CHAPTER IV

RESULTS AND DISCUSSION

This chapter presents the results of esterification of palm fatty acids in supercritical methanol in the absence of catalyst. Firstly, the effects of different operating conditions such as temperature (250-300 °C), molar ratio between palm fatty acids and methanol (1:1-1:2), and reaction time (10-80 minutes) on methyl ester yield was determined. Then the results on the effect of water content in fatty acid (0 - 30 vol %) on the methyl ester yield were presented. In addition, the effect of percentage of water (0-30 vol %) and reaction time (0-30 min) on methyl ester hydrolysis was determined, which demonstrated the importance of hydrolysis in biodiesel production. Lastly, the results of supercritical methyl esterification of palm fatty acid were compared with those of supercritical tranesterification of purified palm oil and that of esterification of fatty acid with conventional acid catalyzed process.

4.1 Supercritical esterification in batch reactor

4.1.1 Effect of reaction temperature on methyl ester production

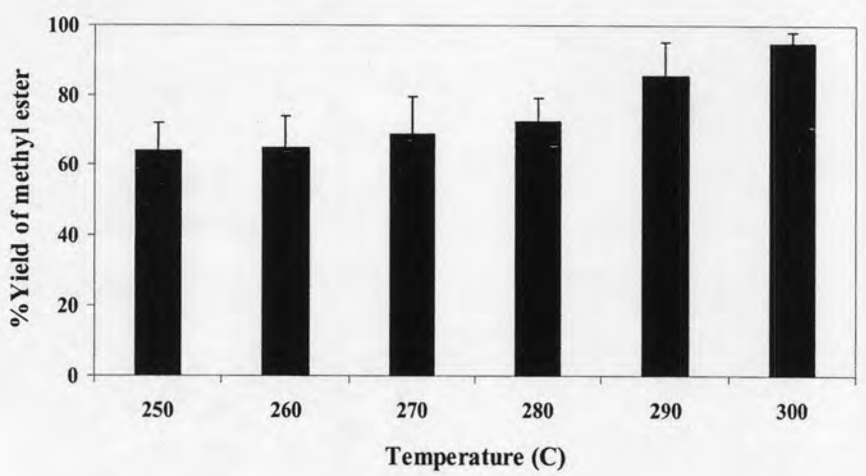

Figure 4.1 Effect of temperature on methyl esterification of palm fatty acids at 240-300 °C, reaction time 30 minutes and molar ratio of fatty acid to methanol of 1:6.

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 4.1. Note that the temperatures specified in Figure 4.1 were measured at the furnace adjacent to the reactor vessel but not at the center of the reaction vessel. It can be seen from this result that the temperature between 250-280 °C, the percent yield of methyl ester only 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 temperature 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. Specifically from the result, the sharp increase in the product yield was observed around the mixture critical temperature, which could be calculated for the molar ratio of fatty acid to methanol of 1:6, to be 282 °C*. This was the actual reaction temperature at the center of the vessel when the system temperature T_1 was set to 290 °C. At higher temperature, the percent yield increased further to 94 %, which was obtained at 300 °C.

4.1.2 Effect of molar ratio of palm fatty acids to methanol

The molar ratio of alcohol to raw material (oil, palm fatty acid) is one of the most important factors that control the cost of operation. 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 percent yields for the results shown in the figure 4.2 were obtained after the reaction was carried out for 30 min.

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* Using Lydersen's method of group contribution with application of Lorentz-Berthelot-type mixing rules (Bunyakiat et.,al, 2006). See appendix C for detailed sample calculation.

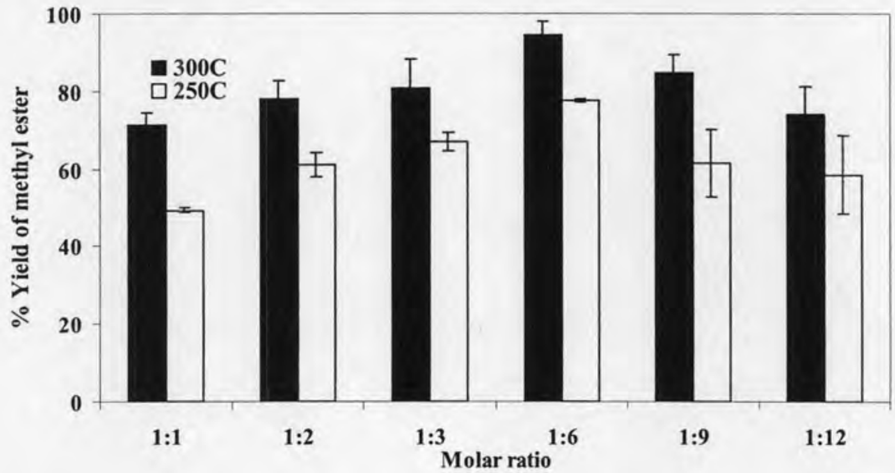


Figure 4.2 Effects of molar ratios on methyl esterification of palm fatty acids at250 and 300 °C, reaction time 30 minutes.

