

## Enhancement of the Two-Stage Process for Producing Biodiesel from High Free Fatty Acid Mixed Crude Palm Oil

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### ABSTRACT

A two-stage process (esterification followed by transesterification) was investigated in biodiesel production from mixed crude palm oil (MCPO) having high free fatty acid (FFA). For the required methyl ester content greater than 96.5 wt%, the two-stage process could produce biodiesel obtaining 95% yield under a molar ratio of 10:1 of methanol to FFA and 10 wt% of sulfuric acid based on FFA, and a molar ratio of 6:1 of methanol to initial triglyceride (TG) and 0.6 %wt/v of sodium hydroxide based on the initial TG at 60 °C with a total production time of 11 hr 35 min.

**Keywords:** biodiesel, esterification, palm oil, two-stage process and transesterification

### INTRODUCTION

Generally, transesterification is used to produce biodiesel from vegetable oil or animal fat containing low free fatty acid (FFA) content through a reaction with alcohol and an alkaline catalyst (Ma and Hanna, 1998; Gerpen *et al.*, 2004; Prateepchaikul *et al.*, 2007). When biodiesel is produced from high FFA oils by transesterification, the high FFA content in the oils reacts with the metallic alkoxide to produce soap (saponification) (Brown *et al.*, 2003; Gerpen *et al.*, 2004). In addition, if oils contain a high moisture content, saponification and hydrolysis occur. These reactions cause a lower yield and washing difficulty. The problem can be solved via four methods: enzymatic-catalyzed transesterification, acid-catalyzed transesterification, a supercritical carbon dioxide technique and a two-stage

process (Ma and Hanna, 1998; Gerpen *et al.*, 2004; Marchetti *et al.*, 2005). However, the two-stage process was chosen to produce biodiesel in this study because this process requires lower temperature and lower pressure than the other processes.

At present, the two-stage process for producing biodiesel from crude oil consists of two methods: saponification followed by transesterification, and esterification followed by transesterification. Nevertheless, esterification followed by transesterification was preferred in this investigation to produce biodiesel from oil containing high FFA content in an undegummed state, because it requires shorter time and involves lower production loss than from the process of saponification followed by transesterification (Jansri and Prateepchaikul, 2011). In this procedure, acid catalyst esterification

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(the first stage) was employed to reduce the FFA by converting it into biodiesel. Then, alkali-catalyzed transesterification was subsequently used to convert glycerides—triglyceride (TG), diglyceride (DG) and monoglyceride (MG)—into biodiesel.

Previously, crude tobacco seed oil, fryer grease, jatropha seed oil, mahua oil, mixed crude palm oil, rubber seed oil and used cooking oil, all having a free fatty acid content of around 5 to 40 wt%, have been investigated in biodiesel production by the latter two-stage process (Cannakci and Gerpan, 2001; Crabbe *et al.*, 2001; Kac, 2001; Ramadhas *et al.*, 2004; Ghadge and Raheman, 2005; Marchetti *et al.*, 2005; Veljković *et al.*, 2006; Prateepchaikul *et al.*, 2007; Tiwari *et al.*, 2007;). FFA contained in the oil was reduced to less than 1–2 wt% in the conversion into biodiesel (methyl ester) in 1 to 8 hr. The suitable conditions for converting the FFA into biodiesel were a 5-20:1 molar ratio of methanol to oil and 2–3 wt% of sulfuric acid at 60 °C.

After this first stage, impurities such as sulfuric acid, water and gum were separated out of the solution. The oily top phase containing less than 2 wt% of FFA was used as a raw material in transesterification. It was found that over 90 wt% of methyl ester was obtained in 1 to 2 hr using a molar ratio of methanol to oil of around 3-9:1, with the amount of alkaline catalyst (sodium hydroxide or potassium hydroxide) around 1–2 wt% at 60 °C.

Although there have been many studies on biodiesel via the two-stage process, the retention time of each stage took a long time, especially for biodiesel production from MCPO under Prateepchaikul's condition (2007). Therefore, improvement of this condition will reduce the time required to obtain biodiesel.

## MATERIALS AND METHODS

### Materials

MCPO (un-degummed and containing

FFA around 8–12 wt%) was used as the feedstock for biodiesel production and was obtained from a local palm oil mill in Hat Yai, Songkhla, Thailand. Sulfuric acid, sodium hydroxide and methanol of 98% purity commercial grade were purchased from a local chemical store. Sulfuric acid, diethyl ether, iso-propanol and hexane, all of analytical grade, were purchased from Lab Scan Analytical Science, Thailand. Analytical grade sodium hydroxide pellets, sodium periodate, potassium hydrogen phthalate, ethanediol and bromothymol blue were purchased from Ajax Fine Chem., New Zealand. Analytical grade phenolphthalein and formic acid were purchased from Merck KGaA, Germany. Benzene and hydranal-coulomat AG No. 34836, also of analytical grade, were purchased from Honeywell, Germany, and Danreac Quimica, E.U., respectively.

