



Factors Affecting Biodiesel Production from Non-edible Vegetable Oil Via Base-catalyzed Transesterification Process: Synthesis

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Abstract: Biodiesel (fatty acid alkyl ester) has received attention as greener, renewable, alternative source of energy; and its utilization as diesel fuel is becoming an auspicious source of energy that can substitute the non-renewable petroleum products. It can make significant contributions in diminishing the emission of harmful gaseous due to combustion of conventional fuel sources and hence, it is helpful to overcome challenges associated with energy crisis coupled with environmental pollution, climate change and global warming. Biodiesel is a carbon-neutral fuel source, biodegradable, non-toxic and can be synthesized from locally available non-edible vegetable oils via base-catalyzed transesterification process. This study presents the insight of operational variables or factors that influence the processing and yield of biodiesel (fatty acid alkyl ester) through transesterification of non-edible vegetable oils. These operational variables include, the amount of free fatty acid (FFA) in the non-edible vegetable oils, moisture in the oils, the amount and types of alcohol used, the non-edible vegetable oil to alcohol molar ratio, time allowed for the reaction, intensity of mixing, temperature, types of catalyzed used, concentration of catalyst and purity of reactants. The considered variables for preparation of biodiesel should be optimized to achieve the maximum possible conversion of reactants and thereby provide the highest possible yield of biodiesel product at the minimum possible operational cost.

Keywords: Biodiesel, Biofuel, Free Fatty Acid, Non-edible Vegetable Oil, Transesterification, Triglyceride

1. Introduction

Recently, the growth of demand in exploitation as well as usage of energy, the rise in oil price, the increase in fossil fuel consumption in industry and in transportation sectors, global warming due to the emissions of harmful gaseous into atmosphere, depletion of petroleum reserves, the increase in carbon dioxide (CO₂) level due to combustion of conventional fossil fuels have exacerbated the regional and global environment [1]. These environmental issues induce the emergence of alternative, renewable, biodegradable and environmentally friendly energy sources like biofuels (i.e. biodiesel) for transportation substituting the limited petroleum reserves; and thereby mitigating climate change

while ensuring the sustainable development. Biofuel (i.e. Biodiesel) is considered as the promising renewable, eco-friendly and alternative fuel across the globe [2]. It has an immense potential for replacement of diesel fuel because it is relatively cleaner, greener, biodegradable and non-toxic energy source [3-5].

Biodiesel, a renewable energy source, is a fuel with chain fatty acid mono-alkyl esters synthesized from non-edible vegetable oils, waste cooking oil, microalgae and fats via transesterification of chemical reaction with appropriate alcohol and suitable catalysts [6- 9]. Predominantly, biodiesel consists the fatty acid alkyl esters; and the corresponding alkyl end of fatty acid alkyl ester ranges from methyl (CH₃) to butyl (C₄H₉) [10, 11]. Biodiesel exhibits good fuel

characteristics and the viscosity of biodiesel is lower than its corresponding triglycerides; and hence, preferable or suitable for utilization in an engine without the requirement for alteration of the engine structure [12-14]. It consists 10-11% O₂ (oxygen) by weight, has no aromatic hydrocarbons and possesses a higher Cetane number [15, 16]. Upon its combustion, these properties are helpful in minimizing emissions of greenhouse gases (GHG), particulate matters, carbon monoxide and unnecessary hydrocarbons into atmosphere [17-19]. Therefore, biodiesel offers a feasible solution to energy crisis, environmental degradation and the markedly diminishing conventional fossil fuels.

Availability of wide range of biodiesel production feedstocks or raw materials such as vegetable oils, fats derived from animal tissue and recycled waste cooking oil across the globe has been the main factor that forces researchers for further investigation in biofuel industries [20]. Nonetheless, the utilization of fats obtained from animals and edible oils for the synthesis of the biofuel induces the dispute of food supply versus fuel competitions in the long run [21-24]. Thus, the exploitation of oils extracted from the non-edible vegetables to prepare and use the fuel (i.e. biodiesel) is becoming a predominant feedstock while meeting the international fuel standards. The present study aims at providing the insight of factors affecting biodiesel synthesis from non-edible vegetable oil via base catalyzed transesterification mechanism.