At the reaction temperature of 250 and 300 °C, the percent yield of methyl ester increased as the molar ratio of methanol increased from 1:1 to 1:6. The increase in percentage yield with the increase in the amount of methanol is due to the fact that the larger numbers of molecules of methanol have greater opportunity to interact with the molecules of palm fatty acids. Furthermore, the critical temperature of the reactant mixture decreases with increasing amount of methanol. The mixture critical temperatures were summarized in Table 4.1. Based on this information, the system temperature of 300 °C is below the critical temperature of the reactant mixture whose ratio of methanol is below 1:6 and exceeded the mixture critical temperatures for all reactions with molar ratio of methanol of 1:6 or higher. It is expected therefore that the percent methyl ester would increase with increasing methanol ratio. 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 lower the overall yield. The most suitable molar ratio was found at 1:6, in which the maximum yield of methyl ester was 74 and 95 % at 250 °C and 300 °C respectively.

It should also be noted that at 250 °C, the effect of molar ratio was similar to that at 300 °C in that the maximum yield was obtained at 1:6. However, the percent yield of methyl ester were about 20-30 % lower than that at the reaction temperature of 300°C for all the molar ratios. This was because the temperature of 250 °C (or 242 °C at the center reaction vessel) was below the mixture critical temperatures for all ratios of methanol.

Table 4.1 The critical properties of fatty acids from palm fatty acid and methanol at various compositions

Molar ratio	T_c (K)	T_c (°C)	P_c (atm)	V_c (L/mol)	Z_c
1:1	606.48	333.48	24.24	0.48	0.23
1:2	587.18	314.18	32.34	0.35	0.23
1:3	575.02	302.02	38.36	0.28	0.23
1:6	555.17	282.17	49.66	0.21	0.22
1:9	545.12	272.12	55.98	0.18	0.22
1:12	538.96	265.96	60.01	0.16	0.22
1:48	520.73	247.73	72.43	0.13	0.22

4.1.3 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 FFA:methanol of 1:6 at 250 and 300 °C. As shown in Figure 4.3, the results indicated that at the high temperature of 300 °C, the percent conversion 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 conversion 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 conversion of methyl ester of 92% was 70 min.

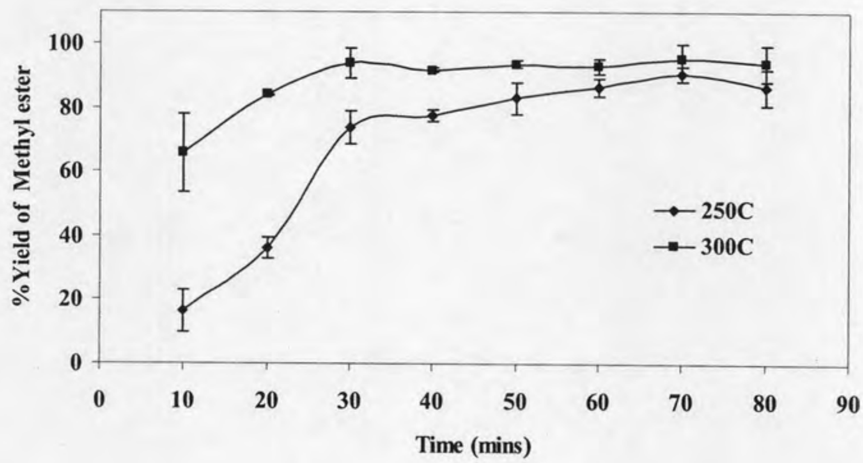


Figure 4.3 Effect of reaction time on methyl esterification of palm fatty acids at 250 and 300 °C, reaction time 30 minutes and molar ratio of fatty acid to methanol of 1:6.

From these results, it can be seen that at lower temperature of 250 °C, longer reaction time was required than at 300 °C. Note again that the temperature here is the set temperature measured at the furnace, not the reaction temperature. The system employed in this study required the heating time of about 15 min for the reaction temperature at the center of the vessel to reach the steady temperature, which is usually 8 °C below the set point temperature controlled at the furnace. This implied that the actual reaction time to obtain the desired yield should be shorter if preheating of the reactants and the reaction vessels was provided. More efficient preheating might be achieved with use of continuous process with preheating of the reactants, the operation which is recommended for the future study.