### Two-stage biodiesel production batch process

The biodiesel production from high FFA mixed crude palm oil by the two-stage batch process (esterification followed by transesterification) was carried out in a 2000 mL round-bottomed flask equipped with a six-blade disk turbine 10 cm in diameter, together with a thermocouple, a fixed condensing coil and a sampling port. While this reactor, which contained the solution, was immersed in a constant-temperature water bath ( $\pm 1$  °C) to control the reaction temperature, the solution of each reaction was stirred at 300 rpm ( $N_{RE} = 2,520$ ) throughout.

### Esterification (first stage process)

To commence the esterification (the first-stage process), MCPO, analyzed for FFA content by a titration technique (Link, 1989) was weighed and heated until the MCPO temperature rose to the predetermined temperature. Then, methanol was added slowly into the flask and mixing was performed for 5 min to blend the mixture. Subsequently, sulfuric acid (catalyzed in esterification) was added slowly in the flask and

mixing was performed until the reaction time was reached. Finally, the stirring was stopped and the final solution was poured into a separating funnel and left for 2 hr to separate the solution into two phases: a top phase (oily phase: oil, methyl ester and some impurities) and a bottom phase (waste phase or black phase: water, un-reacted methanol and sulfuric acid). The top phase was kept to produce biodiesel using transesterification.

The effects of the amount of methanol on the FFA reduction were determined at molar ratios of methanol to FFA of 4:1, 10:1 and 16:1 in the MCPO catalyzed by  $\text{H}_2\text{SO}_4$  at 10 wt%. In addition, the effects of the amount of sulfuric acid on the FFA reduction were determined at 5, 10 and 15 wt% in a fixed methanol molar ratio of 10:1 based on the FFA content. Each reaction was carried out at 60 °C. Moreover, a 10:1 molar ratio of methanol to FFA catalyzed by 10 wt% sulfuric acid was used to investigate the effect of reaction temperature on the FFA reduction at 55, 60, and 65 °C.

#### **Transesterification (second stage process)**

At the beginning of transesterification (the second stage), the pre-treatment oil (the top phase) was poured into the flask and heated until the solution temperature rose to the predetermined value. During heating, the solution was titrated to check the acid value for preparing the amount of sodium hydroxide, which was required to neutralize the solution. After that, the sodium methoxide solution—formed by mixing methanol and sodium hydroxide (neutralization and catalyst)—was added slowly to the flask and then the reaction was allowed to continue for the required time. Agitation was then stopped and the final solution was poured into the separating funnel again and left for 1 hr to separate the red phase (crude biodiesel) out of the glycerol phase (the bottom phase).

A molar ratio of methanol to the initial TG of 3:1, 6:1 and 9:1 in the MCPO catalyzed

by 0.6 %wt/v of sodium hydroxide based on the initial TG was determined to investigate the effects of the methanol ratios on the methyl ester (ME) conversion. The effects of the amount of sodium hydroxide on ME conversion, at 0.3, 0.6 and 0.9 %wt/v of sodium hydroxide based on the initial TG—0.25, 0.50, and 0.75 %wt/v of sodium hydroxide based on the MCPO—in 6:1 molar ratio of methanol to TG was investigated. Each reaction was performed at 60 °C. In addition, the effects of reaction temperature on ME conversion were investigated under similar reaction temperatures of 55, 60 and 65 °C by using 6:1 molar ratio of methanol to TG and 0.6 %wt/v of sodium hydroxide.