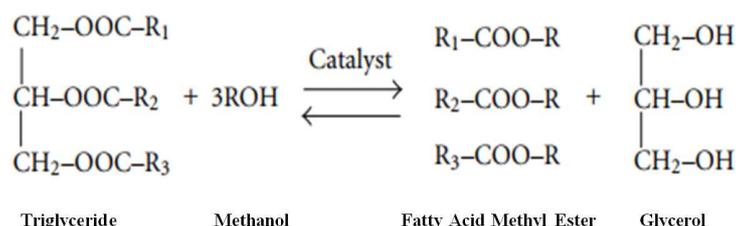


Figure 1. The chemical reaction between triglyceride and methanol using suitable catalyst (i.e. base) producing biodiesel and glycerol [44].

3. Factors Influencing Biodiesel Formulation by Transesterification Mechanism Using Base Catalyst

Synthesis of biodiesel through base-catalyzed transesterification process is influenced by diverse operational variables, including: amount FFA content in the feedstock [45], moisture in the oil [28], alcohol employed [46], Oil to alcohol molar ratio [47], time allowed for the reaction [48], mixing intensity [49], temperature [50], catalyst employed [42] and purity of reactants [12]. Hence, proper control and manipulation of these operational variables will improve the yield and characteristics of biodiesel.

3.1. Amount of FFA in the Oil

Transesterification reaction won't take place when percentage of FFA in the oil is greater than three percent [51].

2. The Transesterification Reaction Catalyzed by Base

Biodiesel can be synthesized in a number of methods, including thermal cracking (pyrolysis) [25], oil dilution or blending [26], micro-emulsion [27], and via base-catalyzed transesterification process [28]. Among these, the transesterification reaction catalyzed by base is the most convenient way for synthesizing biodiesel [29]. The transesterification process involves the organic reaction between vegetable oils and alcohols, usually CH₃OH (methanol) and C₂H₅OH (ethanol) using appropriate catalysts, such as heterogenous base catalysts [30-34], homogeneous base catalysts [35, 36], acid catalysts [37, 38] and bio-catalysts [39, 40] or without the requirement of catalyst [41]. Moreover, the base-catalyzed transesterification reaction is a step-wise stripping of glycerin from the fatty acids of the considered non-edible vegetable oil with proper base catalysts [42]; and thereby substituting it with anhydrous alcohols (i.e. methanol) and hence, producing the desired product (i.e. Biodiesel) and the by-product (i.e. glycerol). This process is also affected by variations in operation parameters like types of alcohol, molar ratio of vegetable oil to alcohol, mixing intensity, temperature, catalyst concentration as well as oil moisture content [43]. The stoichiometric chemical reaction of transesterification process can be provided as follow:

Instead, high amount of FFA in the oil induces the saponification reaction (i.e. formation of water and soap) thereby diminishing the effectiveness and efficiency of catalyst, forming gel, increasing biodiesel viscosity and making glycerol separation cumbersome. Therefore, the problem with transesterification of non-edible vegetable oil of higher FFA (%) can be solved by employing two-step transesterification; firstly, a homogeneous acid pretreatment of the oil [52-55], conducting esterification reaction (i.e. until FFA is less than 0.5%) to produce ester. Secondly, a transesterification process catalyzed with base must be employed; and thereby completing the process [56-59]. Non-edible oil to be trans-esterified must be subjected to titration while employing the phenolphthalein indicator to measure the amount of selected catalysts for the reaction [60].

3.2. Oil Moisture Content

The water content in the non-edible vegetable oil highly affects the base-catalyzed transesterification mechanisms as

the moisture in oil induces and accelerates the hydrolysis of ester with concomitant saponification reaction [28, 61]; and hence, it diminishes the formation of ester [61]. The moisture content of non-edible oil is more critical issue for esterification reaction catalyzed by acid than the base-catalyzed transesterification reaction. Moreover, it is formed as side product of acid catalyzed esterification mechanism (i.e. during conversion of free fatty acid into ester) [62]. Preheating of oil at 120°C favors the removal of water content before dispatch [63] and then, the oil is subjected to cooling to 60°C [64]. The moisture presented in the final product (i.e. Biodiesel) can be removed by using anhydrous magnesium sulfate-MgSO₄ [65] and anhydrous sodium sulfate-Na₂SO₄ [51] while avoiding the backward reaction and increasing the biodiesel yield. Thus, to get about ninety percent yield of biodiesel, moisture content of the oil must be less than 0.5% [38].