4.2 Effect of water on yield of methyl esterification product

4.2.1. Effect of water content in fatty acid on yield of methyl ester

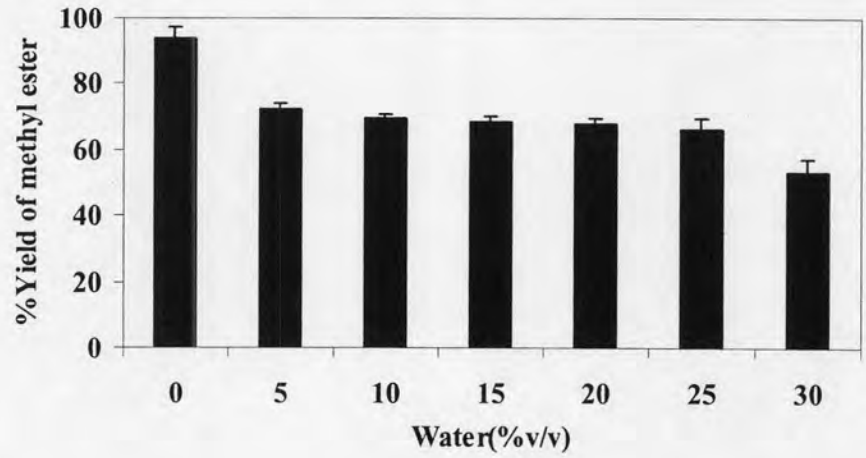
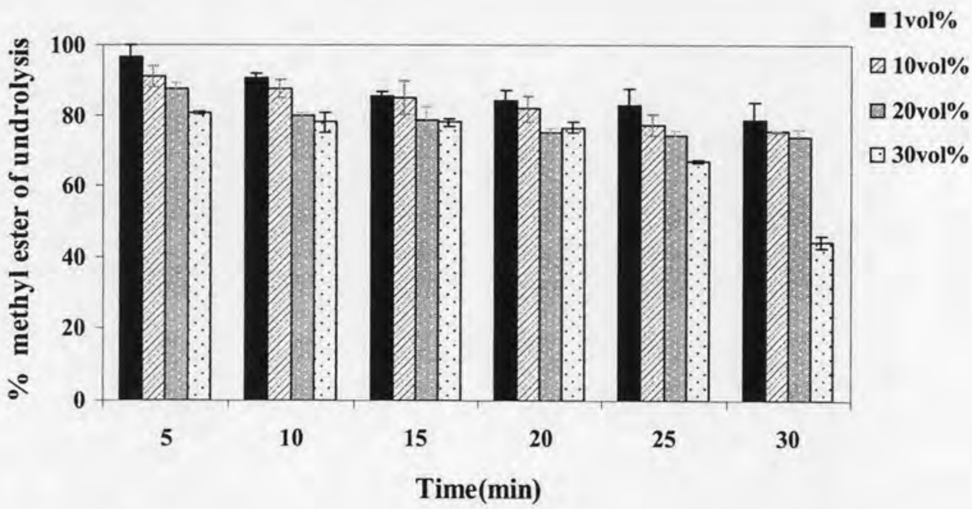


Figure 4.4 Effect water on percent yield of methyl ester at 300 ◦ C, 30 minutes.

