

Acid-Catalyzed Esterification: A Technique for Reducing High Free Fatty Acid in Mixed Crude Palm Oil

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ABSTRACT

Acid-catalyzed esterification for reducing high free fatty acid (FFA) in mixed crude palm oil (MCPO) was investigated in a constant-temperature hot water bath based on parameters such as the speed of stirrer, the catalyst concentration (H_2SO_4), the molar ratio of methanol to oil and reaction temperature. The samples were analyzed by Thin Layer Chromatography for determining the decrease of FFA in MCPO. The high FFA in MCPO was rapidly reduced to less than 1%wt in the first 30 seconds under the reaction conditions of a 3:1 molar ratio of methanol to oil and 0.8%wt H_2SO_4 at 60 °C.

Key words: acid-catalyzed esterification, free fatty acid, MCPO, palm oil

INTRODUCTION

Generally, biodiesel is the production of a chemical process: transesterification, which is the reaction of triglyceride with methanol by using alkali catalyst. Raw materials which were used in this process must be anhydrous and low free fatty acid (FFA). The moisture and high FFA (>1%wt) will cause saponification reaction, which results in lower yield and washing difficulty. Therefore, the methodology of FFA reduction was required for preparing the oil solution to produce biodiesel in transesterification.

Veljković *et al.* (2006) studied the two-stage process of tobacco seed oil. H_2SO_4 was used as catalyst for reducing FFA in tobacco seed oil in the first stage. It indicated that 2%wt H_2SO_4 was the optimized catalyst, which reduced FFA to less

than 2%wt in 25 minutes for the molar ratio of methanol to oil of 18:1.

Canakci *et al.* (2001) used two-step pretreatment to reduce FFA content in yellow grease from 12%wt and brown grease from 33%wt to less than 1%wt before producing biodiesel by transesterification.

Ramadhas *et al.* (2004) studied acid-catalyzed esterification for reducing the high FFA contained in rubber seed oil. It was found that this method could reduce FFA of the oil to less than 2%wt.

Zullaikah *et al.* (2005) studied a two-step acid-catalyzed process for the production of biodiesel from rice bran oil. High FFA (>20%wt) in rice bran oil was converted more than 98%wt FFA at 60 °C in 2 hour using 2%wt H_2SO_4 and a 5:1 molar ratio of methanol to oil.

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Thaweesinsopha *et al.* (2005) and Thaweesinsopha (2006) used acid-catalyzed esterification for reducing FFA in mixed crude palm oil (MCPO). They found that FFA in MCPO was reduced to less than 2%wt in 1 hour at 60 °C by using 3%wt H₂SO₄ as a catalyst and 10%wt methanol.

High FFA MCPO, which is the mixing of palm fiber oil and palm kernel oil, was used as the feedstock. The main objectives of this study were to develop the reaction conditions such as reaction time, amount of acid catalyst, which were used in our previous work and to prepare the feedstock for biodiesel production. Consequently, the reaction conditions such as the speed of stirrer, the molar ratio of methanol to oil, the amount of catalyst, and reaction temperature for reducing the FFA content by acid-catalyzed transesterification were investigated.

MATERIALS AND METHODS

Materials Mixed crude palm oil containing high FFA (8 -12%wt) was obtained from local palm oil mill in Hat Yai, Songkla, Thailand. H₂SO₄ (95%), and methanol (95%) are of commercial grade. Hexane, diethyl ether, formic acid, and benzene, which were used in thin layer chromatography/ flame ionization detector (TLC/ FID), are all of analytical grade.

Apparatus The reducing of high FFA in MCPO was conducted in a 2000 ml round bottom flask equipped with a mechanical stirrer, thermocouple, fixed condensing coil, and sampling port. The reactor was immersed in a constant-temperature hot water bath. The temperature control accuracy was $\pm 1^\circ\text{C}$. In addition, when the samples were washed with NaOH solution, the strong base solution transferred the FFA in each bath to soap (Brown *et al.*, 2003) that caused TLC/ FID determined the FFA values less than 1%wt in 30 seconds. Therefore, the samples were washed with hot water only for reducing the impurities in

the samples.

