



Chiang Mai J. Sci. 2008; 35(1) : 23-28

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Contributed Paper

# Production Methyl Esters from Palm Fatty Acids in Supercritical Methanol

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Received : 27 September 2007

Accepted : 17 October 2007

## ABSTRACT

This study investigated the biodiesel production via a noncatalytic esterification reaction in supercritical methanol. The palm oil fatty acids were chosen as the raw material because of its availability as a low cost byproduct of palm oil industry. The variables affecting the methyl ester (biodiesel) conversion were investigated, which included molar ratio of fatty acids and methanol (1:1 to 1:12), reaction temperature (250 to 300°C) and reaction time (from 10 to 80 min). The results from this study showed that esterification of palm oil fatty acids in supercritical methanol gave the high conversion of 94 % and was obtained at the fatty acids/methanol molar ratio of 1:6 and at 300°C after 30 min. Furthermore, water whose content in fatty acid between 0-30 %v/v was found to lower the yield of methyl ester by hydrolyzing methyl ester back to fatty acids, and the degree of hydrolysis increased as water content and reaction time increased. When compared the result of methyl ester yield obtained from methyl esterification of fatty acids with methyl transesterification of purified oil, it was found that the esterification of palm fatty acids requires lower operating conditions (molar ratio 1:6 versus 1:45 and time 30 min versus 50 min, respectively). When compared with conventional acid catalyzed process, supercritical methyl esterification of fatty acids required shorter reaction time (30 min versus 9 hr) and no neutralization process was needed. This suggests that palm fatty acids offer high potentials as more economical raw material for production of biodiesel.

**Keywords:** Biodiesel, Fatty acid, Supercritical, Esterification, Transesterification.

## 1. INTRODUCTION

The decrease of world petroleum reserves and the atmospheric pollution caused by petroleum based-fuels has necessitated the need for an alternative source of energy. Biodiesel, an alternative fuel, presents a suitable renewable substitute for petroleum base-fuel. This fuel is biodegradable and non-toxic

compared to petroleum diesel. It is usually produced by the transesterification of vegetable oil or animal fat with short chain alcohol. Biodiesel production by transesterification can be carried out either by catalytic or non catalytic means. The reaction is commonly carried out in the presence of

homogeneous base or acid catalysts. Alkali process is very sensitive to the purity of reactants, the presence of minor amount of free fatty acid (FFA) and moisture in the reaction mixture produces soap [1]. Acid catalyzed process does not produce soap, however it requires a long time for the reaction to complete. A two-step transesterification process in which acid catalyzed transesterification is followed by alkali catalyzed reaction has been developed to improve the yield of biodiesel production from oil with high FFA content [2]. Although the reaction time could be reduced, no recovery of catalyst and high cost of reaction equipment were still the main disadvantages of this process.

In the homogeneous transesterification with liquid catalysts, recovery of the catalyst was not possible. Heterogeneous catalyst can therefore be used, nevertheless, there still appear to be some problems with this technique and finding a suitable catalyst that is active, selective, and stable under the specified process conditions is the major challenge [3]. Alternatively, transesterification using enzyme catalyst such as lipase can also convert oils and fats into methyl esters [4]. Although the method is more environmentally friendly, the high cost of enzymes makes the process unattractive for industrial scale.

Other than the catalytic transesterification, Saka and Kusdiana (2001) proposed a method of biodiesel production via non-catalytic transesterification of vegetable oils in supercritical methanol [5, 6]. Compared with the catalytic processes, the reaction was found to be complete in a very short time and purification of the product is much simpler and more environmentally friendly. However, the reaction requires high temperatures of 350–400 °C and high pressures of 45–65 MPa, thus resulting in high production cost.

One approach to bring down the cost of production would be the use of inexpen-

sive raw material. In Thailand, palm oil is the most suitable for production of biodiesel in large scale due to its availability. Purified palm oil however is too expensive (0.74 USD per liter) to be economically feasible. Palm fatty acid (0.37 USD per liter), a by-product of palm oil refinery, on the other hand, is one of the most attractive raw materials due to its low cost. Furthermore, it is generally obtained in a purified form during the refining process of crude oil. Therefore palm fatty acid is a potential raw material for the production of biodiesel. This study was carried out to investigate the effect of operating conditions and effect of water on yield of methyl ester produced by supercritical methyl esterification of palm fatty acids.

