

Methyl Ester Derived from Used Frying Oil by Two-Step Chemical Process

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ABSTRACT: Utilization of used frying oil as a raw material for biodiesel production process is of interest due to the higher price and the future depletion of petroleum diesel. However, used frying oil contains large amount of free fatty acid (FFA) which adversely affects alkaline transesterification reaction, a commonly used method for biodiesel production. The FFA in the oil is therefore needed to be firstly reduced by acid esterification to a certain value (less than 1%) prior to the transesterification process. This research proposes biodiesel (methyl ester) production by two-step chemical process; sulfuric acid catalyzed esterification followed by potassium hydroxide catalyzed transesterification. Influences of reaction temperature, reaction time, methanol to oil molar ratio and amount of catalyst on FFA content of the product obtained by esterification as well as yield and properties of methyl ester (ME) obtained by transesterification were experimentally investigated. The experimental results showed that increases in reaction temperature, methanol to oil molar ratio, and reaction time as decreases in quantity of catalyst led to the faster reduction of FFA content. The FFA content could be reduced from the original 2.87% to the minimum 0.30% when the esterification process was performed at reaction temperature of 60°C, molar ratio of 18:1, catalyst amount of 0.5 %wt, and reaction time of 120 minutes. Percentage yield of ME could be enhanced by increasing reaction temperature and quantity of catalyst, and decreasing methanol to oil molar ratio and reaction time. The yield of ME was maximized (93.125%) when the transesterification was reacted at temperature of 60 °C, molar ratio of 3:1, catalyst amount of 1%wt and reaction time of 60 minutes. Flash point and kinematic viscosity of the ME undergoing the two stage chemical reaction were in the acceptable ranges of the ASTM standard. Flash point and viscosity of the ME tended to decrease with increasing reaction temperature, catalyst quantity, molar ratio and reaction time.

Keywords: biodiesel, esterification, methyl ester, transesterification

1. INTRODUCTION

Attributed to the high price, the limited quantity, and the negative ecological impact

of fossil fuels, exploring alternative energy resources is of growing importance in recent years. The alternative fuel should be technically feasible, economically

competitive, environmentally acceptable, and readily available [1]. Biodiesel, derived from vegetable oils or animal fats, is recommended for use as a substitute for petroleum-based diesel. It is biodegradable, non-inflammable, non-toxic and has a favorable combustion–emission profile, producing much less carbon monoxide, sulfur dioxide and unburned hydrocarbons than petroleum-based diesel [2].

Out of the four ways (blending, micro-emulsions, thermal cracking, and transesterification) to convert vegetable oils and animal fats into biodiesel, transesterification is the most viable process adopted [3-4]. This is because this process is relatively simple and properties of biodiesel obtained are very close to those of diesel fuel. Transesterification is the process of using an alcohol in the presence of a catalyst to chemically break the molecule of triglycerides in the raw oil into alkyl esters (biodiesel) with glycerol as a by-product [5]. Although there are many commonly used alcohols including methanol, ethanol, propanol and butanol, methanol is most preferable due to its low cost and its physical and chemical advantages (polar and shortest chain alcohol) [6-8]. According to the type of catalyst used, transesterification can be divided into acid, alkaline, and enzymatic catalyzed process. Compared to acid and enzymatic-catalyzed processes, alkaline catalyzed process has been proved to be more practical nowadays. This is due to its fast reaction rate (lower temperature and shorter reaction period requirement) [9-10]. However, one limitation of the alkali-catalyzed process is its sensitivity to the purity of reactants; especially water and FFA [11]. Amount of FFA beyond a certain limit (0.5-3%) may cause soap formation, resulting in high consumption of catalyst and difficulties in the downstream recovery and purification of the biodiesel [5,12-13]. To convert high FFA oils and fats to biodiesel, two-step chemical process (acid catalyzed pretreatment followed by alkaline catalyzed transesterification) is