In biodiesel production with alkali and acid catalysts, it is well known that the vegetable oil used as raw material for transesterification should be water-free since the presence of water has negative effects on the reaction as water interferes with the catalyst and reduces catalyst efficiency (Komer et al., 2001). For the alkaline catalyzed method, the conversion was slightly reduced when more water was added. In acids catalyst method, only as little as 0.1% of water added to the reaction mixture could lead to the reduction of the yield by 6% (Canaki and Gerven 1999). This however was not found to be the case for supercritical methyl transesterification. Kusdiana and Saka (2001) demonstrated that in the presence of water up to 30% w/w, triglycerides can be successfully transesterified to methyl ester in the supercritical methanol method with very minimal loss in conversion. Although esterification of FA in this study was conducted also in supercritical state, the difference in the raw materials (FA vs. triglycerides) as well as the differences in the reaction systems employed in this study compared with Kusdiana and Saka (2001) may give different results. In this study, the effect of the presence of water between 0-30% v/v water to FA 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 4.5 shows that the presence of water indeed lowered the percent yield of methyl ester. Water between 5-25 vol% of water to fatty acid lower the yield of methyl ester by nearly 22-28 %, while 30 vol% of water to fatty acid, the yield dramatically decreased to 42% .The decrease in methyl ester yield could be a results 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. This result agreed with previous study by Kusdiana and Saka (2004) which reported approximately 2-5% reduction in conversion of oleic acid to methyl oleate in the presence of water. Their study was conducted for the reaction with the molar ratio of 1:42 (oleic acid: methanol) at 350 °C with water contents between 0-30% for 4 min, the conditions that were different from those used in this study. Nevertheless, the same trend was observed in which the conversion of fatty acids to methyl oleate was somewhat reduced when the water content was increased. In this study, much higher reduction in methyl ester are attributed to the prolong reaction time employed. These results would therefore suggested that, in order to maximize the yield of methyl esterification product of fatty acid, care must be taken to remove water from the reaction mixtures and to prevent extended reaction time.

4.2.2 Hydrolysis of methyl ester



The Figure 4.5 Effect of various water on hydrolysis methyl ester for various reaction time 30 minutes at 300 ° C

From the result in the previous section, water was found to reduce the methyl ester yields and that its effect increases with water content and reaction time. Although the reasons for this decrease has not been fully elucidated, one of the possible reasons was believed to be a result of hydrolysis reaction, in which methyl ester produced was hydrolyzed and converted back to fatty acid and methanol. Therefore, in order to understand the effect of hydrolysis on the methyl ester yield, experiments were conducted to determine the effect of water content between 0-30% (v/v) and the hydrolysis time 0-30 minutes on the amount of methyl ester hydrolyzed. Figure 4.6 shows the result of the amount of methyl ester remained unhydrolyzed. From this figure, the degree of hydrolysis increased with the increased amount of water as higher amount of water have greater opportunity to attack the molecules of methyl ester. Furthermore, as the reaction time increased, hydrolysis of methyl ester increased. For 30 min reaction of methyl ester with 30% water, 46% of the methyl ester was unhydrolyzed. This result confirmed the importance of hydrolysis in the methyl ester production. At high temperature 300 °C, water is considered to be in subcritical state (the temperature is between boiling point temperature and critical temperature). At this condition, water has high ion product (Kw), which means that water readily dissociate into hydronium and hydroxide ions. The increased in these ions would play an important role in hydrolysis which breaks up the large methyl ester back to fatty acid.

4.2.3 Hydrolysis of methyl ester in presence of methanol

The result in the previous section demonstrated the significance effect of hydrolysis in the reduction of methyl ester production in presence of water. Nevertheless, the hydrolysis reaction conducted in the previous section was carried out in the absence of methanol. In the actual methyl esterification system however, excess methanol was used and the methanol content remained in the reaction mixture was significant. Thus, in order to examine the effect of hydrolysis in the system that has greater resemblance to the actual process, in this section, the hydrolysis was carried out in the presence of methanol. The reactions were conducted at 300 °C for 30 min. The amount of methyl ester, methanol, and water used in the hydrolysis reaction in this set of experiments was calculated from what would be the ratio of the final mixtures obtained after the esterification was completed. For example, for methyl esterification at 1:6 molar ratio, the final products would consist of 1 mol of methyl ester, 1 mole of water, and 5 mol of the remaining methanol, given a 100% conversion. For this ratio, the molar ratio of the reactants for the hydrolysis reaction be 1:5:1 for methyl ester: methanol: water. For methyl esterification at 1:9 molar ratio, the ratio of the reactants for hydrolysis reaction would be 1:8:1. These two ratios were chosen for the hydrolysis study here. The first was the molar ratio that yielded the highest amount of methyl ester, and the second was chosen to determine the effect of higher percentage methanol present on the methyl ester yield. The percent of methyl ester remained unhydrolyzed for these two conditions are summarized in Table 4.2. For the molar ratio of 1:5:1, 8% of methyl ester was hydrolyzed by water in the presence of methanol. Hydrolysis of methyl ester without the presence of methanol found in the previous section (section 4.3.2) was much higher (20% methyl ester hydrolyzed at 30 min with 1% water). This result shows that the presence of methanol lower the degree of hydrolysis as water concentration would be lower. However, if the ratio of methanol further was increased as in 1:8:1, one would expect smaller effect of hydrolysis, and thus higher methyl ester should remain unhydrolyzed compared with 1:5:1. On the other hand, larger amount of methyl ester was hydrolyzed (only 88% of methyl ester remained). These results actually agreed with the previous results in which the yield of methyl ester was found to be smaller at the FA to methanol molar ratio of 1:9 (84%), compared with 1:6 (94%).This again could be explained by the fact that the methanol used in the experiment was commercial grade and has only 95% purity. The presence of water in the starting methanol could be responsible for the reduction in the methyl ester yields observed.

