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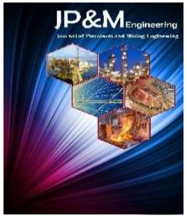

Transesterification reaction conditions and low-quality feedstock treatment processes for biodiesel production- A review

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Abstract

Biodiesel is a type of biofuel that has a composition and combustion properties similar to petrodiesel fuel. Renewable resources such as vegetable oil, algae, and animal fats are crucial feedstocks for biodiesel production. Biodiesel is a renewable and clean fuel as it reduces carbon monoxide, carbon dioxide, hydrocarbons, and particulate matter emissions compared with petroleum-based diesel fuel. The conversion of vegetable oil to alkyl esters (biodiesel) depends upon certain parameters that affect the biodiesel production process such as catalyst concentration, methanol to waste cooking oil ratio, temperature, mixing rate, and reaction time. In this paper, the effect of reaction parameters on the yield quantity and properties will be shown

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Introduction

Diesel or petro-diesel is a non-renewable fossil fuel that is derived from crude oil and it is likely to be exhausted shortly [1, 2]. Since diesel comes from non-renewable resources, this leads to a rise in energy costs especially with the decline of crude oil production [3, 4]. Biodiesel is a promising fuel for diesel engines in wake of its renewable nature and environmental benefits and is the best substitute in diesel engines. In comparison to petroleum diesel fuel, biodiesel is better due to lower emissions and sulfur-free. Biodiesel composition and physicochemical properties are very similar to petrodiesel. Therefore, the importance of biodiesel is the reduction of dependency on imported petroleum. Biodiesel is compatible with diesel engines so it can be used alone as fuel or blended with petroleum diesel to increase lubricity in engines. Biodiesel is produced via transesterification reaction of triglycerides which are the main component of vegetable oils and they are about 90-98% of the total oil mass[5, 6].

Transesterification reaction occurs when the triglycerides react with alcohol in the specified time, temperature, mixing rate, and in presence of catalyst producing a mixture of fatty acids alkyl esters (biodiesel) and glycerol[7]. The transesterification reaction is catalyzed by the addition of a base, acid, or enzymatic catalyst. Alkaline catalyzed transesterification is the most common process because it is economical, faster, and less processing steps than other processes[5, 8]. The conversion of triglycerides to alkyl esters (biodiesel) depends upon certain parameters that affect the biodiesel production process such as catalyst concentration, methanol to waste cooking oil ratio, temperature, mixing rate, and reaction time[6, 9, 10].

Biodiesel should conform to either ASTM D6751 in the USA or EN14214 in the European Union. The quality of biodiesel fuel is decided by successful usage in vehicle engines and the substitution of non-renewable fossil fuels. When achieving the standard limits, biodiesel can be used in vehicle engines without modifications or precautions while maintaining the engine's durability and reliability[6]. The properties of the biodiesel must be within the standard specifications to be used in internal combustion engines [7, 11].

Transesterification

Transesterification is the process that organic group (alkyl) of an alcohol is substituted with the organic group of a triglyceride. Transesterification reactions are done with utilization of a catalyst either an acid or a base catalyst[5]. Transesterification can be occurred by using of enzymes. Equation 1 shows the transesterification reaction

(1)

Transesterification process relies mainly on free fatty acid and water. Measurement of free fatty acid is a necessary before transesterification as it determines which type of catalyst will be more effective. Alkaline transesterification is most effective in feedstocks with free fatty acid (FFA) content less than 1%. KOH is the common catalyst used in alkaline transesterification and sulfuric acid is the common catalyst in acid transesterification[5, 12].

Results

Transesterification reaction depends on various factors that affect the final yield of biodiesel and its specifications such as reaction temperature, methanol to oil molar ratio, type of catalyst, catalyst concentration, mixing rate, and reaction time [8, 12, 13].

Reaction Temperature

The reaction temperature is necessary to increase the reaction rate and it is preferred to be lower than the boiling point of methanol, which is 65 °C[14]. The transesterification reaction is strongly affected by the reaction temperature, as the temperature increases the rate of reaction increases and enhancing biodiesel formation. Moreover, the elevated temperature might enhance the saponification reactions which became significant with increasing the reaction time[15, 16]. If the reaction temperature is higher than the boiling point of methanol, methanol will evaporate and the reaction will lose one of the reactants. Consequently, biodiesel quantity will decrease and more methanol will be required to compensate for the deficit in methanol[17, 18]. In contrast, the very low temperature will not be sufficient to activate molecules to colloid with other molecules leading to the same result of elevated temperature. Therefore, the reaction temperature should not exceed the boiling point of alcohol as alcohol vaporizes and biodiesel is consequently not produced[19].