recommended by many authors [6,14-17]. During the first step acid catalyzed pretreatment, the FFA in oils and fats is reduced because it is converted to fatty acid alkyl ester and in the second step transesterification, triglycerides is converted to ester. During the past decades, production of biodiesel from non-edible oils via two-step chemical process has been widely studied. Such non-edible oils include tobacco seed oil [14], rubber seed oil [6], karanja oil [15], jatropha oil [16] and mahua oil [17]. The optimum conditions for the first step pretreatment and the second step transesterification varied depending on type of oil used. At present, the high cost of biodiesel is the major obstacle to its commercialization. It is reported that approximately 70–95% of the total biodiesel production cost arises from the cost of feed stock [18-19]. Utilization of used frying oil, instead of neat oil, to produce biodiesel is an effective way to reduce the raw material cost. In this work, two-step chemical process is proposed to prepare biodiesel from used frying oil. At the first step, sulfuric acid was introduced to catalyze the reaction between FFA in the used frying oil and methanol. At the second step, potassium hydroxide was added to catalyze the reaction between triglyceride (TG) and methanol. Influences of reaction temperature, reaction time, methanol to oil molar ratio and amount of catalyst on FFA content of the product obtained by esterification as well as yield and properties of methyl ester (ME) obtained by transesterification were experimentally investigated.

2. MATERIALS AND METHODS

2.1 Materials

Used frying oil was collected from a local market in Mahasarakham province, Thailand. It was heated at 120°C for 1 h to evaporate moisture and was then filtered by cloth and filter paper (8µm) to remove food

residues and impurities. Methanol (99.99%), sulfuric acid (99%), and potassium hydroxide (pellet) were purchased from Merck Chemical.

2.2 Acid Esterification

The pretreated used frying oil was placed in a beaker equipped with a magnetic stirrer heating plate to control the stirring rate and temperature of the reaction mixture. Sulfuric acid-methanol solution previously prepared was then added into the oil. Esterification reactions were carried out at temperature range of 40–60 °C, amount of catalyst (H_2SO_4) of 0.5-3%wt., methanol to oil molar ratio of 6:1-18:1 and reaction period of 60-120 minutes. After the reaction, the products were poured into a separatory funnel and allowed to settle overnight producing two distinct liquid phases. The lower layer (oily phase) was separated and its FFA content was determined according to standard titration method. The product with minimum FFA content was used for further process by the alkaline transesterification.

2.3 Alkaline Transesterification

The acid pretreated oil with minimum FFA content was processed by alkaline transesterification in a beaker equipped with a magnetic stirrer heating plate. The reaction was conducted at 40-60°C with 3:1-9:1 methanol-to-oil molar ratio using 0.25-1%wt potassium hydroxide as a catalyst, for reaction period of 60-120 minutes. After completion of the transesterification, the reaction mixtures were poured into a decantation funnel and allowed to settle overnight to produce two separating phases: the upper ester phase and the lower glycerol phase. The lower layer, containing glycerol and impurities, was then drawn off. The upper layer containing ME, was washed with warm distilled water three times to obtain purified ME. The purified ME was weighted to determine ME yield defined as the weight percentage of purified ME relative to the weight of raw oil. The

product was then kept in reagent bottles for further analysis of fuel properties.

2.4 Characterization of fuel properties

The purified ME was evaluated in a series of tests to determine kinematic viscosity at 40°C by a viscometer, flash point by Cleveland open cup method, and calorific value by a bomb calorimeter, according to the ASTM standard.

3. RESULTS

3.1 Acid Esterification

Four major factors affecting reduction of FFA content are: reaction temperature, reaction time, molar ratio of alcohol to oil and catalyst amount.

3.1.1 Effects of reaction time and temperature on FFA reduction

The effect of reaction time and temperature on FFA reduction is shown in Fig. 1.

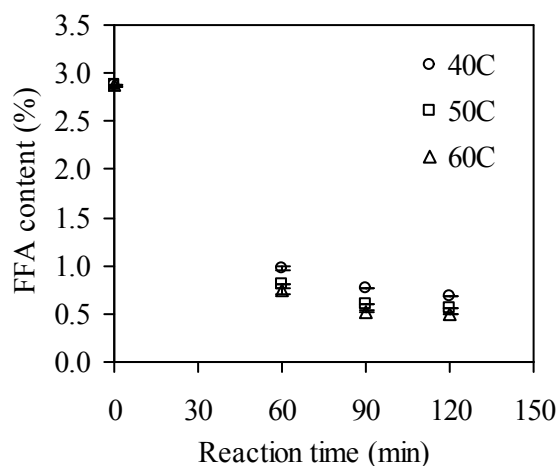


Figure 1: Variation of free fatty acid content during acid esterification at various reaction times and temperatures, with 6:1 methanol-to-oil molar ratio and 2%wt sulfuric acid

The FFA content in the used frying oil was found to abruptly decrease from 2.87 to 0.74-0.97, corresponding to FFA conversion of 66-74%, during the first 60 minutes of

reaction. When time continuously elapsed, the amount of FFA was gradually decreased to the equilibrium value. Insignificant reduction in FFA content after 90 minutes might be due to the effect of water produced during the esterification of FFA, which prevented further reaction [17].