Methodology The MCPO was weighed and heated. Then the methanol was added to the flask and performed for mixing oil and methanol. After that H₂SO₄ was added as a catalyst into the oil. 2 ml sample at the retention time, $t = 0, 1, 3, 5, 7, 9, 12, 15, 18, 21, 25, 30$ minutes, were collected from the reactor. After that the sample were collected at every 5 minutes for 30 minutes (May, 2004). The reactions of the samples were stopped immediately by immersing in cold water (5°C) until the temperature of the samples reached ambient temperature. Then the samples were washed with hot water.

Experiments were carried out with different stirring speeds, varying the molar ratio of methanol to oil, varying the amount of catalyst and at different temperature.

Effect of speed of stirrer at 200, 300 and 400 rpm on the reducing of high FFA held in MCPO was investigated using a 6:1 molar ratio of methanol to oil at a temperature of 60°C, catalyzed by 0.8%wt H₂SO₄.

Effect of molar ratio of methanol to oil at 1:1, 3:1, and 5:1 for reducing high FFA in MCPO was investigated using 0.8%wt H₂SO₄ at 60°C and a stirring rate of 300 rpm.

Effect of the amount of catalyst (H₂SO₄) at 0.4, 0.8, and 1.2%wt on the reaction of high FFA in MCPO was investigated using a 3:1 molar ratio of methanol to oil, at temperature of 60, and a speed of stirrer at 300 rpm.

Effect of temperature on high FFA reduction of MCPO at 55, 60, and 65°C was investigated using a molar ratio of methanol to oil of 3:1, catalyzed by H₂SO₄ (0.8%wt) and a 300 rpm speed of stirrer.

Analysis The samples were analyzed by TLC/FID. Analyses were performed using an Itronscan MK6 with Chromarod type S-III quartz rod (Mitsubishi Kagaku Iatron Inc., Japan). The flame ionization detector used 160 mL/min hydrogen flow rate and 2.0 L/min air flow rate.

The samples were diluted in hexane and the sample solution was spotted on each rod. The rods were developed in hexane/diethyl ether/formic acid (50:20:0.3 vol/vol/vol) for 20 min, air-dried for 5 min, then developed in hexane/benzene (1:1 vol/vol) for 30 min, oven-dried at 105°C and then analyzed. Scan speed was 30 sec/rod. The mass ratio of methyl ester, tri-, di-, mono-glyceride and free fatty acid was determined.

RESULTS AND DISCUSSION

Acid-catalyzed esterification analysis

A characteristic concentration curve for treatment FFA in MCPO under the conditions of a 0.8%wt H_2SO_4 and a 3:1 molar ratio of methanol to oil at 60°C are shown in Figure 1. The tendency of FFA consumption suddenly decreased from the beginning of the reaction in the first 30 seconds and then lowered until equilibrium. The inclination of Triglyceride (TG) and monoglyceride reduced slowly but the diglyceride (DG) trend increased slightly, which were showed in linear curve. The rapid formation tendency of methyl ester as shown

in a sigmoid curve was observed within the first 1 min and then formed steadily, primarily due to esterification of FFA. As for the description of the typical concentration curve of esterification, beside the FFA esterification, MG, DG, and TG were also transesterified. There was the cause for the reduction in the MG and TG content and the increase in the DG content.

Conversion of FFA into methyl ester

Esterification reaction was the treatment technique of high FFA which contained in MCPO. It was the reaction between FFA in MCPO and methanol with acid catalyst (H_2SO_4). In chemical reaction of esterification, carboxyl function group of FFA was substituted with a CH_3O^- group of methanol to produce methyl ester and water as shown in Equation 1.