3.3. Type of Alcohol Employed and Oil to Alcohol Molar Ratio

The selection of alcohol(s) for the base-catalyzed transesterification reaction depends upon their effectiveness or operational performance and their respective cost [46]. The transesterification mechanism necessitated the applications of lower alcohols, like methanol (CH₃OH), ethanol (C₂H₅OH) and butanol (C₄H₉OH). Among these, methanol is a predominantly utilized alcohol for transesterification reaction process [48, 66-69] and methanol is more available and substantially cheaper in price than ethanol; and hence, the corresponding biodiesel derived from methanol is more preponderating commercial product than biodiesel derived from other alcohols [70]. Moreover, methanol is preferable to ethanol because it does possess lower boiling point than ethanol and hence, the recovery of unreacted alcohols from the downstream is relatively easier [71]. On the other hand, when the isopropanol or ethanol is employed in transesterification reaction, it exhibits formation of azeotrope with molecules of water; and thereby causing the alcohol-water separation cumbersome in the distiller [54].

During the base-catalyzed transesterification reaction, fatty acid triglyceride of one mole reacts with three mole of alcohol (i.e. usually methanol) to produce three mole of alkyl (i.e. methyl) ester as well as one mole of tri-hydroxy alcohol (i.e. glycerol) [72]. With this regard, the oil to alcohol molar ratio has significant effect on the rate of conversion of triglyceride into the alkyl ester (Biodiesel) [73]. According to the principle of Le Chatelier's, the gradual rise in concentration of reactants enhances the product formation rate and vice-versa. Hence, increasing the concentration of alcohol enhances the biodiesel formation rate [55]. A maximum triglyceride conversion into alkyl ester (Biodiesel) takes place at 1:6 oil to alcohol molar ratio [47, 67, 74-77]. The efficiency of reactant conversion remains constant upon further increasing molar ratio of oil to alcohol. Nonetheless, higher molar ratio of oil to alcohol beyond optimum point makes alcohol recovery cumbersome [78].

3.4. Reaction Time

To diminish biodiesel synthesis operational cost via base-catalyzed transesterification of triglyceride in the non-edible vegetable oil, the optimum reaction time should be employed. The best conversion of reactants and completion of the chemical reaction relies on reaction time and it has been found that 60 minute is the optimum reaction time that provides the best biodiesel yield [47, 48, 76]. About 99% of biodiesel can be obtained when the transesterification reaction is conducted for longer time. However, extra reaction time beyond the optimum favors hydrolysis of fatty acid alkyl ester (biodiesel) or the backward reaction is promoted; and hence, diminishes the product yield [28, 36, 79]. Besides, longer residence time of reaction reduces the specific gravity of the desired product exponentially and ceases with asymptotic values relatively with provided time [48].

3.5. Intensity of Mixing

The base-catalyzed transesterification reaction is a slow process due to the immiscibility of alcohols and oils; and due to the occurrence of the chemical reaction in the interfacial surface between fatty acid triglycerides and alcohols [80]. Inadequate mass transfer between triglycerides and alcohol interface is slow and critical step and hence, it is considered as a rate limiting step for the transesterification reaction [49]. Thus, agitation is necessitated to enhance the contact surface area between the non-miscible phases [81]; and thereby achieving the completion of the reaction process while enhancing the yield of the desired product [49]. Moreover, mixing favors the diffusion of alcohol molecules into triglycerides and rises the interfacial collision between particles. The higher the mixing intensity favors the shorter reaction time and increase the rate of conversion of reactants [82]. Nevertheless, beyond the considered speed of agitator, the rise in the biodiesel yield will be insignificant. Hence, optimum agitator speed should be employed for a variety of biodiesel feedstocks depending upon the respective physical properties of reactants. In this regard, it has been demonstrated that the higher conversion of reactants was observed by adjusting the speed of agitator between 100 and 200 revolutions per minute [83].