As also shown in Fig. 1, at a specific reaction time, Increase in reaction temperature caused the faster reduction rate of FFA content. Since the acid esterification is an endothermic reaction, reaction rate and equilibrium constant are therefore enhanced by temperature.

3.1.2 Effects of catalyst amount and methanol to oil molar ratio on FFA reduction

Influence of catalyst amount on the FFA reduction at different methanol to oil molar ratios is presented in Fig. 2.

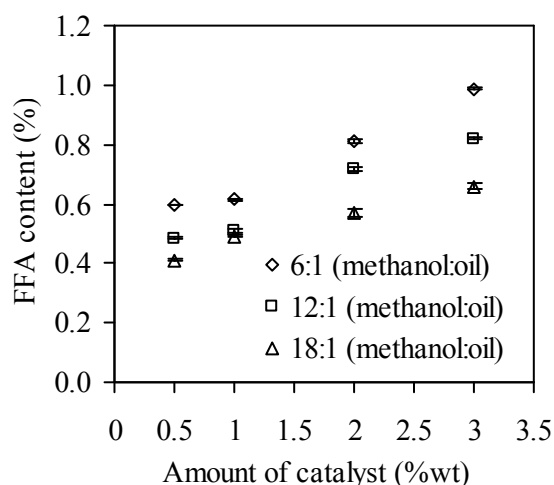


Figure 2: Variation of free fatty acid content during acid esterification with different amount of catalyst and methanol to oil molar ratios, at reaction temperature of 50°C for 60 min

Unexpectedly, an increase in sulfuric acid amount resulted in reduction of FFA conversion. By observation, the excess addition of sulfuric acid also darkened the color of the product. In addition to catalyst amount, molar ratio of methanol to oil is another important parameter affecting the FFA reduction efficiency. An excess of methanol is necessary for accelerating the

esterification of FFA. That was the result why using larger amount of methanol (18:1 molar ratio) could reduce FFA content faster than using smaller amount of methanol (6:1 molar ratio). The FFA content could be reduced to the minimum value (0.30%) when the process was conducted at reaction temperature of 60°C, molar ratio of 18:1, catalyst amount of 0.5 %wt, and reaction time of 120 minutes.

3.2 Alkaline Transesterification

3.2.1 Effects of reaction time and temperature on the ME yield

Changes of ME yield during alkaline transesterification with molar ratio of 3:1 and using 0.5%wt potassium hydroxide as catalyst are depicted in Fig. 3.

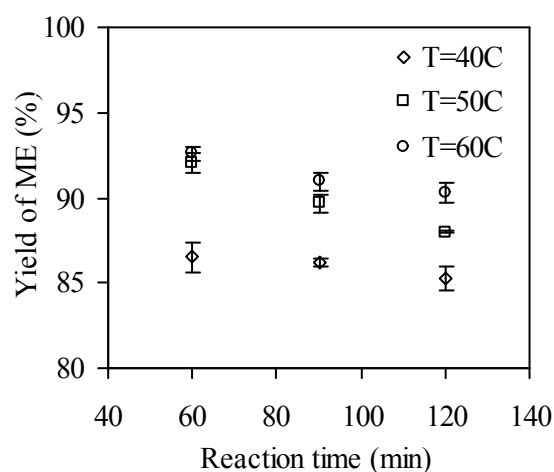


Figure 3: Effects of reaction time and temperature on yield of methyl ester prepared by transesterification with 3:1 methanol-to-oil molar ratio and 0.5%wt potassium hydroxide

It was noticed that yield of ME was influenced by both the reaction time and temperature. The yield increased with increasing reaction temperature and decreasing reaction time. This was because high temperature led to a drastic decrease in viscosity of used frying oil that was favorable to increase the solubility of the oil in the methanol and improve the contact between oil and methanol molecules, thereby reaching a better conversion of

triglycerides [20]. Furthermore, the negative impact of reaction time can be described by the fact that longer reaction period enhances the hydrolysis of esters (reverse reaction of transesterification), resulting in a loss of esters as well as causing more fatty acids to form soap [20].