#### **Monitoring**

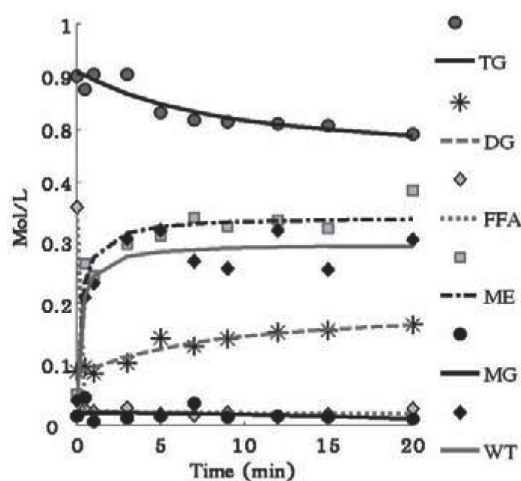
The progress of the two-stage process reaction was monitored periodically by the composition of the solution using TLC/FID (thin layer chromatography/flame ionization detection) according to Prateepchaikul *et al.* (2007), the appearance of water by the Karl Fischer titration technique and the appearance of glycerol (GL) by a titration technique (Thai Industrial Standards Institute, 1980). After adding the catalyst in each step, the sample of 2 mL was withdrawn after a retention time of 0, 0.5, 1, 3, 5, 7, 9, 12, 15, 18, and 20 min (May, 2004). The sample reaction was stopped immediately by immersing in cold water (5 °C) (Jansri *et al.*, 2007). Before purifying the sample for analyzing the concentration of TG, DG, MG, FFA, and ME with TLC/FID in esterification and transesterification, each un-washed sample in the first stage was analyzed for water content by the Karl Fischer titration technique and in the second stage the GL content in each sample was analyzed by the titration technique. The sample for the TLC/FID analysis had its impurities removed by washing with 250 mL hot water (80 °C) three times (Jansri *et al.*, 2007) because the residue methanol in each sample would interfere with the signal of the TLC/FID (Sherma, 2000).

## RESULTS AND DISCUSSION

The two-stage process (esterification followed by transesterification) was used to convert un-degummed mixed crude palm oil having an FFA content around 8–12 wt% into biodiesel of more than 96.5 wt% purity. After completing the procedure, sample results were verified using TLC/FID, the Karl Fischer titration technique and one other standard titration, which were determined in terms of percentage by mass.

### Esterification (first stage process)

A characteristic concentration curve for treating high the FFA content in the MCPO under the conditions of a 10:1 molar ratio of methanol to FFA in the MCPO catalyzed by 10 wt% of sulfuric acid based on the FFA in the MCPO at 60 °C is shown in Figure 1 and indicates that the FFA composition suddenly decreased after the first 30



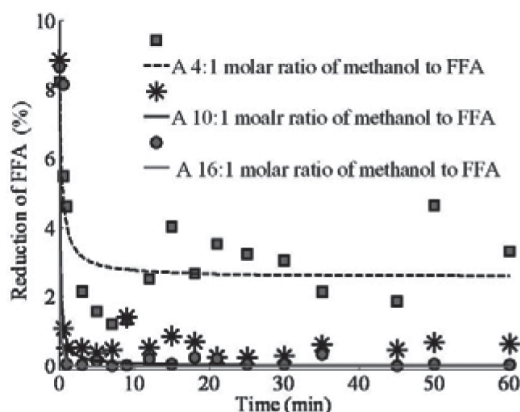
**Figure 1** Variation of reaction mixture concentrations during esterification under the condition of a 10:1 molar ratio of methanol to free fatty acid (FFA) in mixed crude palm oil (MCPO) catalyzed by 10 wt% of sulfuric acid based on FFA in MCPO at 60 °C (TG = triglyceride; DG = diglyceride; ME = methyl ester; MG = monoglyceride; WT = water).

sec and then very slowly decreased until it reached equilibrium. The rates of decrease of TG and MG were gentle, however, the concentration of DG increased slightly. The rapid formation of ME and water (WT) according to a sigmoidal curve was observed within the first minute and then formation was steady, primarily due to esterification of the FFA and/or transesterification of TG, DG, and MG.

The above description of typical concentration curves of esterification indicated that besides the acid-esterification reaction, TG, DG, and MG were also converted into ME by transesterification. In addition, the hydrolysis reaction could be promoted by water (WT), which was the byproduct in this process. These processes might have caused changes in the concentration of TG, DG and MG. Although, the acid-transesterification reaction and the hydrolysis reaction occurred in this process, only esterification was considered and investigated, especially the disappearance of FFA in the investigation of the effects of the methanol ratio, of the amount of sulfuric acid and of the reaction temperature.

First, the effect of the methanol ratio on the FFA reduction was investigated under the conditions of methanol molar ratios on FFA in the MCPO of 4:1, 10:1 and 16:1 catalyzed by 10 wt% of sulfuric acid based on FFA at 60 °C. The results, shown in Figure 2, indicate that the FFA was reduced rapidly to less than 1 wt% in 30 sec using molar ratios of 10:1 and 16:1 methanol to FFA.