El-Gendy et al[6] reported that the optimum reaction temperature value would be around 50 to 65 °C; higher or lower temperatures except within range would not give a significant yield. They also stated that the relation between temperature and the final yield is proportional as temperature increases, final yield increases. Thaiyasuit et al.[20] reported the temperature should not exceed the boiling point of methanol and showed that the optimum reaction temperature ranges between 55 °C and 60 °C.

Molar Ratio

The transesterification reaction requires an alcohol to be completed as alcohol reacts with triglycerides producing biodiesel and glycerol. Methanol is an important reactant as it merges with triglyceride to produce methyl ester (biodiesel)[21]. Producing one mole of fatty acid methyl ester (biodiesel) requires three moles of methanol with one mole of triglyceride for the reaction to occur so when the molar ratio of alcohol to oil is lower than 3:1, the reaction will not occur or give poor results. Excess amount of methanol is not recommended as more methanol will deteriorate the properties of biodiesel as the presence of 1wt. % of methanol decreases the biodiesel flash point from 170 ºC to less than 40 ºC[15, 22]. Excess methanol also increases the production cost because more purification steps to recover the methanol so more equipment and power are needed. High methanol percentage increases glycerol product that enhances the reaction back to reactant formation and lower yield[23].

Molar ratio should be maintained in suitable range neither lower than 3 nor higher than 9. The optimum methanol to oil ratio value is around 6 to 9 beyond this value no significant effect on the final yield quantity[5, 24]. All experiments that have high methanol to oil ratio and reasonable values of other factors exhibit high yield so biodiesel yield is directly proportional to M:O ratio to a certain limit. The minimum methanol to oil ratio required is 3:1 to complete the reaction. The most applied industrial processes use 6:1 ratio[25, 26]. Yaakob et al[9] demonstrated that the optimum methanol to waste cooking oil ratio is approximately 9:1.

The Calculation of molar ratio percentage was done as following, the molecular weight of used cooking oil was 900 g/mol as the main components of used cooking oil are palmitic oil and oleic acid while the molecular weight of methanol was 32 g/mol. The percentage 1:1 equal 900:32, and so during utilization weight of oil 100 g and methanol to oil ratio 6:1, the weight of methanol will be as below:

$$\text{Methanol Wt.\%} = \frac{\text{molecular weight of methanol} * \text{M:O ratio} * \text{weigh of oil (g)}}{\text{molecular weight of Oil}} \quad (2)$$

For example, the calculation of methanol to oil molar ration 6:1 is as following:

Methanol Wt. % = $\frac{32*6*100}{900}$ = 21.3 g, For other different molar ratio is shown in table 3.1.

Table 1: Methanol weight (g)

No.	Molar ratio	Methanol weight (g)
1	6:1	21.3
2	9:1	32
3	3:1	10.7
4	0.54:1	1.92
5	11.46:1	40.7

Type of catalyst

There are four types of catalyzed transesterification which are alkaline, acid, heterogeneous and enzyme catalyst. The most applied catalyst in alkaline transesterification is potassium hydroxide and sodium hydroxide[27]. Encinar et al.[28] reported that potassium hydroxide is best catalyst that enhance highest yield for the transesterification of used frying oils. Pinzi et al.[29] investigated the activity of KOH and NaOH in transesterification of used cooking oil and made a comparison between them. The result was KOH activity higher than that of NaOH activity, the reaction became faster in case of using KOH and soap formation become lower[30]. Heterogeneous catalysts are more active than the homogeneous one but more expensive. The famous heterogeneous catalysts are titanium dioxide and calcium oxide[31]. Acid catalyst activity is lower than alkaline one in addition it gives lower yield but it is used in case of free fatty acid higher than 1%[32]. The most famous acid catalyst is sulfuric acid (H_2SO_4) and hydrochloric acid (HCL). Enzyme catalysts are more expensive, lower in activity but produce a high yield[26, 29].

