Methanolysis process catalyzed by homogeneous alkaline catalyst: effect of free fatty acid content on saponification reaction

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Abstract: *In biodiesel production, soap formation creates phase separation problems during the purification process resulting in low biodiesel yield and ester content. This research evaluates the effect of FFA contents (0.2-1.1 wt%) during the transesterification reaction of refined palm oil (RPO). In comparison, saponification of fatty acid methyl ester (FAME) with varying FFA contents (0.2-1.1 wt%) is determined. From a microscopic point of view, soap should act as a mass-diffusion barrier affecting a lower reactant mass flux to the reaction zone. Regarding soap formation in biodiesel production, high FFA leads to soap formation in FAME and RPO due to neutralization and saponification reaction. This work suggests that the soap formation behaviour in biodiesel production should be addressed; and thus, the optimal FFA content in oil should be determined.*

I. Introduction

Biodiesel is defined as a mixture of alkyl esters which produced from the reaction between vegetable oils, animal fats, or waste oils containing triglyceride (TG) as the main component and short-chain alcohols (typically methanol or ethanol) in the presence of a suitable catalyst [1]–[3]. There are widely production methods; such as esterification, transesterification, and two-step method (esterification and transesterification). The reaction is called transesterification reaction as shown in Eq. (1).

$$TG + 3\ Alcohol \xrightleftharpoons{\text{Catalyst}} 3\ Ester + Glycerol \qquad . (1)$$
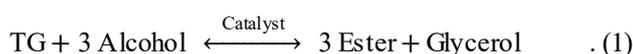
In the reaction, there are two types of catalysts which are a heterogeneous (solid) and a homogeneous (liquid) catalyst. The solid catalyst, either acid or base catalyst, is advantaged for low soap formation, but it is relatively time-consuming in the reaction. It required a high amount of alcohol and consequent separation equipment [1]–[3]. On the contrary, the liquid catalyst such as alkaline hydroxide and alkaline methoxide is widely used in commercial biodiesel plants. It consumes less time, low alcohol usage, and is well mixed in the reaction. However, it could facilitate the saponification reaction and requires a high amount of water in a latter washing process [4], [5].

The soap formation is also the main reason for the biodiesel yield loss. For commercial target, the low-cost feedstocks such as crude palm oil and waste cooking oil are interesting for biodiesel production. However, the presence of free fatty acids (FFA) and moisture contents in these oils lead to a serious problem of soap formation. They can speed up the hydrolysis of triglycerides (Eq. 3) and esters (Eq. 4) by increasing FFA to further react with the alkaline catalyst to form soap. The chemical reactions of soap formation in biodiesel production are shown in Eq. (2-7). It is formed by FFA neutralization (Eq. 2) and saponification of triglyceride (Eq. 5) [6] and FAME (Eq. 6) [6] during transesterification in the presence of a homogeneous base catalyst. The saponification reaction is highly undesirable because it not only consumes the catalyst but also causes a problem in phase separation and emulsion formation during purification stages. Hence, it reduces biodiesel yield. Therefore, the FFA content in the feedstocks is essential to render saponification during the transesterification process. Some studies have demonstrated the influence of FFA on transesterification using an alkaline catalyst to determine the optimal conditions. Kwiecien et al [6] demonstrated that ester content in the glycerol phase increases with increasing of soap content caused by the FFA neutralization and presence of water. The free fatty acid (FFA) neutralization reactions are described in Eq. (2).

$$FFA + KOCH_3 \longrightarrow Soap + Alcohol \qquad . (2)$$

The hydrolysis reactions of triglyceride and ester are described in Eq. (3-4).

$$TG + 3Water \longrightarrow 3FFA + Glycerol \qquad (3)$$

$$Ester + Water \longrightarrow FFA + Alcohol \qquad (4)$$

The saponification reactions of triglyceride and ester and potassium methoxide are described in Eq. (5-6).

