

Biodiesel produced by homogeneous alkaline catalyst: effect of catalyst concentration on saponification reaction

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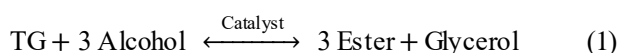
Abstract: During transesterification reactions, catalyst affects the final ester content which is also impacted by the soap formation. This research aims at examining the effect of catalyst amount (0.5-2.42 wt%) during the transesterification reaction of refined palm oil containing 0.49 wt% FFA. It was found that the optimal catalyst content to meet biodiesel property standard i.e. ester content greater than 96.5% was 1.0 wt% of oil. Catalyst addition lower than 0.7 wt % resulted in diesel that did not meet the required ester content standard. Catalyst addition higher than 1% did not result in further conversion improvement but it increases the production costs. From a microscopic point of view, soap could act as a mass-diffusion barrier affecting a lower reactant mass flux to the reaction zone. The actual events in liquid-liquid mass transfer transesterification are possible. This work suggests that the drawbacks associated to high catalyst utilization (production cost and soap formation) should be addressed; and thus, the optimal catalyst concentration be determined.

Keywords: Biodiesel, catalyst, saponification, transesterification.

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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).



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

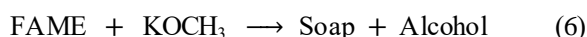
water. The free fatty acid (FFA) neutralization reactions are described in Eq. (2).



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



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



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 (KOCH_3) 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.

The aim of this study is to evaluate the effects of catalyst contents on soap formation during the transesterification reaction of refined palm oil. This study also aims at illustrating the microscopic view 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 (KOCH_3 , 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

The experiment was conducted in a 1-liter 3-necked flat-bottomed flask equipped with a condenser and a 500-rpm magnetic stirrer. The reaction conditions of transesterification were (TABLE I): 300g of refined palm oil (approx. 0.49 wt% FFA), varying KOCH_3 amount of 0.5 to 2.42 wt% oil and molar ratio of methanol/oil of 6:1. RPO was poured into the glass reactor, heated to 50 °C followed by the potassium methoxide solution. During the mixing, approximately 1 mL of the mixture was sampled and immediately analyzed with an LCD digital microscope (Novel NLCD-307, 2.0 Mega Pixels CMOS Chip) at 100X magnification for illustrating the microscopic photograph of saponification reaction. The mixture was then stirred for 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. and approx. 3 ml of three replicated samples were collected using a volumetric pipette. After sampling, the mixture was allowed to settle for 2 h for phase separation, then it was washed with tap water and finally dried using a 250-rpm heater-stirrer at 105 °C for 3 h. The ester content was analyzed by both chemical method [18] and GC-FID (EN 14103).

Table I. Conditions in methanolysis of refined palmoil.

Run#	RPO	MeOH	KOCH ₃		FFA	Water
	g	g	wt%	g	wt%	wt%
1	300	67.92	2.42	7.26	0.49	0.13
2	300	67.92	1.94	5.82	0.49	0.13
3	300	67.92	1.45	4.35	0.49	0.13
4	300	67.92	1.00	3.00	0.49	0.13
5	300	67.92	0.67	2.01	0.49	0.14
6	300	67.92	0.50	1.50	0.49	0.14

C. Analytical methods

The water content of raw materials and methanol was analysed by Karl Fischer method (ISO 12937) [19]. FFA content was analysed by titration (Method AOAC 940.28) [20]. Ester content was analysed by a chemical method [18]. The final FAME product, which was obtained from the suitable reaction conditions, was quantified directly in Gas chromatography equipped with flame ionization detector according to EN 14103. Glycerol content in the sample was determined by titration method (BS Official Method 5711-3: 1979). The catalyst and soap contents in samples were tested using an acid-base titration method (AOCS Official Method Cc 17-79).

III. RESULTS AND DISCUSSIONS

Reaction parameters, such as reaction time, reaction temperature, FFA content, water content, and catalyst concentrations have a significant impact on conventional transesterification process. To evaluate the purity of biodiesel, the ester content (wt% referred to biodiesel mass) in the final biodiesel phase was determined. In this study, catalyst concentration is selected as a studied reaction variable. The results are shown in Tables 1 and 2.

Soap content was analysed for both crude biodiesel and crude glycerol phases. From the weight ratio of both phases, the total soap content could be calculated. The remaining catalyst was also analyzed for both phases. The remaining catalysts and soap contents are presented in Table 2. From our previous work [15], one could assume that the barrier to mass transfer at the outer surface of methanol droplet is composed of glycerol, soap, diglyceride, and monoglyceride.