On the other hand, the molar ratio of methanol to FFA in the MCPO of 4:1 could not reduce the FFA to less than 1 wt%. Therefore, to drive the forward reaction to obtain the highest yield of the product according to Le Châtelier's Principle, a higher molar ratio was required in the reaction (Brown *et al.*, 2003). In addition, a reaction temperature close to the boiling point of methanol at ambient pressure was used; therefore, methanol could continuously evaporate during

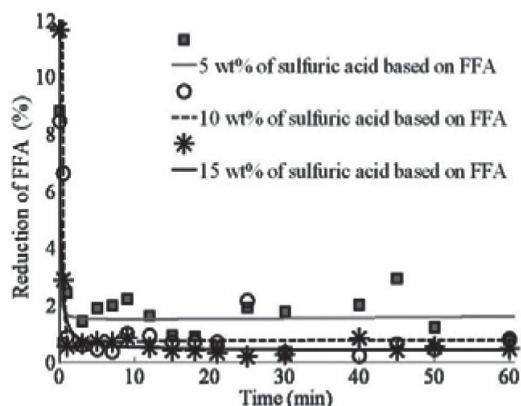


**Figure 2** Effect of methanol molar ratio on free fatty acid (FFA) reduction.

the reaction. Moreover, the higher molar ratio of methanol to FFA had an influence on the rate of FFA reduction. During periodical FFA monitoring, no substantial differences were found in the reduction of FFA under molar ratios of methanol to FFA of 10:1 and 16:1. Therefore, to save on methanol consumption, a 10:1 molar ratio of methanol to FFA in the MCPO was used to reduce the FFA in the MCPO to around 8–12 wt% by esterification.

Then, the investigation focused on the effect of the amount of sulfuric acid on the FFA reduction. Sulfuric acid in amounts of 5, 10, and 15 wt% based on the FFA content was used as a catalyst for reducing the FFA in the MCPO by esterification under the conditions of a 10:1 methanol molar ratio of the FFA in the MCPO at 60 °C. The results indicated that the rapid reduction of the high FFA content in the MCPO was dependent on the composition of the amount of catalyst, with the 8–12 wt% FFA that was contained in the MCPO being reduced with 5, 10, and 15 wt% of sulfuric acid based on FFA, as shown in Figure 3.

Nevertheless, the concentration of sulfuric acid at 5 wt% was not sufficient to reduce the FFA to less than 1 wt% of the MCPO because its concentration was diluted with the solution

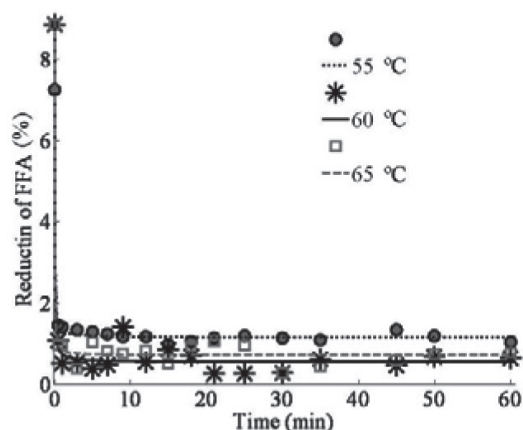


**Figure 3** Effect of sulfuric acid on free fatty acid (FFA) reduction.

(the mixture between MCPO and methanol) in this process. At the higher amounts of catalyst (10 and 15 wt% based on FFA), the rate of the reaction was found to be approximately the same (FFA < 1 wt%). Therefore, 10 wt% sulfuric acid based on the FFA in the MCPO (the lower suitable concentration) was selected to reduce 8–12 wt% of the FFA in the MCPO to less than 1 wt% of the MCPO because greater use of sulfuric acid, which is a strong liquid acid, would have a greater adverse effect on the environment.

Although the esterification reaction is typically an exothermic reaction, it was necessary to continuously increase the temperature to drive the reaction to reach the required FFA concentration because the reaction temperature strongly influences the reaction rate. Therefore the reaction should be conducted under a suitable reaction temperature even though the reaction could proceed to near completion even at room temperature (Brown *et al.*, 2003). So, finally, the various reaction temperatures of 55, 60, and 65 °C were investigated under the conditions of a 10:1 molar ratio of methanol to FFA and 10 wt% of sulfuric acid based on the FFA in the MCPO. Even though the results, shown in Figure 4, indicate there were no substantial differences in reaction time when the temperature was varied at 55, 60,