$$TG + 3KOCH_3 \longrightarrow Soap + Alcohol \qquad (5)$$

$$FAME + KOCH_3 \longrightarrow Soap + Alcohol \qquad (6)$$
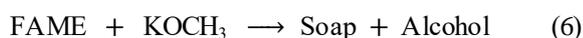
The key parameters affecting the yield of biodiesel in biodiesel production are FFA and moisture contents. According to industrial biodiesel companies such as Lurgi GmbH [7] and Crown Iron Works [8], these have specified feedstock properties as maximum acidity 0.1 % or 0.5 % and maximum moisture and volatiles as 0.1 % or 0.05 %. These impurities are significant to soap formation in the transesterification process. Among the other reaction parameters, FFA content, catalyst type, and its concentration, and reaction time play key roles in biodiesel yield, which is related to soap formation. The reaction kinetics are significant in biodiesel production. The immiscibility of alcohol and triglyceride causes a mass-transfer barrier during the transesterification process [9]. For a two-phase reaction, mass transfer with a chemical reaction and two-film theory are well described by Levenspiel [10]. Slinn (2008) proposed a mass transfer limited model adapted from Levenspiel (1999): the immiscibility of oil and methanol causes rigid glycerol droplets to form at the interface of methanol and triglyceride [11]. Tubino et al. (2014, 2016) proposed that methanolysis with alkaline catalysts should be heterogeneous [12], [13]. Noureddini and Zhu (1997) proposed a reaction mechanism consisting of an initial mass transfer controlled region followed by a kinetically controlled region [14]. Our previous works studied the actual events in liquid-liquid mass transfer transesterification via microscopic visual observations at room temperature [15]–[17]. The miscibility of biodiesel (FAME) and refined palm oil (RPO) from homogeneous alkaline catalysis (KOCH₃) via mass transfer by diffusion was studied on a concave glass slide as a micro-reactor. The study of soap formation behavior was included in the microscopic observations. Convective mass transfer in alkaline-catalyzed transesterification was evaluated.

This study aims to evaluate the effect of free fatty acid (FFA) on soap formation during the transesterification reaction of refined palm oil and the saponification reaction of fatty acid methyl ester (FAME). This study also aims at

illustrating the reaction zone of saponification reaction using an LCD digital microscope.

II. EXPERIMENTAL ANALYSIS

A. Chemicals and materials

Refined palm oil (RPO) with approx. 0.1 wt% of FFA and 0.1 wt% of moisture content, and a commercial-grade FAME (approx. 98.0 wt% purity) were obtained from the Specialized R&D Center for Alternative Energy from Palm Oil and Oil Crops, Prince of Songkla University, Thailand. A commercial-grade methanol (MeOH, 99.8 wt% purity) was purchased from P-General Co. Ltd. Commercial grade potassium methoxide (KOCH₃, 32 wt% in methanol) was bought from AGC Chemicals (Thailand) Co., Ltd. The RPO and FAME were premixed with PFAD (90 wt% FFA) for 0.22 to 1.11 wt% FFA. All raw materials, RPO and FAME were dewatered by heating at 105 °C for 3 h, and then analyzed to control the remained moisture (<0.05 wt%) by a Karl Fisher coulometer.

B. Experimental methods

Study of the effect of FFA content on saponification reaction in biodiesel production

Three replicated experiments were conducted in a 1-liter 3-necked flat-bottomed flask equipped with a condenser and a 500-rpm magnetic stirrer. The reaction conditions of saponification were: 100g of refined palm oil (RPO) with varying FFA approx. 0.22-1.11 wt%. The RPO (0.1 wt% FFA) was premixed with PFAD (90 wt% FFA) for 0.22 to 1.11 wt% FFA. KOCH₃ concentration 1.50 wt% oil and molar ratio of methanol/oil of 6:1. A sample of RPO was poured into the glass reactor, heated to 50 °C of reaction temperature followed by the potassium methoxide solution. The mixture was then stirred for the next 10 min, and approx. 3 ml of three replicated samples were collected using a volumetric pipette at 10 min. Three replicated samples were transferred into the pre-weighed 250 ml Erlenmeyer flasks containing 50 ml of isopropanol to immediately halt the reaction, and then analyzed for catalyst and soap contents. For biodiesel (FAME), the same procedure was carried out.

Study of the reaction zone of saponification reaction in biodiesel production

The microscopic observation of saponification reaction on a microreactor at room temperature (about 27 °C) was illustrated to determine the zone of reaction. A concave glass slide was used as a microreactor. This trial was performed by microscopic observation (Novel NLCD-307, 2.0 Mega Pixels CMOS Chip, at 100X magnification) of the mass diffusion and chemical reaction between the alkaline-methanol and triglyceride phases. A small pool of RPO (approx. 10 μL) at room temperature was put on the concave glass slide and centered under the LCD 307 microscope. A very fine drop of methanol-potassium methoxide -phenolphthalein solution (1 μL) was dropped in the pool of RPO. The concentration of potassium methoxide-methanol is 0.1515 mol/L. A reversed

trial was done by putting a fine drop of RPO (1 µL) to the center of the concave slide, then a small amount of methanol-potassium methoxide -phenolphthalein solution (approx. 10 µL) was dropped in and the photo was taken. These trials were repeated several times. For biodiesel (FAME), the same procedure was performed.