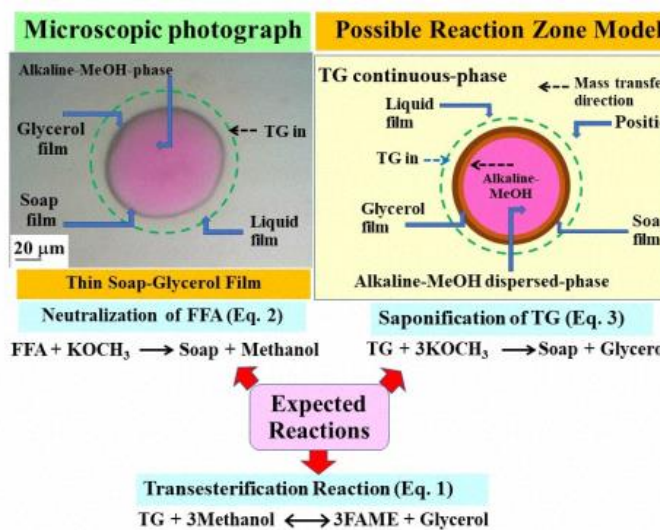
The effect of catalyst amounts on the soap formation in the transesterification process is summarized in Table II. The catalyst concentrations were varied in the range 0.50-2.42 wt%, while FFA and water contents were maintained constant, as seen in Runs #1-6. The results show that increasing catalyst concentration gives higher soap content. The addition of approximately 1.0 wt% of KOCH₃, the molar ratio of methanol to oil at 6:1 and 10 minutes reaction time gave a final ester content in biodiesel greater than 96.5 wt%, meeting biodiesel specification standards. Potassium methoxide content below 0.70 wt% of RPO (Runs #5-6) resulted in unacceptable biodiesel quality with insufficient ester content. Use of catalyst amount above 1.0 wt% did not cause significant changes in the conversion; but it could be increase biodiesel production cost. The ester content increased with increasing catalyst concentration due to the reduction of activation energy during catalytic process, yielding the transesterification reaction proceeds to product-side.

In the microscopic views (Fig. 1), the two phases of alcohol and oil from saponification are observed. Soap acts as an emulsifier that suspends methanol droplets in the methanol-triglyceride (TG) continuous solution phase (Fig. 1C). The pink color indicates alkaline-phenolphthalein-methanol drops separated from the miscible methanol-TG solution. The transesterification of oil (Eq. 1) and saponification of triglyceride (Eq. 5) are expected reactions. 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 [15], [17].

Table II. Conversion by methanolysis of refined palmoil.

Run#	Ester content	Remaining Catalyst	Soap	Glycerol analysis			
				Ester-rich phase		Glycerol-rich phase	
				wt%	mol	g	mol
1	98.13	0.060	0.044	0.92	0.010	29.44	0.320
2	98.13	0.041	0.040	1.28	0.014	28.57	0.311
3	98.54	0.029	0.033	1.02	0.011	27.34	0.297
4	97.72	0.016	0.025	1.00	0.011	27.19	0.296
5	91.58	0.009	0.019	1.41	0.015	26.76	0.291
6	88.31	0.006	0.015	1.28	0.014	23.65	0.257

Note: Experimental conditions: initial methanol-to-oil molar ratio of 6:1, 50 °C, 500 rpm, 10 min reaction time. The data reported are averages of three-replicate experiments with standard deviation (S.D.) < 0.05.



C: 400X

Fig 1. Microscopic photographs and possible reaction zone: saponification and transesterification of triglyceride (modified from Chanakaewsomboon et al 2019 [15])

IV. CONCLUSIONS

The addition of catalyst was studied to find the optimum compromise between final ester content, soap formation, and production cost. Microscopic observation investigates the actual events in liquid-liquid mass transfer transesterification. Soap could act as a mass-diffusion barrier affecting a lower reactant mass flux to the reaction zone. The optimal catalyst concentrations to meet the biodiesel standard (> 96.5 wt% ester content) was 1.0wt%. During transesterification reactions utilizing low catalyst, the catalyst is easily consumed to form soap which results in low remaining catalyst amount for further reaction. For those scenarios, low ester contents are obtained. Higher catalyst concentration, however, has significant drawbacks; higher catalyst consumption and higher content of soap formed. Moreover, high catalyst concentration accelerated the saponification of FAME. Thus, the optimum catalyst utilization which would lower soap formation should be investigated.

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