3.2.2 Effects of catalyst amount and methanol to oil molar ratio on the ME yield

Apart from reaction time and temperature, catalyst amount and molar ratio of alcohol to oil are other important parameters affecting the ME yield and purity. As illustrated in Fig. 4, when the catalyst amount increased from 0.25 to 0.5%wt, the yield raised from 77-88 to 84-92%. With further increase in catalyst amount, however, the yield remained relatively constant. This was because addition of an excessive amount of catalyst caused soap formation, leading to an increase of viscosity and formation of gel. This interfered with the reaction and hindered glycerol separation, resulting in no obvious increase of the yield [21]. Addition of a large amount of methanol, acting as an emulsifier, increased solubility, thus making separation of glycerol more complicated. The remaining glycerol helped drive the equilibrium to back to the left, resulting in a decrease of the yield [22].

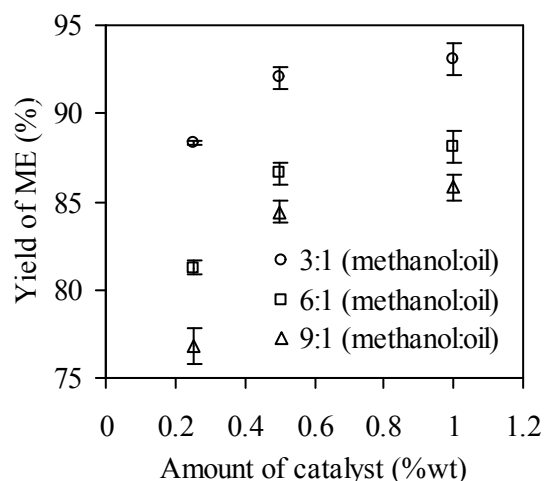


Figure 4: Effects of amount of catalyst and methanol to oil molar ratio on yield of methyl ester prepared by transesterification at reaction temperature of 50°C for 60 min

The yield of ME was maximized (93.125%) when the transesterification was reacted at the temperature of 60 °C, molar ratio of 3:1, catalyst amount of 1%wt and reaction time of 60 minutes.

3.2.3 Flash points of ME prepared by different conditions

Flash point is the lowest temperature at which the vapors of a combustible liquid will ignite momentarily in air. The flash point of biodiesel is generally higher than the petro-diesel, which is safe for transport purpose. Influences of operating parameters viz. reaction time, reaction temperature, amount of catalyst, and methanol to oil molar ratio of the alkaline transesterification step on flash point of ME obtained are summarized in Figs. 5-6.

It was clearly seen that the four parameters had negative effect on flash point. Flash points of the ME prepared by all reaction conditions were in the range of 150-175°C which were higher than the lower limit that indicated in the ASTM standard (130 °C).

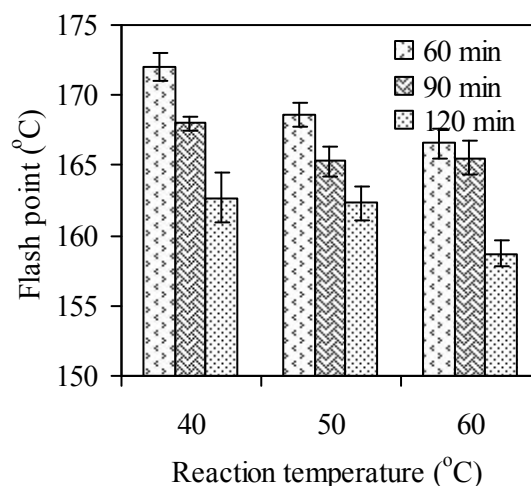


Figure 5: Flash point of methyl ester prepared by transesterification at various reaction times and temperatures, with 3:1 methanol-to-oil molar ratio and 0.5%wt potassium hydroxide

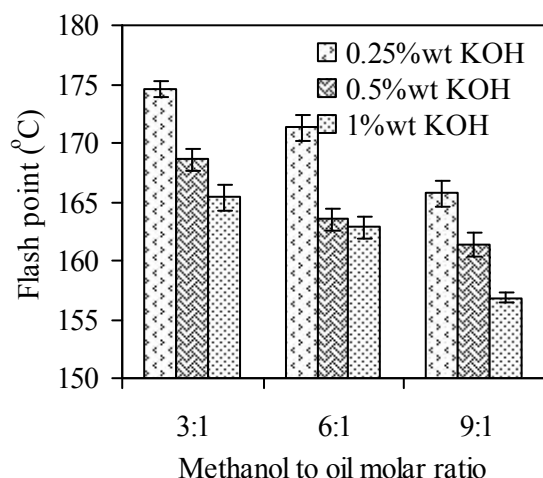


Figure 6: Flash point of methyl ester prepared by transesterification with different methanol to oil molar ratios and amount of catalyst, at reaction temperature of 50°C for 60 min

