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APPENDICES

APPENDIX A

EXPERIMENTAL DATA FOR ANALYSIS

A-1 Experimental data of catalytic transesterification reaction of purified palm oil and catalytic esterification reaction of palm fatty acid in batch reactor

Table A-1.1 The present of methyl ester at molar ratio of methanol to purified palm oil of 42:1, molar ratio of methanol to palm fatty acid of 6:1, at a temperature 290 °C, mass ratio of SO_4^{2-}/ZrO_2 catalysts (SZ1) to purified palm oil and palm fatty acid were varied within the range of 0-1 % for reaction time 10 minutes

mass ratio	% yield	
	purified palm oil	palm fatty acid
non-cat	29.3	61.04
0.25%cat	68.48	75.59
0.5%cat	79.415	77.72
0.75%cat	73.92	75.67
1%cat	74.94	69.66

Table A-1.2 The present of methyl ester at the various temperature between 200-300 °C, methanol:purified palm oil molar ratio of 42:1, methanol:palm fatty acid molar ratio of 6:1 and SO_4^{2-}/ZrO_2 catalysts (SZ1):reactants mass ratio of 0.5 % for reaction time ten minutes

Temp.(°C)	% yield	
	purified palm oil	palm fatty acid
210	66.05	75.02
230	68.23	73.92
250	77.89	79.65
270	78.37	78.46
290	79.415	77.72

Table A-1.3 The present of methyl ester at methanol:purified palm oil molar ratio of 42:1 and methanol:palm fatty acid molar ratio of 6:1, reaction temperature 290 °C, SO_4^{2-}/ZrO_2 catalysts (SZ1):reactants mass ratio of 0.5% and reaction time between 0-15 minutes

time (min)	% yield	
	purified palm oil	palm fatty acid
0	69.88	77.23
1	-	78.195
3	-	76.8
5	77.11	76.4
10	79.415	77.72
15	78.11	76.1

Table A-1.4 The present of methyl ester at the reaction temperature 290 °C for the range of molar ratio between 6:1-42:1 for purified palm oil and 3:1-12:1 for palm fatty acid, SO_4^{2-}/ZrO_2 catalysts (SZ1):reactants mass ratio of 0.5 % for 10 minutes of purified palm oil and 1 minute of palm fatty acid

Molar ratio	% yield		Avg.	SD
	purified palm oil			
6:1	36.81	35.56	36.185	0.883883
12:1	77.06	74.28	75.67	1.965757
24:1	80.05	77.13	78.59	2.064752
42:1	80.4	78.43	79.415	1.393

Molar ratio	% yield		Avg.	SD
	palm fatty acid			
3:1	67.99	66.23	67.11	1.244508
6:1	78.67	77.72	78.195	0.671751
9:1	82.78	76.81	79.795	4.221427
12:1	81.5	65.46	73.48	11.34199

Table A-1.5 The present of methyl ester at the reaction temperature 290 °C, methanol:purified palm oil molar ratio of 42:1, methanol:palm fatty acid molar ratio of 6:1, SO_4^{2-}/ZrO_2 catalysts:reactants mass ratio of 0.5 % and reaction time 10 minutes of purified palm oil and 1 minute of palm fatty acid for SO_4^{2-}/ZrO_2 catalyst as preparation at different conditions and commercial grade

catalysts	% yield	
	purified palm oil	palm fatty acid
SZ1	79.415	78.195
SZ2	75.3	76.1
SZ3	20.59	54.48
comercial	26.92	53.76

Table A-1.6 The present of methyl ester at the reaction temperature 290 °C, methanol:purified palm oil molar ratio of 42:1, methanol:palm fatty acid molar ratio of 6:1, SO_4^{2-}/ZrO_2 catalysts:reactants mass ratio of 0.5 % and reaction time 10 minutes of purified palm oil and 1 minute of palm fatty acid for recycling SO_4^{2-}/ZrO_2 catalysts (SZ1)

Time	% yield		Avg.	SD	% yield		Avg.	SD
	palm fatty acid				purified palm oil			
first	78.67	76.75	77.71	1.357645	74.64	80.4	77.52	4.072935
second	64.26	70.91	67.585	4.70226	27.4	34.04	30.72	4.695189

APPENDIX B

CALCULATION OF PERCENT YIELD OF METHYL ESTER

B-1 Calculation of molecular weight of palm fatty acids

The molecular weight of palm fatty acids is calculated from the weighted average of the molecular weight of the five key fatty acids: palmitic acid, oleic acid, stearic acid, linoleic acid, and linolenic acid. The compositions of palm fatty acids are shown in Table B-1.1

Table B-1.1 Composition and molecular weight of key components in of palm fatty acids.