3.6. Reaction Temperature

A base-catalyzed transesterification reaction is affected by reaction temperature [84]. Increasing the temperature of the reaction increases reaction rate and thereby enhances yield of biodiesel [50, 72]. In addition, the higher temperature tends to minimize the required time to achieve maximum possible conversion of reactants [70]. However, the reaction temperature should be kept below alcohol's boiling point because increasing temperature beyond alcohol's boiling point induces vaporization of alcohol and bubble formation that suppress the transesterification mechanism [52, 76]. On the other hand, keeping temperature far below alcohol's boiling point increases the fatty acid alkyl ester (biodiesel)

viscosity [85]. Thus, the operation should be conducted at optimum temperature of reaction between 63-68°C so as to provide maximum yield of the desired product [54].

3.7. Catalyst Type and Concentration

Catalysts (i.e. chemical and biological) are substances that promote chemical reaction rate by diminishing primary activation energy. During transesterification reaction of non-edible vegetable oil and alcohol, catalysts play significant roles in the process [86]. Moreover, a number of catalysts (i.e. heterogeneous, homogeneous and enzymatic catalysts) can be utilized for biodiesel synthesis [87]. For instances, the homogeneous alkali catalysts and their respective methoxides are preponderantly employed in biodiesel processing industries because of their availability, low cost, ease of handling and transportation [46-48, 67, 75, 78]. The use of potassium methoxide (base catalyst) in the transesterification reaction, with concentrated sulfuric acid (H_2SO_4) catalyst as pretreatment or esterification reaction [42, 88], provides the maximum possible yield of biodiesel [48]. Nonetheless, one of the major drawbacks of using homogeneous base catalyst is its soap formation and the difficulty of its recovery from the end product [88]. In order to overcome such challenges, heterogeneous base catalyst has been considered as it withstand the effect of FFA and moisture in the oil [52]. Hence, the use of several heterogeneous catalysts (i.e. solid acid and alkali catalyst) is helpful to enhance rate of transesterification mechanism. A solid acid catalyst can be employed for oil of high FFA as it exhibits higher stability, eliminates problems of corrosion, replaces liquid acids and no deactivation of the catalyst surface [72, 89] relatively when compared with solid heterogeneous base catalyst [38].

The concentration of catalyst to be employed is related to the amount of FFA in non-edible oil. Oil of higher FFA necessitated addition of more acidic and alkaline catalysts respectively to inhibit the deactivation of catalyst and to compensate the acidity of the oil [42]. However, the addition of extra catalyst induces the formation of gel and emulsion thereby raising the viscosity of fatty acid alkyl ester (biodiesel) which in turn impede glycerin separation from the biodiesel [67, 90]. Hence, the utilization of optimum catalyst concentration (1%wt.) should be considered to enhance reactant's conversion rate thereby maximizing the yield [72].

4. Conclusion

Environmental degradation, air pollution due to the release of harmful gaseous emissions, growth of demand in exploitation and usage of energy globally along with the rapidly diminishing petroleum products (i.e. Automotive Diesel Oil-ADO, kerosene, Motor Gas Regular-MGR) necessitated the search for alternative, renewable and sustainable fuel sources for the replacement of conventional fossil fuel (i.e. petroleum). In this respect, biodiesel is considered as greener, renewable, alternative source of energy, environmentally benign and synthesized from locally available biological feedstocks. It

can be produced via base-catalyzed transesterification reaction, dilution, pyrolysis (thermal cracking) and micro-emulsion. It's production process (i.e. via base-catalyzed transesterification mechanism) necessitated adequate knowledge, good technical skills and deep understanding of the nature of operational variables, including: purity of reactants, fatty acid content of non-edible vegetable oils, oil moisture contents, types and concentration of catalyst employed, temperature, agitation speed, reaction time and molar ratio of oil to alcohol. Therefore, it is recommended that the considered operational variables should be controlled accordingly and optimized carefully while obtaining the best yield of the desired product and realizing viability of the production process.

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