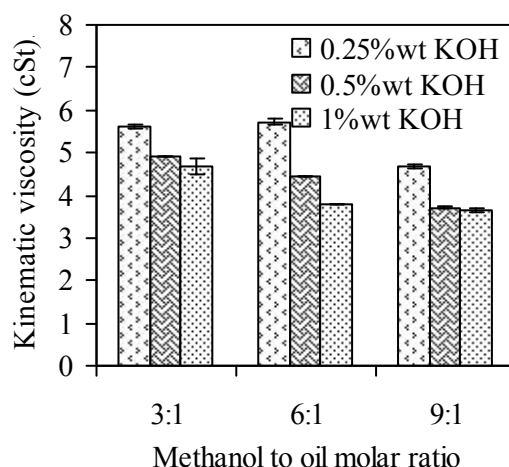


Figure 8: Kinematic viscosity of methyl ester prepared by transesterification with different methanol to oil molar ratios and amount of catalyst, at reaction temperature of 50°C for 60 min

3.2.4 Kinematic viscosities of ME prepared by different conditions

The viscosity is a very important property related to the biodiesel utilization in direct injection diesel engines. High value of viscosity gives rise to a poor fuel atomization, incomplete combustion, and carbon deposition on the injectors. Kinematic viscosities of ME produced by reaction at some different conditions are represented in Figs. 7-8.

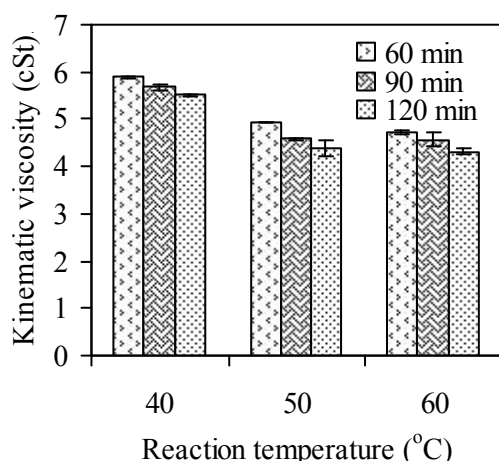


Figure 7: Kinematic viscosity of methyl ester prepared by transesterification at various reaction times and temperatures, with 3:1 methanol-to-oil molar ratio and 0.5%wt potassium hydroxide

The viscosities tended to decrease as increasing reaction time, reaction temperature, amount of catalyst, and methanol to oil molar ratio. This might be described by the fact that increases in the four parameters made the reaction more complete, resulting in low impurities. This result was in accordance with that reported by Encinar et al. [23]. The kinematic viscosities of all ME produced in this work ranged from 3.5-6 cSt which are desirable according to the ASTM standard (1.9-6 cSt).

3.2.5 Calorific values of ME

Calorific values of ME prepared in this work were in the range of 39-42 MJ/kg which were 6-13% less than those of petroleum diesel (45 MJ/kg).

5. CONCLUSION

Two stage chemical process of acid catalyzed esterification followed by alkaline catalyzed transesterification was adopted to prepare biodiesel (methyl ester) from used frying oil. Reaction temperature, reaction time, methanol to oil molar ratio and catalyst were found to strongly affect reduction of FFA content of the product

during the first step esterification as well as the yield and fuel properties of the ME produced in the second step transesterification. Reduction rate of FFA content can be accelerated by increasing reaction temperature, methanol to oil molar ratio, and reaction time and decreasing catalyst amount. FFA content was minimized (0.30%) when the esterification was conducted at reaction temperature of 60°C, molar ratio of 18:1, catalyst amount of 0.5 %wt, and reaction time of 120 minutes. Yield of ME was raised by increasing reaction temperature and amount of catalyst and decreasing methanol to oil molar ratio and reaction time. The maximum yield (93.125%) was obtained when performing the transesterification at the temperature of 60°C, molar ratio of 3:1, catalyst amount of 1%wt and reaction time of 60 minutes. Flash point and kinematic viscosity of the ME produced were in the ranges of 150-175°C and 1.9-6 cSt respectively which met the specification of ASTM standard. Calorific value of the ME ranged from 39 to 42 MJ/kg.

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