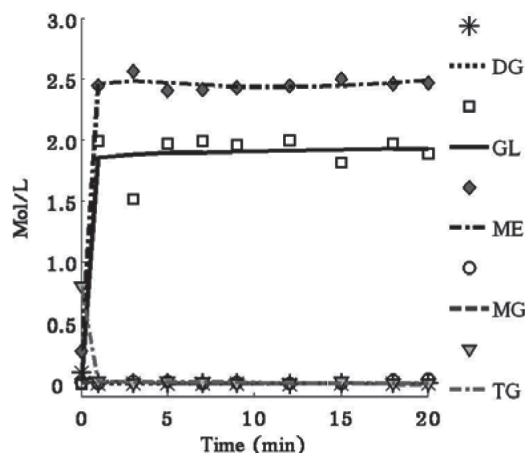
**Figure 4** Effect of reaction temperature on free fatty acid (FFA) reduction.

and 65 °C, the reaction temperature has been reported to have an influence on the reaction rate of esterification (Brown *et al.*, 2003).

The results indicated that the reduction of the FFA in the MCPO to 1 wt% was achieved at 55, 60, and 65 °C. The FFA concentration could be decreased more rapidly when the reaction temperature was increased from 55 °C to 60 and 65 °C. However, there was an insubstantial increase in the reduction of FFA when the reaction temperature was increased from 60 to 65 °C. Therefore, the reaction temperature of 60 °C was considered suitable for reducing the FFA at around 8–12 wt% contained in the MCPO by esterification.

#### Transesterification (the second stage process)

A characteristic concentration curve in transesterification of de-acidified MCPO is shown in Figure 5 under the conditions of a 6:1 molar ratio of methanol to the initial TG in the MCPO and 0.6 %wt/v of sodium hydroxide based on the initial TG in the MCPO at 60 °C and indicates that the rate of appearance of ME and GL was initially high and then rapidly reached equilibrium. The concentration curve followed a sigmoidal curve, more or less.



**Figure 5** Variation of reaction mixture concentrations during transesterification under the conditions of a 6:1 molar ratio of methanol to initial TG in MCPO catalyzed by 0.6 wt% of sodium hydroxide based on TG in MCPO at 60 °C (DG = diglyceride; GL = glycerol; ME = methyl ester; MG = monoglyceride; TG = triglyceride).

On the other hand, the mechanism of the TG disappearance was controlled by the mass transfer reaction so that a decrease in the TG concentration was observed within the first minute. It was also found that the tendentious curves of DG and MG composition increased in the first minute and then decreased until equilibrium was reached. The aforementioned description indicated that both the ME and GL concentrations were dependent on changes in the concentration of TG, DG, and MG in the transesterification reaction. According to the study objective, only the ME conversion was periodically monitored to investigate the effect of the methanol ratio, of the amount of sodium hydroxide and of the reaction temperature in the transesterification process.

First, the de-acidified MCPO was used as a raw material for investigating the effect

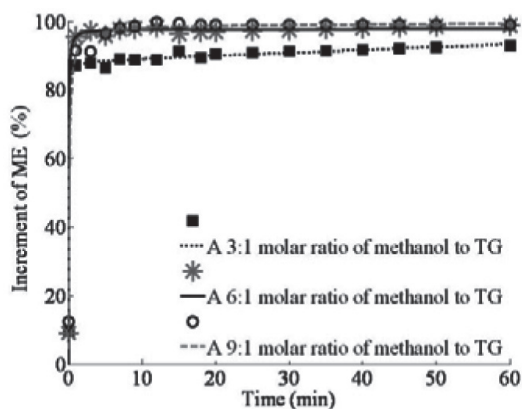
of methanol ratios on the ME conversion. The conditions of a methanol molar ratio of 3:1, 6:1 and 9:1 to the initial TG in the MCPO were investigated and were catalyzed by 0.6 %wt/v of NaOH based on the TG at 60 °C. The results, shown in Figure 6, indicate that 96.5 wt% of the ME was obtained rapidly when 6:1 and 9:1 molar ratios of methanol to the initial TG were used. Alternatively, with the methanol ratio based on an initial TG of 3:1, the ME conversion could be increased slightly but its concentration did not reach the required 96.5 wt% purity standard level within 1 hr.

Similar to the esterification reaction, it was found that the higher molar ratio of methanol to initial TG also had an influence on the transesterification reaction rate. In fact, it has been reported that biodiesel production cannot reach the biodiesel standard when the methanol ratio is used according to this stoichiometry (Ma and Hanna, 1998; Gerpen *et al.*, 2004). According to Le Châtelier's Principle (Brown *et al.*, 2003), a higher molar ratio is required in the reaction to drive the forward reaction to achieve the highest yield of the product.

