversion [28]. Supriya et al. studied production of jatropha methyl ester using calcium oxide derived from eggshell and they observed the conversion was good and properties of ester were within ASTM limit. They found the catalyst can be used upto six times without loss of catalytic activity [29]. Brito et al. transesterified used vegetable oil by using several Y- type zeolites with different proportions of Al_2O_3 content. They found Reaction temperature and space time were very vital for ester conversion [30]. Kotwal et al. transesterified sunflower oil by loading KNO_3 on flyash. They found loading 5 % by wt. of KNO_3 on flyash would yield maximum conversion of 87.5%. The optimized reaction parameters were molar ratio of methanol to oil of 15:1, reaction time of 8 hour, at reaction temperature 443K, 15 % catalyst loading. They observed the catalytic activity decreased with reusing the catalyst [31]. Babajide et al. also studied use of South African fly ash for transesterification [32]. Taufiq-yap et al. studied transesterification of jatropha curcas oil by using calcium based mixed oxides catalyst. They found the CaZnO and CaMgO can be used up to 3 to 4 times. The optimum parameters were the molar ratio 15, reaction time 6 hour, catalyst amount 4% by wt. to yield more than 80% conversion [33]. Schultz et al. prepared novel polymeric catalyst Amberlyst BD20 to convert FFA. They found the Amberlyst BD20 performed better in comparison to H_2SO_4 for higher FFA content [34]. Dalai et al. used various heterogeneous catalysts for production of biodiesel and compared their performance and found $Ba(OH)_2$ performed better. They found canola ester mix with methanol served as a good lubricity additive [35]. Jacobson et al. studied several heterogeneous solid catalysts and found zinc stearate conditioned on silica gel was better compared to other catalyst under investigation. The optimum parameters were reaction temperature of 200^{0}C, molar ratio 18, stirring speed 600rpm, and catalyst amount 3 % by wt. to yield 98% conversion [36]. Enzyme catalyzed approach for production of biofuel is really good for the environmental concern but cost is too high. Owing to the economical factor, the uses of lipase enzymatic catalysts are not sensible. Cost has been always acted as a hindrance for the production of biodiesel in industrial scale [37, 38, 39].

CONCLUSIONS

Keeping in view several insightful opinions and vital works of researchers around the world regarding the catalyzed production of biodiesel, following conclusions can be made.

a. More than 300 oil yielding crops has been identified and the researches on production of liquid biofuel by using various catalysts will continue for sustainable growth of a country. Still few proved promising like Jatropha, Karanja in India. Out of many fuel modifications process transesterification process proved promising. Both homogeneous and heterogeneous catalysts are widely studied by various researchers. Due to its low cost, environmental friendly and reusability characteristics heterogeneous catalysts from natural sources are encouraged for the transesterification process.

b. Primarily methanol or ethanol is utilized for transesterification reaction out of various alcohols available. Acid catalyst is better for treating more free fatty acids content vegetable oil for biodiesel production.

c. The maximum production of biodiesel depends on five important parameters, i.e. temperature, time, molar ratio of oil/ alcohol, catalyst amount and stirring speed.

d. Biodiesel is not popular in the market because of its cost. Due to higher cost incur by using enzymatic lipase, it is not suggested to use in the production process.

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