## 2. MATERIALS AND METHODS

### 2.1 Chemicals

Palm fatty acid sample used in this study was given by Burapha Munkong Company (Saraburi, Thailand). Methyl ester standard (methyl palmitate, methyl Stearate and methyl oleate) were obtained from Wako Chemicals, USA. Methanol and hexane (analytical grade) was from Fisher scientific, UK.

### 2.2 Supercritical methanol esterification reaction

A batch type reactor was used for production of biodiesel from palm fatty acid in supercritical methanol. A 8.8 ml stainless steel reactor (AKICO, Japan) was charged with a calculated amount of liquid methanol and palm fatty acid with a molar ratio of 1:1 to 1:12. The reaction vessel was heated with a heater to the desired reaction temperature (250 °C - 300 °C), after which the reaction continued for a set time period (from 10 – 80 min). After each reaction, the vessel was removed from the heater and placed into a water bath to quench the reaction. The reaction products were discharged from the reactor and were

allowed to settle and separated into three phases. The top phase was the unreacted methanol which was removed by evaporation. The remaining phases consisting of the upper phase and the lower phase were methyl ester (biodiesel) and water, respectively. Analysis of methyl ester in products was carried out by using a gas chromatograph (GC).

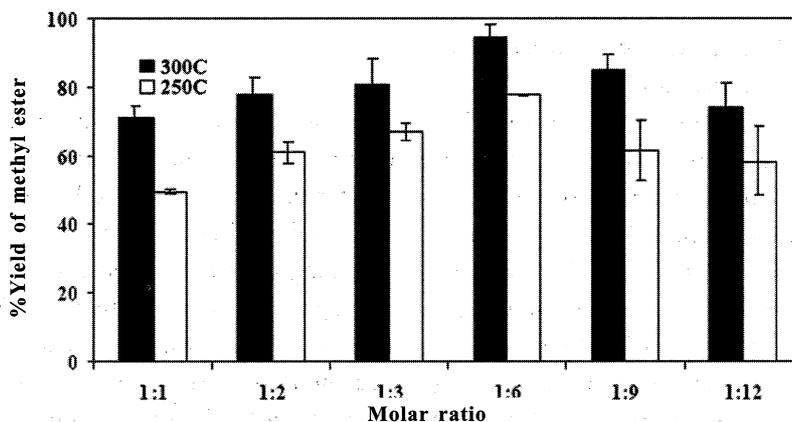
### 2.3 Methyl ester analysis

The amount of methyl ester in the reaction products were analysed by GC (Shimadzu 14B). The system consisted of a column (Rtx 5, 30m, 0.25 mm ID, 0.25 mm) and flame ionization detector (FID). Samples were prepared by adding 0.1 ml of oil to 6 ml of n-hexane using eicosane as an internal standard. For each GC analysis, two micro liters of the sample were injected into the column. The temperature program for the GC oven starts with the temperature of 150 °C and the holding time of 2 min, followed by an increase in temperature with the ramp rate of 5 °C/min to the final temperature of 250 °C with the holding time of 5 min.

## 3. RESULTS AND DISCUSSION

### 3.1 Effect of molar ratio of palm fatty acids to methanol

In this work, the effect of molar ratio of palm fatty acids to methanol on percent yield of methyl ester was determined for the range of molar ratio between 1:1 and 1:12 at the reaction temperature of 250 and 300 °C. The results on the percent yields shown in Figure 1 were obtained after the reaction was carried out for 30 min. The results showed that when molar ratio increased (between 1:1 and 1:6), the yield of methyl ester increased. The increase in yield with the increase in the amount of methanol is due to the fact that the larger numbers of molecules of methanol resulted in the greater opportunity to interact with the molecules of palm fatty acids. Furthermore, the critical temperature of the reactant mixture decreased with increasing amount of methanol. However, the yields of methyl ester for the molar ratio of 1:9 and 1:12 were found to be lower. This result could be attributed to the high water content in the reactants as the high percentage of the analytical grade methanol (95 %) was used. Water would react readily with methyl ester under subcritical water condition, thus lowering the overall yield. The most suitable molar ratio was found at 1:6, in which the maximum yield of methyl ester was 74 and 94 % at 250 °C and 300 °C respectively.