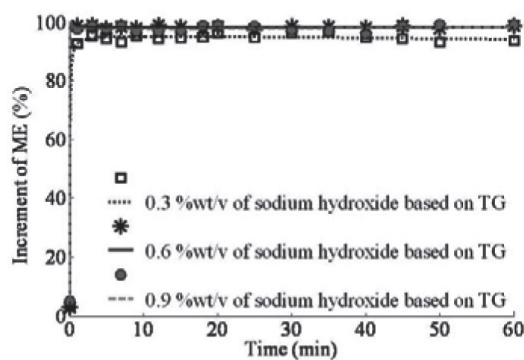
In addition, methanol could continuously evaporate during the reaction because the

reaction temperature was near the boiling point of methanol at ambient pressure. However, although no substantial differences were found among the methanol ratios (methanol:TG) of 6:1 and 9:1, a large amount of methanol interfered with the glycerol separation because of increasing solubility. This was one of the causes of lower ester yields. The remaining glycerol in the biodiesel can promote a reversible reaction. Therefore, a 6:1 molar ratio of methanol to the initial TG was determined to be used to produce biodiesel.

Subsequently, the effect of the amount of sodium hydroxide on the ME conversion was investigated under various sodium hydroxide levels of 0.3, 0.6 and 0.9 %wt/v based on the TG and a 6:1 molar ratio of methanol to the initial TG at 60 °C. The results (Figure 7) indicated that the concentration of ME to more than 96.5 wt% rapidly increased with an amount of sodium hydroxide of 0.6 and 0.9 %wt/v based on the initial TG. While the 0.3 %wt/v level of sodium hydroxide could be used to produce biodiesel, the concentration of ME did not reach 96.5 wt% because of the dilution of sodium hydroxide in the solution (the mixture between the de-acidified MCPO and methanol) in this process. In addition, although sulfuric acid was gravitationally separated out of the solution at the end of the first reaction, some sulfuric acid remained in the de-acidified MCPO.



**Figure 6** Effect of methanol molar ratio on methyl ester (ME) conversion. (TG = tryglyceride).



**Figure 7** Effect of sodium hydroxide on methyl ester (ME) conversion. (TG = tryglyceride).

During the transesterification reaction, if the amount of neutralizing sodium hydroxide (titration) was not sufficient in the acid-base reaction, some catalyst sodium hydroxide might be used. Therefore, the small amount of sodium hydroxide was not enough to be used as a catalyst in this process. The rates of the reaction were found to be approximately the same at the 0.6 and 0.9 %wt/v levels of sodium hydroxide based on the initial TG. Therefore, the smaller figure was used as the catalyst to produce biodiesel to achieve the concentration of 96.5 wt%.

The reaction temperature has a strong influence on the rate of the biodiesel production because the reaction was typically endothermic. When the temperature was increased, the final conversion also increased. Therefore, to drive the reaction to reach the requirement of ME purity immediately, the reaction should be conducted at a suitable reaction temperature. The conditions of a 6:1 molar ratio of methanol to the initial TG in the MCPO and 0.6 %wt/v of sodium hydroxide based on the TG in the MCPO were used to investigate various reaction temperatures of 55, 60 and 65 °C.

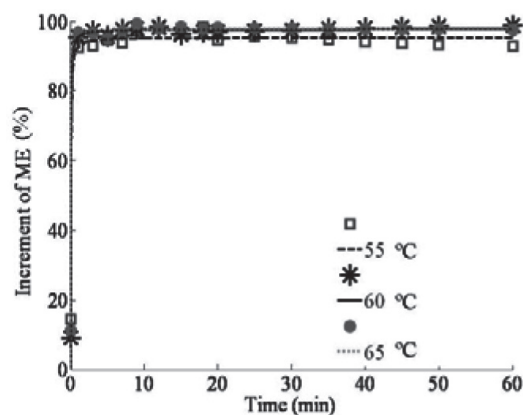
The results in Figure 8 show that when the reaction was allowed to continue for a long time, there were no substantial differences in the reaction times with variations in temperature of 55,

60 and 65 °C. It was found that 96.5 wt% of ME concentration was obtained within the first 5 min at 60 and 65 °C. Although, the reaction should be carried out close to the boiling point of methanol (64.8 °C) at atmospheric pressure, the results indicated that a reaction temperature of 60 °C was sufficient to produce biodiesel from de-acidified MCPO by transesterification.

### Reaction time

The two-stage process (esterification followed by transesterification) was used to produce biodiesel from MCPO having a high FFA content. The FFA in the MCPO was reduced to less than 1 wt% under the conditions of a 10:1 molar ratio of methanol to the FFA in the MCPO and 10 wt% of sulfuric acid based on the FFA in the MCPO at 60 °C. Then, the de-acidified MCPO was used as a raw material to produce biodiesel, having an ME concentration greater than 96.5 wt% under the conditions of a 6:1 molar ratio of methanol to the initial TG in the MCPO and 0.6 %wt/v of sodium hydroxide based on the initial TG in the MCPO. Both reactions satisfied the requirements at 60 °C.