Table 4.2 The reproduce esterification for methyl ester product.

Molar ratio	**% Methyl ester**
1:5:1	92.55
1:8:1	88.44

4.3 Comparison of supercritical methyl esterification with supercritical transesterification and conventional acid catalyzed process

4.3.1Comparison with supercritical tranesterification

The biodiesel production by supercritical methyl esterification reaction of fatty acids was compared with that by transesterification of palm oil in supercritical methanol. The bar graph in Figure 4.8 is the percent methyl ester obtained from transesterification of purified palm oil at various molar ratios of oil and methanol between 1:6 and 1:45. The experiment was conducted at 2 temperatures at 250 and 300 °C and the percent conversion shown here was obtained after 50 min. From the figure 4.6, it could be seen that the highest molar ratio of methanol of 1:45 resulted in the highest yield of 80 % for transesterification of purified palm oil.

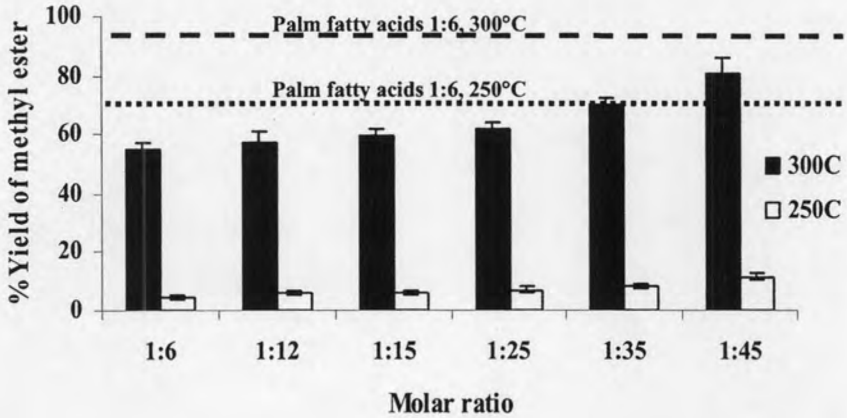


Figure 4.6 Effect of the molar ratios of methanol to palm oil on the percent conversion of methyl ester at 250 and 300 °C

Compared transesterification with purified palm oil, esterification, shown for the reactions at 250 and 300 °C with the molar ratio of fatty acid to oil of 1:6 gave higher yields as shown by the dashed and dotted lines in the figure. The results here demonstrated that the smaller amount of methanol was required for the biodiesel production from fatty acids. Specifically, one could compare the amount of the methanol required to produce 100 g of biodiesel by methyl esterification and transesterification of purified palm oil could be compared, and the results are summarized in Table 4.3. In order to produce 100 grams of biodiesel at 300°C, supercritical esterification of palm fatty acids requires only 75 grams, while supercritical transesterification of purified palm oil requires as high as 198 grams of methanol.

Table 4.3 Comparisons of the quantity of methanol required to produce biodiesel.

Reaction	Methanol(g)	Biodiesel(g)
Esterification	75	100
Transesterification	198	100

Considering the transesterification at 250 °C (50 min), the yield was much lower than that obtained with esterification of fatty acid at the same temperature. Transesterification at 250 C gave less than 15% methyl ester yield in 50 min, whereas the yield of esterification of palm fatty acids at 250 °C for 30 minutes and molar ratio 1:6 was as high as 74% biodiesel. It can therefore be concluded from these results that the production of biodiesel from fatty acids requires milder reaction conditions and shorter period of time than transesterification of palm oil.

4.3.2 Comparison with acid catalyzed esterification

Production of biodiesel from FFA could also be performed conventionally with acid catalyzed transesterification. The reaction was carried out with (%) sulfuric acids at the molar ratio 1:6 for the reaction time 30 minutes at reaction temperature 67 °C. The result is shown in Table 4.4, which shows that only 75 % methyl ester yield was obtained in 5 hrs. In order to produce methyl ester up to 90 %, long reaction as long 9 hrs was required.

Table 4.4 Effect of reaction time on methyl ester produced by acid catalyzed esterification of palm fatty acids.

Time (Hrs)	% Yield
5	75
9	90