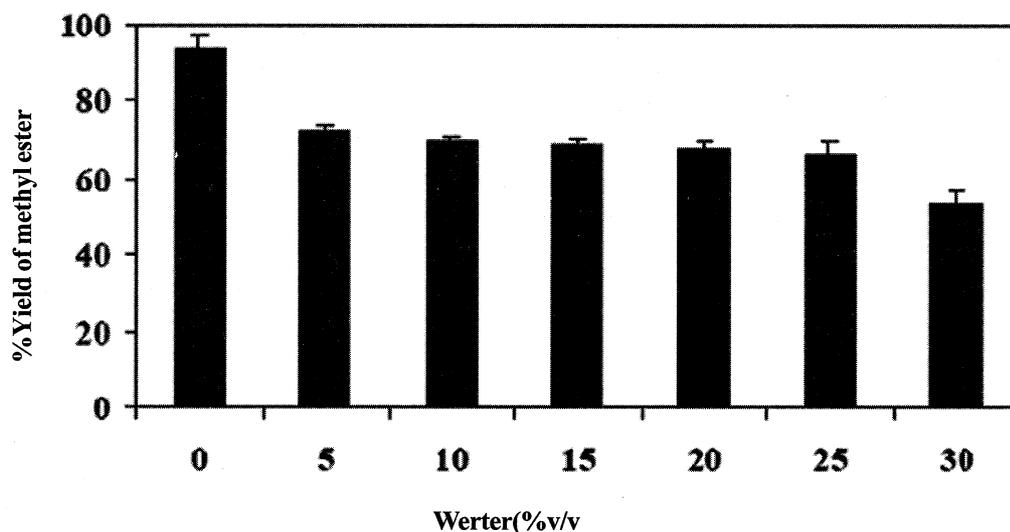


**Figure 1.** Effects of molar ratios on methyl esterification of palm fatty acids at 250 and 300 °C, reaction time 30 minutes.

### 3.2 Effect of water content in fatty acid on yield of methyl ester

In this study, the effect of the presence of water between 0-30% v/v water to palm fatty acids on the supercritical methyl esterification was determined. The study was carried out at the reaction temperature 300 °C for 30 min. The result in Figure 2 shows that the presence of water indeed lowered the percent yield of methyl ester. Water

between 5-25 vol% of water to palm fatty acids lowered the yield of methyl ester by nearly 22-28 %, while for 30 vol% of water to fatty acid, the yield dramatically decreased to 42%. The decrease in methyl ester yield could be the result of lower methanol concentration with increased water content. Moreover, water might react with methyl ester by hydrolysis reaction which converted biodiesel back to fatty acids and methanol.