The results, shown in Figures 2, 3, 4, 6, 7 and 8, indicate that the reaction reached 1 wt% of the FFA and 96.5 wt% of the ME in a reaction time of 30 sec and 5 min, respectively. However, the reaction should be allowed to continue for a longer time to protect against a reversible reaction (Noureddini and Zhu, 1997; Peters *et al.*, 2006). It was found that 20 min was a suitable time for esterification and transesterification. In the first-stage process, 20 min of the reaction time was used to convert the FFA in the MCPO into ME. After that, the solution was left for 2 hr to separate the solution into pre-treated MCPO and wasted solution. Then, the de-acidified oil was used to produce biodiesel by transesterification in the second-stage process with a reaction time of 20 min and then the solution was left for 45 min to separate into biodiesel and glycerol. After that, the crude biodiesel was cleaned after 8 hr by



**Figure 8** Effect of temperature on methyl ether (ME) conversion.



a spray-and-bubble technique. In conclusion, the total reaction time for producing biodiesel from the MCPO with a high free fatty acid content using this process was around 11 hr and 35 min.

It was found that the retention time of this process was less than Prateepchaikul's process (2007) because the de-gummed step before starting to reduce the FFA content had been eliminated. In fact, during the reduction of the FFA, sulfuric acid was used as a catalyst in esterification; in addition, it was a catalyst for removing gum that was contained in the MCPO. Moreover, the reaction in this study reached the required level very quickly even though a small amount of

reagent was used because the reaction had plenty of mixing intensity; therefore, the reagent was promoted to mix well.

### Properties of biodiesel production from MCPO

The properties of biodiesel produced from un-degummed and de-acidified MCPO (with a yield of 95 v% based on the MCPO), which was carried out by the two-stage process under suitable conditions, were compared with other biodiesel standards as shown in Table 1. It was found that the biodiesel produced succeeded in meeting the requirements for a biodiesel standard.

**Table 1** Properties of methyl ester from mixed crude palm oil (MCPO).

Parameter	CPOME*	Biodiesel standard				
		Austria (ON)	Germany (DIN)	Italy (UNI)	Thailand (ASTM and EN)	USA (ASTM)
Methyl ester (wt%)	98.75	-	-	≥ 98	≥ 96.5	-
Density at 15 °C (kg.m <sup>-3</sup> )	878.7	850–890	875–890	860–900	860–900	-
Viscosity at 40 °C (cSt)	4.28	3.5–5.0	3.5–5.0	3.5–5.0	1.9–8	1.9–6.0
Flash point (°C)	167	≥ 100	≥ 110	≥ 100	≥ 120	≥ 130
Sulfur (%wt)	0.0004	≤ 0.02	≤ 0.01	≤ 0.01	≤ 0.0015	-
Sulfated Ash (%wt)	0.0050	-	-	-	≤ 0.02	-
Water and Sediment (%vol)	<0.05	-	≤ 0.03	≤ 0.07	≤ 0.2	-
Copper Strip Corrosion	Number 1	-	Number 1	-	≤ Number 3	-
Acid Value (mg KOH.g <sup>-1</sup> )	0.25	≤ 0.80	≤ 0.50	≤ 0.50	≤ 0.80	≤ 0.80
Free Glycerin (%wt)	Na	≤ 0.02	≤ 0.02	≤ 0.05	≤ 0.02	≤ 0.02
References		(Meher <i>et al.</i> , 2006; Prateepchaikul <i>et al.</i> , 2007)	(Meher <i>et al.</i> , 2006; Prateepchaikul <i>et al.</i> , 2007)	(Meher <i>et al.</i> , 2006; Prateepchaikul <i>et al.</i> , 2007)	(Department of Energy Business, 2006 )	(Meher <i>et al.</i> , 2006)

\*CPOME = Mixed Crude Palm Oil Methyl Ester.

## CONCLUSION

The suitable conditions for producing biodiesel having more than 96.5 wt% purity in ME content and a 95% yield of biodiesel based on the initial MCPO by the two-stage process involved 0.8 wt% of sulfuric acid, 0.5 %wt/v of sodium hydroxide and a 7.5:1 molar ratio of all methanol based on the initial MCPO and at 60 °C, required 11 hr and 35 min.