Catalyst concentration

Catalyst is a substance required to increase the reaction speed and it is not consumed during reaction. Catalyst concentration is an important factor in transesterification reaction. Rate of reaction is directly proportional to the catalyst concentration consequently, biodiesel yield increases[33]. In the absence of catalyst, the conversion of waste cooking oil to biodiesel requires a higher temperature and a longer time. Increasing catalyst weight will increase biodiesel yield and improve its properties but to a limited percentage as increasing beyond this limit will affect negatively the final yield and its properties[30, 34]. More increasing the catalyst concentration, the conversion decreases as catalyst reacts with FFA forming soap and water and hence water decomposes the triglyceride into monoglycerides and diglycerides so the biodiesel become lower [34]. Excess amount of catalyst leads to soap formation, lower biodiesel yield and harms properties of biodiesel produced. In contrast low catalyst concentration slows the reaction. Therefore, a high temperature and a longer time will compensate low catalyst concentration[35, 36]. The optimum base catalyst concentration value will be around 0.5% - 0.9 wt.% beyond this value no significant effect will occur on the final yield. Whereas, for the acid transesterification the optimum concentration is around 5 wt.% [19, 37].

Mixing rate

Chemical reaction requires mixing between reactants to be completed. Mixing of reactants motivates the collision between the molecules, the interaction between reactants and accelerates the reaction rate. Mixing reduces reaction duration and increases yield[27, 38]. High mixing rate affects reversely on final yield so mixing rate has to be optimized to achieve the highest yield[29, 39]. The optimum mixing rate is ranged from 200 to 400 rpm rate beyond this value the reaction is drawn back and lead to lower yield[5]

Reaction time

Reaction time is the period needed for the reactants to react and produce the required yield. Increasing time of reaction has a reverse effect on yield as the high reaction time will lead to drawback reaction reducing the yield and production cost. Low reaction time is not sufficient for the molecules to collide so it will decrease produced biodiesel[15]. Freedman et al.[40]investigated that the conversion of free fatty acids is directly proportional to reaction time; the reaction is slow at the beginning, then the reaction rate increases very rapidly. The optimum time for alkaline transesterification is around 2 hrs., more time will not affect the final yield on contrast excess reaction duration will motivate the backward reaction lowering the final yield and produce soaps [15, 17, 41]. Jian and Sharma [42] reported that percentage of biodiesel yield increases from 21.5% to 90.6% within 180 min.

Treating High FFA Waste Vegetable Oil

The transesterification reaction is used to convert the waste cooking oil to a fuel suitable for diesel engines without modification. The properties of this new fuel should be similar to the petroleum diesel fuel. Alkaline-catalyzed process is suitable for biodiesel production by trans-esterification when FFA content is below 1%. For higher FFA content alkaline-catalyzed process cannot be used due to gel and soap formation in the reactor. The best method for treating the higher free fatty acid is a combined process with pretreatment to convert the FFA's into ester followed by alkaline-trans-esterification of triglycerides. High content of free fatty acid and water will enhance reaction of catalyst with FFAs consequently soap formation and more separation processes[43, 44]. Soap formation reaction is unwanted reaction because soap reduces biodiesel yield, increases viscosity of products, forms emulsions and makes separation of glycerol from biodiesel more difficult[45]. Equation 3 shows the saponification reaction.

$$\underset{\text{FFA}}{\text{R-COOH}} + \underset{\text{Catalyst}}{\text{NaOH}} \longrightarrow \underset{\text{Soap}}{\text{RCOONA}} + \underset{\text{Water}}{H_2O} \qquad (3)$$

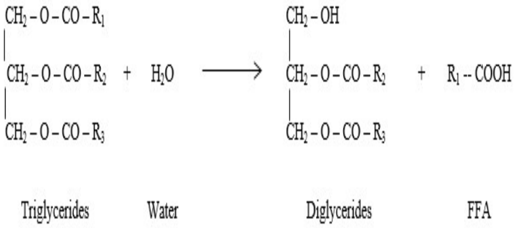
Free fatty acids should be determined and treated before transesterification. Feedstock with free fatty acid more than 1% of oil weight is not processed directly by alkaline transesterification. Soap formation is a big barrier especially in alkaline transesterification as its sensitivity to FFAs. Pretreatment is necessary for base transesterification in case of FFA content is higher than 1% [46]. Equation 4 shows the reaction of pretreating high FFA waste vegetable oil to produce biodiesel and water.