Effect of impurities Generally, when ester was treated with acid or base in aqueous solution, the molecule of ester could be reversed to alcohol and acid compound: hydrolysis as shown in Equation 1 (Brown *et al.*, 2003). In addition, the excess methanol in the samples was interference for detecting the signal of TLC/FID

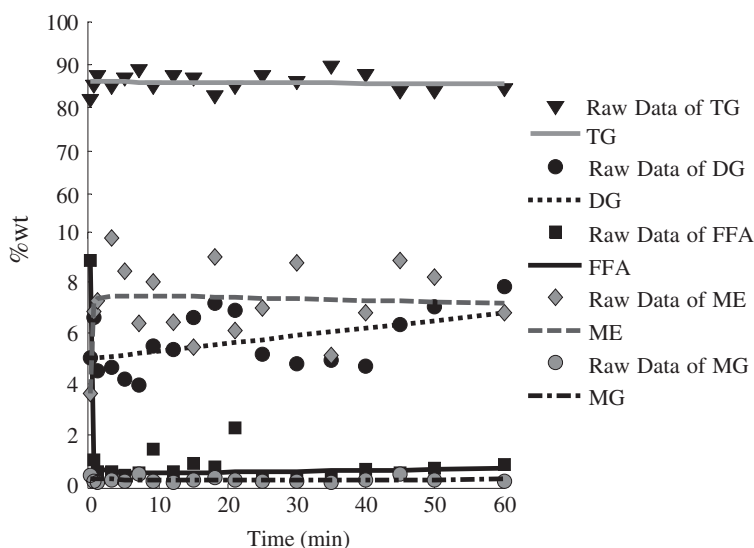
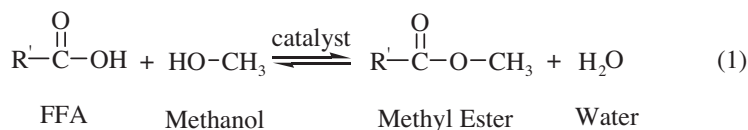


Figure 1 Variations of the reaction mixture composition with acid-catalyzed esterification of MCPO by using a 0.8 %wt H_2SO_4 and a 3:1 molar ratio of methanol to oil at 60°C.



(Sherma, 2000). Therefore, the samples were washed with hot water for reducing the impurities in the samples.

Effect of speed of stirrer The reacting mixture formed two immiscible layers of oil and methanol. Thorough mixing of the two layers was necessary for the reaction to proceed (Thaweensin-sopha *et al.*, 2005 and Thaweensin-sopha, 2006). When the esterification reaction was performed for a long time, there were no significant differences in the variation of the stirrer speed for reducing FFA in 200, 300 and 400 rpm. However, FFA was reduced to less than 1%wt in 30 seconds when the speed of stirrer of this experiment was 300 and 400 rpm as shown in Figure 2. Therefore, a 300 rpm speed of stirrer was suitable for using to reduce FFA in MCPO.

Effect of molar ratio of methanol to oil Figure 3 shows the changes in the acid values of the mixing on the FFA reduction reaction. The rate of reaction was influenced by the molar ratio

of methanol to oil. The results indicated that FFA was reduced to less than 1%wt for high methanol ratios in a half of minute. No significant differences were found in FFA reduction on the molar ratio of methanol to oil of 3:1 and 5:1. As for the reaction, low methanol ratio was considered to reduce high FFA. Therefore, a 3:1 molar ratio of methanol to oil was used to decrease FFA that held in MCPO.

Effect of the amount of catalyst (H_2SO_4) The reduction of high FFA in MCPO was dependent on the consumption of the amount of catalyst. It was found that there was not much effect when the catalyst was increased from 0.8 to 1.2%wt as shown in Figure 4. However, the reduction of FFA with 1.2 and 0.8%wt were almost the same, so 0.8%wt H_2SO_4 was suitable to be used in the esterification reaction.