C. Analytical methods

FFA content analysis

FFA contents in oil and biodiesel were evaluated using an acid-base titration method (AOAC 940.28). Approx. 10 g of sample was transferred into a pre-weighed 250 ml Erlenmeyer flask containing 50 ml of isopropanol and then titrated with 0.05-0.1 N sodium hydroxide (NaOH) solutions using phenolphthalein indicator.

Catalyst and soap contents analysis

The halted sample has tested the contents of catalyst and soap (AOCS Cc 17-79). The sample was analyzed by a two-step titration method with 0.05-0.1 N hydrochloric acid solutions: using phenolphthalein indicator for the catalyst content while bromophenol blue was used for the soap content.

III. RESULTS AND DISCUSSIONS

Study of the effect of FFA content on saponification reaction in biodiesel production

In alkaline-catalyzed transesterification, depletion of catalyst activity is due to its consumption by side reactions: neutralization and saponification. To determine the influence of FFA content on soap formation, experiments were conducted by varying the FFA content of palm oil and biodiesel (FAME) between 0.22 and 1.11 wt% as presented in Figs. 1 and 2. An increase of the FFA content in RPO and biodiesel (FAME) increases the high soap formation by neutralization reaction. As a result, it was observed that the soap amount was higher than the total mole of FFA and water. The results suggest that soap was possibly produced via different sources; neutralization of FFA (Eq. 2) and saponification of triglyceride (Eq. 5) or FAME (Eq. 6). The FFA content in raw materials leads to soap formation [6]. In comparison, biodiesel ease to form soap than palm oil due to the lower mass transfer barrier. From our previous studies [15], high FFA content in RPO creates a large portion of soap that restrains the diffusion of alcohol and catalyst. Formation of soap should reduce the remaining catalyst for further transesterification and thus the lower ester content would be obtained. Therefore, 0.1 and 0.5 wt% (or 0.05 and 0.25 wt% FFA) are at the maximum tolerable acidity in oil for transesterification reported by Lurgi GmbH [7] and by Crown Iron Works [18], respectively. The thick boundary layer of soap does not allow the diffusion of alcohol and catalyst to the reaction zone and has the consequence of slowing down transesterification.
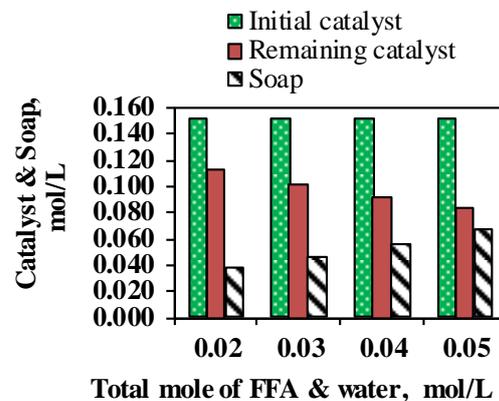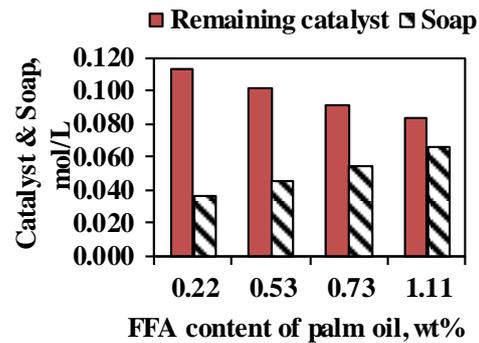

Fig. 1. The effect of FFA content of RPO on saponification reaction in biodiesel production: the varying FFA content in RPO (0.22-1.11 wt%), moisture content (0.05 wt%), total FFA and water (0.02-0.05 mol/L), the potassium methoxide-methanol solution (0.1515 mol/L), the reaction time of 10 min, 50 °C and 500 rpm.