Pre-treatment of high free fatty acid in feedstock will lower the FFA in feedstock and increase alkyl ester yields. There are several options to treat high FFA waste vegetable oils in small-scale systems. These options are:

$$\underset{\text{FFA}}{RCOOH} + \underset{\text{Alcohol}}{CH_3OH} \longrightarrow \underset{\text{Alkylester}}{RCOOCH_3} + \underset{\text{Water}}{H_2O} \qquad (4)$$

Water drying

The feedstock is heated to above 100 °C so as to get rid of water as water causes decomposition of triglyceride to diglycerides or monoglycerides and free fatty acid and hence soap formation so it destroys the transesterification reaction[12]. Utilization of anhydrous of alcohol and catalyst in a process is necessary and the maximum water content shouldn't be more than 0.3 wt. %[6, 47]. Feedstock after water drying must be left in air so as to be cooled to the surrounding environmental temperature before transesterification reaction. Equation 5 shows the effect of water on triglyceride molecule.



$$\begin{array}{l}CH_2-O-CO-R_1\\ |\\ CH_2-O-CO-R_2\\ |\\ CH_2-O-CO-R_3\end{array} + H_2O \longrightarrow \begin{array}{l}CH_2-OH\\ |\\ CH_2-O-CO-R_2\\ |\\ CH_2-O-CO-R_3\end{array} + R_1-COOH \quad (5)$$

Alkaline Pre-treatment (Neutralization)

Alkaline pretreatment includes reaction of FFAs with alcohol to produce alkyl ester and water in presence of alkaline as a catalyst, it is the most profitable and easier pretreatment method to lower the FFAs in oil. It is not preferable to be used with feedstocks that contain FFAs more than 5% by weight as emulsions formed causing loss in biodiesel yield so acid pretreatment is the perfect alternative[20]. Kombe et al.[48] stated that alkaline treatment is done with initial reaction conditions: time is 3 min, ambient temperature, mixing rate of 800 rpm. The mixture is then heated to 65°C for a 20 min to prevent emulsification and break any formed emulsions. Equation 6 shows the neutralization loss in feedstock due to the treatment method.

$$\text{The neutralization loss} = \frac{\text{weight of crude oil} - \text{weight of neutrlized oil}}{\text{weight of crude oil}} * 100 \quad (6)$$

Acid Pre-treatment (Esterification):

Acid pretreatment includes reaction of FFAs with alcohol to produce alkyl ester and water in presence of acid as a catalyst, it is used in case of FFA content in the feedstock is higher than 1% by weight before alkaline transesterification. Acid pretreatment is considered as an esterification because esters are formed from reaction of acid and alcohol[49]. Kombe et al. [50] states that acid pretreatment is done at reaction conditions atmospheric pressure, temperature is 60°C, mixing rate 800 rpm, methanol to oil ration 0.6, sulfuric acid content as a catalyst 2% by weight and the reaction time is 2 h, the mixture is then poured in separating funnel forming three layers; the upper layer is unreacted methanol, the middle layer is alkyl ester and oil and the below layer is water. The middle layer is withdrawn from the separating funnel and processed with the alkaline transesterification to produce biodiesel. Chai et al.[51] reported the free fatty acid should be measured first then acid pretreatment for used cooking oil is done at conditions of the temperature is to be between 55 and 65 °C, the methanol to free fatty acid molar ratio is 40, and sulfuric acid as a catalyst is 10% wt.% of FFAs. In case of FFAs % is found to be between 15 % and 35 %, the optimum methanol to free fatty acid ratio condition is 20 with 5% by weight sulfuric acid[51].

Conclusion

This paper investigates the reaction conditions of the transesterification of vegetable oil to biodiesel production process. The best reaction conditions of biodiesel production process are methanol to oil molar ratio of 6:1 to 9:1, catalyst concentration of 0.5 to 1 wt. %, a reaction time of 1-2 hrs., a temperature of 55-60 °C, and a mixing rate between 200-400 rpm. The produced biodiesel can be used in compression ignition engine if its quality is agreeing the American Standard Testing Method (ASTM) and all properties such as cetane number, acid number, flash point, pour point, cloud point, aniline point, pour point are in the standard range. Accelerate in changing to utilization of biodiesel from waste cooking oil will have a great profit and positive effect on environment, vehicle engines, independency on crude oil, investment and economy as it will create jobs and save foreign currency especially that Egypt consumption of petro-diesel is very high. Egypt consumption of petro-diesel is 13.5 million ton in 2014, Egypt imports 25 % of diesel and 75% from local market, and there is no accurate information about waste cooking oil quantity in Egypt.

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Conflicts of interest

There are no conflicts to declare.

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