## ACKNOWLEDGEMENTS

The authors would like to thank the National Research University Project of Thailand's Office of the Higher Education Commission for financial support.

## LITERATURE CITED

- Brown, T.L., E.H. LeMay and J.R. Burdge. 2003. **Chemistry: The Central Science**. 9th ed. Prentice Hall. New Jersey. 1046 pp.
- Cannakci, M. and J.V. Gerpan. 2001. Biodiesel production from oils and fats with high free fatty acids. **Transaction of ASAE**. 44 (6):1429–1436.
- Crabbe, E., C. Nalasco-Hipolito, G. Kobayashi, K. Sonomoto and A. Ishizaki. 2001. Biodiesel production from crude palm oil and evaluation of butanol extraction and fuel properties. **Process Biochemistry** 37 (1): 65–71.
- Department of Energy Business. 2006. **Methyl Ester Quality for Agricultural Engines in Thailand**. [Available from: <http://www.doeb.go.th>]. [Cited: June 9, 2011].
- Gerpen, J.V., B. Shanks, R. Pruszek, D. Clements and G. Knothe. 2004. **Subcontractor Report: Biodiesel production technology**. NREL. USA. 110pp.
- Ghadge, S.V. and H. Raheman. 2005. Biodiesel production from mahua (*Madhuca indica*) oil having high free fatty acids. **Biomass and Bioenergy** 28: 601–605.
- Jansri, S. and G. Prateepchaikul. 2011. Comparison of biodiesel production from high free fatty acid crude coconut oil via saponification followed by transesterification or a two-stage process. **Kasetsart J. (Nat. Sci.)** 45 (1): 110–119.
- Jansri, S., G. Prateepchaikul and S.B. Ratanawilai. 2007. Acid-catalyzed esterification: A technique for reducing high free fatty acid in mixed crude palm oil. **Kasetsart J. (Nat. Sci.)** 41 (3): 555–560.
- Kac, A., 2001. **The FOOLPROOF Way to Make Biodiesel**. [Available from: <http://journeytoforever.org>]. [Cited: June 20, 2011].
- Link, W.E. 1989. **Method Ca 5a-40: Sampling and Analysis of Commercial Fats and Oils**. 4th ed. A.O.C.S. Official. Urbana. USA.
- Ma, F. and H.A. Hanna. 1998. Biodiesel production: A review. **Bioresource Tech.** 70: 1–15.
- Marchetti, J.M., V.U. Miguel and A.F. Errazu. 2005. Possible methods for biodiesel production. **Renewable and Sustainable Energy Reviews** 11 (6): 1300–1311.
- May, C.Y. 2004. Transesterification of palm oil: Effect of reaction parameters. **Journal of Oil Palm Research** 16 (2): 1–11.
- Meher, L.C., S.D. Vidya and S.N. Naik. 2006. Technical aspects of biodiesel production by transesterification – a review. **Renewable and Sustainable Energy Reviews** 10 (3): 248–268.
- Noureddini, H. and D. Zhu. 1997. Kinetics of transesterification of soybean oil. **JAOC** 74 (11): 1457–1461.
- Peters, T.A., N.E. Benes, A. Holmen and J.T.F. Keurentjes. 2006. Comparison of commercial solid acid catalysts for the esterification of acetic acid with butanol. **Appl. Cat. A: Gen.** 297: 182–188.
- Prateepchaikul, G., M.L. Allen, T. Leevijit and K. Thaveesinsopha. 2007. Methyl ester

- production from high free fatty acid mixed crude palm oil. **Songklanakarín J.Sci. Technol.** 29 (6):1551–1561.
- Ramadhass, A.S., S. Jayaraj and C. Muraleedharan. 2004. Biodiesel production from high FFA rubber seed oil. **Fuel** 84 (4): 335–340.
- Sherma, J. 2000. Planar Chromatography. **Analytical Chemistry** 72 (12): 9R–25R.
- Thai Industrial Standards Institute. 1980. Standard for Crude Glycerine: BS 2621-5: 1964 (specification for glycerol (glycerine) in Thailand) (in Thai). pp. 7–11.
- Tiwari, A.K., A. Kumar and H. Raheman. 2007. Biodiesel production from jatropha oil (*Jatropha curcas*) with high free fatty acids: An optimized process. **Biomass and Bioenergy** 31: 569–575.
- Veljković, V.B., S.H. Lakićević, O.S. Stamenković, Z.B. Todorović and M.L. Lazić. 2006. Biodiesel production from tobacco (*Nicotiana tabacum* L.) seed oil with a high content of free fatty acids. **Fuel** 85 (17-18): 2671–2675.