Study of the reaction zone of saponification reaction in biodiesel production

In this study, the transesterification of oil (Eq. 1) and saponification of triglyceride (Eq. 5) are expected reactions. For soap formation of biodiesel (FAME), it could be reacted with an alkaline substance which is expected from two major reactions, neutralization (Eq. 2) and saponification of FAME (Eq. 6). From Fig. 3A, saponification of alkaline solution on RPO is expected to behave differently from FAME due to the transesterification reaction [15], [16]. Transesterification of triglyceride gives ester and as by-product glycerol. Glycerol is a strongly polar compound, unlike other esters. Glycerol should prefer to stay with methanol, and if the reaction takes place near the interface of alcohol and triglyceride, the glycerol should leave the ester and move to the methanol phase. Fig. 3B, a drop of FAME on the pool of alkaline-methanol solution, indicates diffusion of FAME into the alkaline-methanol solution [15].
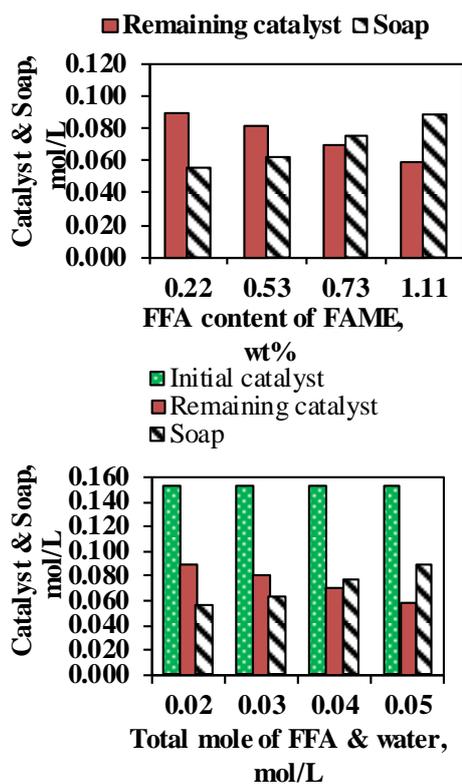
Fig. 2. The effect of FFA content of FAME on saponification reaction in biodiesel production: the varying FFA content in FAME (0.22-1.11 wt%), moisture content (0.05 wt%), total FFA and water (0.02-0.05 mol/L), the potassium methoxide-methanol solution (0.1515 mol/L), the reaction time of 10 min, 50 °C and 500 rpm.

Fig. 3. Possible reaction zone: saponification of triglyceride and FAME (modified from Chanakaewsomboon et al 2019 [15])

IV. CONCLUSIONS

In transesterification via alkaline catalysis, soap formation is a major factor of catalyst depletion and yield loss due to saponification reaction and loss on purification step. The rate of saponification reaction is a complicated solution that depends on many factors such as free fatty acid (FFA) content, water content, alkaline category, catalyst amount, reaction temperature, amount of methanol, and amount of glycerol, and many others factors. This paper demonstrates the effect of FFA contents of palm oil and biodiesel are performed in range 0.2 to 1.1 wt%. Microscopic observation (Novel NLCD-307, 2.0 Mega Pixels CMOS Chip, at 100X magnification) investigates the actual events in liquid-liquid mass transfer transesterification at room temperature. Soap could act as a mass-diffusion barrier affecting a lower reactant mass flux to the reaction zone. High FFA of oils (palm oil and biodiesel) leads to soap formation because of neutralization and saponification reactions. Thus, the optimal FFA content in oil should be addressed.
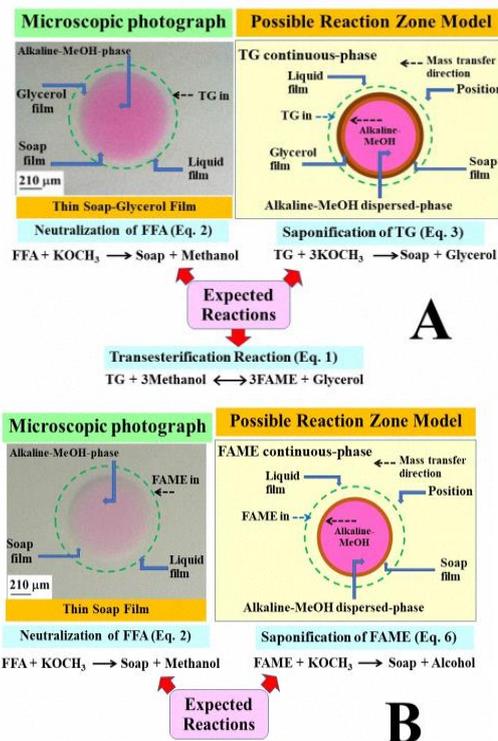
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