EFFECT OF TEMPERATURES, POTASSIUM HYDROXIDE AND POTASSIUM METOXIDE ON SAPONIFICATION OF BIODIESEL

Kannika Angchotipan¹*, Warut Congkumnert¹, Sukritthira Ratanawilai¹ and Chakrit Thongurai¹

¹Prince of Songkla University, Faculty of Engineering, Thailand
*e-mail: nfai_843@hotmail.com

Abstract: The saponification of biodiesel using potassium hydroxide (KOH) and potassium metoxide (KOC₃) was investigated. In this study, the reactions were carried out at four different temperature (30, 40, 50 and 60±1°C), using a mixing speed of 250 rpm, and a constant basic concentration of 0.005 mol% based on oil weight. Samples were collected at various time intervals and analyzed for amount of remain base and soap with titration. Results showed that both the temperatures and different base had effect on the biodiesel saponification rate.

Key Words: Saponification / Biodiesel / KOH / KOC₃

1. INTRODUCTION

Biodiesel is defined as fatty acid methyl or ethyl esters derived from vegetable oils, animal fats and waste cooking oil that can be used in diesel engines in neat form or blended with diesel fuel with little or no engine modification, it can be considered as a potential diesel fuel [1-3]. There are several routes to obtain biodiesel such as esterification [4], transesterification [5], and two-step method [6]. The industrial process widely used today for biodiesel production is transesterification of triglycerides with low molecular weight alcohols such as methanol and ethanol in the presence of catalyst [2, 5, 7].

Transesterification reactions (also called methanolysis or ethanolysis depending on alcohol type) can be performed using acid catalysts, such as sulfuric, sulfonic, phosphoric and hydrochloric acids or basic catalysts, such as metal hydroxides, metal alkoxides, alkaline-earth oxides or hydrotalcites [5]. The basic catalysts are usually preferred to acid catalysts since the higher activity [5], the faster process and the moderated reaction conditions as compared to acid-catalyzed transesterification [1].

However, alkali-catalyzed transesterification process for biodiesel production there is a serious problem of side-reaction that is “Saponification”. Unless free fatty acids (FFAs), which presence in oil, and glycerides, which are key component in oil, it can also occurs from esters, which are product from transesterification, react with alkali (OH) to form soap [8], as shown in Eq. (1).

\[
\text{Esters + OH} \iff \text{Soap + Alcohol} \quad (1)
\]

Soap formations of this reaction effects on alkali-catalyst and purity of biodiesel in transesterification due to they consume the catalyst, reduce the biodiesel yield and complicate the separation and purification steps [1]. Nevertheless, there are not many researches to investigate about effects on saponification of esters.

Consequently, this research interests to study effect of temperature and different base on saponification reaction of biodiesel, is representative of esters, react with base at various temperature for database, improvement and development in biodiesel production by alkali-catalyzed transesterification.

2. MATERIAL AND METHOD

2.1 Material

Biodiesel (Methyl Ester) in this experimental study were supplied and produced from Specialized R&D Center for Alternative Energy from Palm Oil and Oil Crops, Prince of Songkla University, Thailand, with the following characteristics: purity, >98%; density, 0.87 kg/l. Potassium hydroxide of 95% purity was purchased from Lab-Scan Ltd (Ireland). Potassium metoxide of 90% purity was purchased from Fluka (Sigma-Aldrich, Germany). For methanol of 99.8% purity was purchased from P. General Group Company Ltd (Bangkok, Thailand).

2.2 Apparatus and reaction procedure

The reactions were carried out at four different temperatures (30, 40, 50 and 60±1°C) and two different
bases (KOH and KOCH₃) in a 500 mL three-necked reactor, equipped with a reflux condenser and a thermometer. The reactor was immersed in a constant-temperature oil bath and controlled within ±1°C. Agitation was provided with a magnetic stirrer, which was fixed at a mixing speed of 250 rpm all over the experiment. The reactor was initially filled with 200 g of oil and preheated to the desired temperature. A constant base concentration of 0.005 mol% based on oil weight was dissolved in methanol (6 wt% based on oil weight) and added to the reactor.