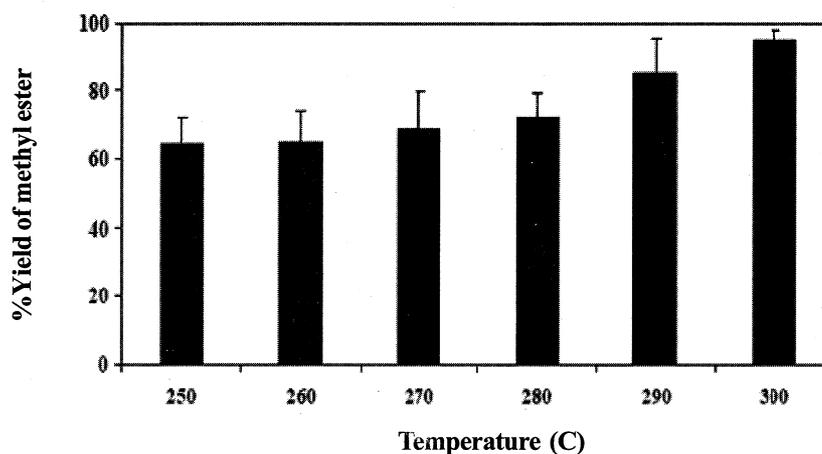


**Figure 2.** Effect of water on percent yield of methyl ester of palm fatty acids at 300 °C, 30 minutes.

### 3.3 Effect of reaction temperature on methyl ester production

To determine the effect of reaction temperature, the reactions of palm fatty acids and methanol with the molar ratio of 1:6 were carried out at 250 to 300 °C for 30 minutes. The result is shown in Figure 3. It can be seen from this result that at the temperature between 250-280 °C, the yield of methyl ester slightly increased with temperature, while at the reaction temperature of 290 °C and higher, the increase in the yield was more pronounced. Generally, the increase in tem-

perature causes the polarity of methanol to decrease, as a result of the breakdown of the hydrogen bonding of methanol, leading to increased solubility of fatty acids in methanol. The complete solubility occurs as the temperature approaches the mixture critical temperature, at which point the reaction mixture became homogeneous and the reaction took place rapidly. At higher temperature, the percent yield increased further to 94 %, which was obtained at 300 °C.

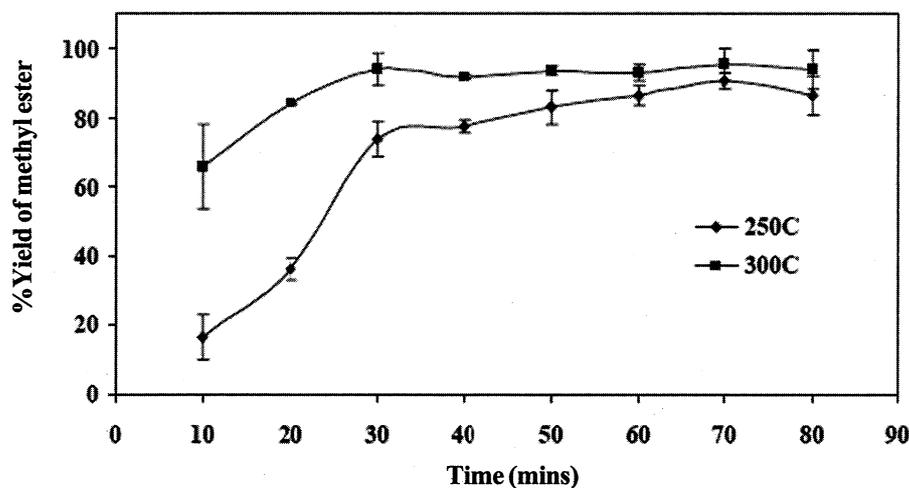


**Figure 3.** Effect of temperature on methyl esterification of palm fatty acids at 250-300 °C, reaction time 30 minutes and molar ratio of fatty acid to methanol of 1:6.

### 3.4 Effect of reaction time on methyl ester production

The effect of reaction time between 10-80 minutes was determined for esterification of FFA at the ratio of palm fatty acids to methanol of 1:6 at 250 and 300 °C. As shown in Figure 4, the results indicated that at the high temperature of 300 °C, the percent yield of methyl ester increased dramatically in the first 30 min and then remained constant. At 300 °C, the most suitable reaction time was

therefore 30 min which resulted in the yield of 94% methyl ester. At 250 °C, the percent yield of methyl ester also increased greatly during in the first 30 minutes and increased quite slowly afterwards. At 250 °C, the reaction time required to reach the maximum yield of methyl ester of 92% was 70 min. From these results, it can be seen that at the temperature of 250 °C, longer reaction time was required than at 300 °C.



**Figure 4.** Effect of reaction time on methyl esterification of palm fatty acids at 250 and 300 °C, reaction time 30 minutes and molar ratio of fatty acid to methanol of 1:6.

#### 4. CONCLUSIONS

The production of biodiesel from palm fatty acids by supercritical methanol esterification reaction is a feasible process. The most suitable conditions are 300 °C, 30 min and molar ratio of palm fatty acids to methanol of 1:6, which result in the yield of methyl ester yield of 94 %. Water has an effect on the methyl ester yield as it hydrolyzed methyl ester back to fatty acid, and the decrease in the yield increased with water content.

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