Effect of temperature The results of FFA reduction of MCPO to less than 1%wt were obtained for 55, 60, and 65°C at a molar ratio of methanol to oil of 3:1, catalyzed by H_2SO_4

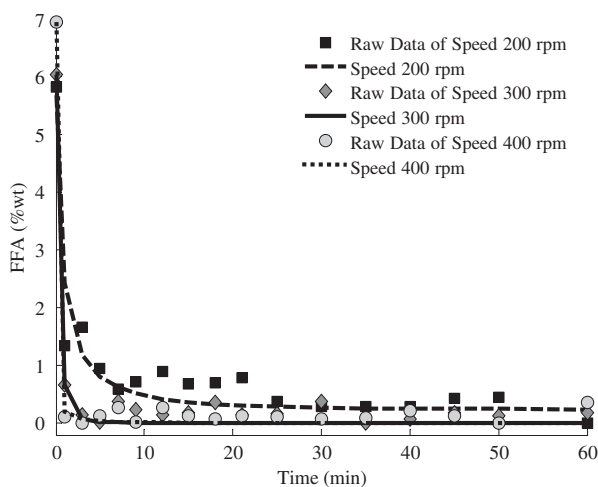


Figure 2 Effect of stirring speed on FFA in MCPO by using a 6:1 molar ratio of methanol to oil at a temperature of 60°C, catalyzed by 0.8 %wt H_2SO_4 .

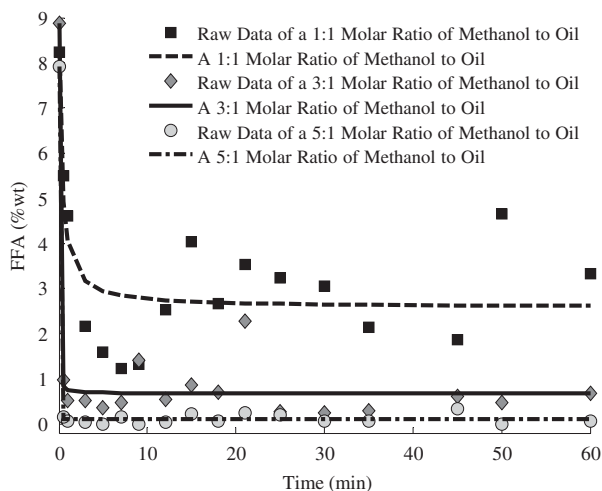


Figure 3 Effect of molar ratio of methanol to oil on FFA in MCPO by using 0.8 %wt H_2SO_4 at 60°C and a stirring rate of 300 rpm.

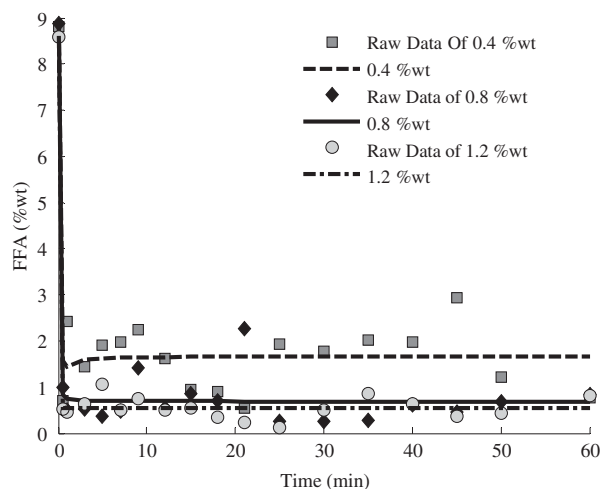


Figure 4 Effect of the amount of acid-catalyst on FFA in MCPO by using a 3:1 molar ratio of methanol to oil, at temperature of 60°C and a speed of stirrer of 300 rpm.

(0.8%wt), and a 300 rpm speed of stirrer. The time for reducing FFA was decreased in 30 seconds when the temperature increased from 55 to 60 and 65°C. Even though there were no significant differences in reaction time when the temperature was changed, they had an influence on reaction rate of esterification. As a result, the reaction temperature at 60°C was sufficient for reducing high FFA to below 1%wt.

CONCLUSION

Acid-catalyst esterification was investigated to treat high free fatty acid (FFA), which contained in mixed crude palm oil (MCPO) by varying the speed of stirrer, the catalyst concentration (H_2SO_4), the methanol ratios and temperature. The reaction condition that reduced FFA to less than 1%wt in 30 second, was a 3:1

molar ratio of methanol to oil at 60 and catalyzed by 0.8%wt H₂SO₄.

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