2.3 Sampling and analysis

Sampling: Samples were withdrawn quickly with a syringe at various times (1, 3, 5, ..., 10, 15, 20, ..., 30, 40, 50, ..., 75, 90, 105 minutes and so on) until not found amount of base and 5 ml of the sample was added into solvent (alcohol) then shaken and immerse into an ice bath to stop the reaction immediately. Then the samples were analyzed to determine amount of remain base and soap with titration.

Analysis: The amount of remain base of samples was determined by adding a sample to a larger quantity of alcohol then added a phenolphthalein indicator solution and titrating with 0.01N hydrochloric acid until reach the colorless end point. For the soap measurement, 4-5 drops of bromophenol blue indicator solution was added and the titration continued to the yellow end point [9].

3. RESULTS AND DISCUSSIONS

3.1 Effect of temperature on biodiesel saponification

The temperature is one of the most important variables affecting a consumption of base and amount of soap formation, the saponification reactions of biodiesel were carried out with a fixed mixing speed of 250 rpm and a constant base concentration of 0.005 mol% based on oil weight (dissolved in methanol 6 wt% based on oil weight) at temperature 30 (room temperature or not have heating), 40, 50 and 60°C for KOH and KOCH₃, respectively, is shown in figures 1-4.

Fig. 1. Illustration of the effect temperature and time on remaining of KOH at 30, 40, 50 and 60°C

Fig. 2. Illustration of the effect temperature and time on amount of soap formation at 30, 40, 50 and 60°C by using KOH

Fig. 1 and 2 show that temperature had a significant effected on base consumption rate and soap formation rate. They were found that the reaction rate increased with increasing the temperature which observed from amount of base that was rapidly reacted to form soap and vanished within 5, 7, 15 and 40 minutes at 60, 50, 40 and 30°C, respectively.

Fig. 3. Illustration of the effect temperature and time on remaining of KOCH₃ at 30, 40, 50 and 60°C

Fig. 4. Illustration of the effect temperature and time on amount of soap formation at 30, 40, 50 and 60°C by using KOCH₃

Fig. 3 and 4 show the influence of temperature (30, 40, 50 and 60°C) on disappear rate of base and soap formation rate. They can be observed that temperature had a significant influence on those rates because base disappearing and soap formation rate at 40, 50 and 60°C happened quickly when compare with not have heating.
(30°C). On the other hand, the temperatures had effect on those rates increase rapidly within first 20 minutes, and slowly increase during interval from 20 minutes to 50 minutes. At 30°C, the base consumption and soap formation rate keep relatively stable and show no significant increase after 50 minutes. While at the other temperatures, base disappeared within 50 minutes.

3.2 Effect of different base on biodiesel saponification

To determine the effect of different base (KOH, KOCH3) on consumption of base and amount of soap formation that occur at 60°C (because this temperature is most used in transesterification for biodiesel production) using a mixing speed of 250 rpm, and a constant base concentration of 0.005 mol% based on oil weight is shown in figures 5-6.

![Graph 5. Illustration of the relationship between remaining of base and time at 60°C by using different base](image)

The result showed that different base make to different consumption rate of base and amount of soap that occur. When we used KOH found that rapid decreasing remain base which relate to increasing content of soap, which its formation will consume base make to decrease catalyst content in alkali-catalyzed transesterification, as compare with KOCH3.

![Graph 6. Illustration of the relationship between amount of soap and time at 60°C by using different base](image)

4. CONCLUSION

Results showed that both the temperatures and different base had effect on the biodiesel saponification rate. The temperature was found to have a significant effect on consumption rate of base and soap formation rate when using KOH whereas it had a slightly effect on those rates for using KOCH3, and the reaction rate increased with increasing the temperature. For base difference, was found that consumption of KOH and soap formation rate faster than KOCH3.

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6. REFERENCES