Palm fatty acids	% Weight Fraction	Molecular weight
Palmitic acid	42.8	256.43
Oleic acid	40.5	282.47
Stearic acid	4.5	284.5
Linoleic acid	10.1	280.45
Linolenic acid	2.1	278.43

The data in Table B-1.1 can be used to compute the molecular weight of palm fatty acids as shown below:

1 mole of palm fatty acids

M_w = Sum (M_{Fa} x % Weight fraction fatty acids) **B-1.1**

Where

M_w = Molecular weight of fatty acids

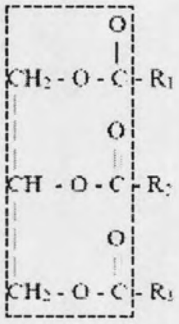
M_{Fa} = Molecular weight of each fatty acids

Such as (Data in the table B-1.1) apply in equation B-1.1

$$= (0.428 \times 256.43) + (0.405 \times 282.47) + (0.045 \times 284.5) + (0.101 \times 280.45) + (0.021 \times 278.43)$$

$$= 271.13$$

B-2 Calculation molecular weight of purified palm oil



Triglyceride

R1, R2, R3: carbon chain of the fatty acids

Table B-2.1 Fatty acid composition in purified palm oil sample

Fatty acid	wt %
Lauric	0.10
Myristic	1.00
Palmitic	42.80
Stearic	4.50
Oleic	40.50
Linoleic	10.10
Linolenic	0.20

Molecular weight of triglyceride

$$Mw_{TG} = 3R_{aver} + 173 \qquad \text{.................. B-2.1}$$

$$R_{aver} = \sum\left(\frac{\%Fa_n}{100} \times Mw_n\right) \qquad \text{................. B-2.2}$$

Where

Mw_{TG} = molecular weight of triglyceride

R_{aver} = average molecular weight of fatty acid

$\% Fa_n$ = percent of fatty acid in vegetable oil

Mw_n = molecular weight of fatty acid

Example Find molecular weight of palm oil

Such as (Data in the table B-2.1) apply in equation B-2.1 and B-2.2

$$R_{aver} = \left(\frac{0.1}{100}\times 200\right)+\left(\frac{1}{100}\times 228\right)+\left(\frac{42.8}{100}\times 256\right)+\left(\frac{4.5}{100}\times 284\right)$$

$$+\left(\frac{40.5}{100}\times 282\right)+\left(\frac{10.1}{100}\times 280\right)+\left(\frac{0.2}{100}\times 278\right)$$

$$= 267.08$$

$$3R_{aver} = 3\times 267.08 = 801.23$$

$$Mw_{TG} = 801.23 + 173 = 974.23$$

B-3 Calculation of reactants

Molar ratio of methanol to reactants: $\dfrac{N_{MeOH}}{N_{reactant}}$

Volume of reactant: $\left(\dfrac{Mw_{reactant}\times N_{reactant}}{\rho_{reactant}}\right)+\left(\dfrac{Mw_{MeOH}\times N_{MeOH}}{\rho_{MeOH}}\right) = V_{reaction}$

Volume of methanol: $V_{reaction} - V_{reactant} = V_{MeOH}$

Example Base on molecular weight of purified palm oil and methanol is 974.23 and 32.04, respectively. The density of purified palm oil and methanol is 0.92 and 0.79, respectively. The volume of reaction used for all preparation was 5 ml.

Molar ratio of methanol to purified palm oil: $\dfrac{N_{MeOH}}{N_{oil}} = \dfrac{42}{1}$

$$N_{MeOH} = 42N_{oil}$$

Volume of purified palm oil: $\left(\dfrac{974.23\times N_{oil}}{0.92}\right)+\left(\dfrac{32.04\times 42N_{oil}}{0.79}\right) = 5$

$$N_{oil} = 0.00181$$

$$V_{oil} = \frac{974.23\times 0.00181}{0.92}$$

$$= 1.92 \text{ ml}$$

Volume of methanol: $5 - 1.92 = 3.08$ ml

B-4 Calculation of catalyst

Example Base on volume of purified palm oil is 1.92 ml. The density of purified palm oil is 0.92 g/ml. The catalyst to purified palm oil mass ratio of 0.5 %

Weight of catalyst = volume of purified palm oil x density of purified palm oil x catalyst to purified palm oil mass ratio

= 1.92 x 0.92 x 0.5 /100

= 0.0088 g

B-5 Calculation of the percent methyl esters yield

The percent methyl ester yield is defined as

$$\%\text{Yield of methyl ester} = \frac{W_{ME}}{W_{Fa} \times (x_i)} \times 100 \qquad \text{………… B-5.1}$$

$$W_{ME} = W_{MP} + W_{MS} + W_{MO} + W_{ML}$$

Where

W_{ME} = weight of methyl ester (g)

W_{Fa} = weight of fatty acid (g)

W_{MP} = weight of methyl palmitate (g)

W_{MS} = weight of methyl stearate (g)

W_{MO} = weight of methyl oleate (g)

W_{ML} = weight of methyl linoleate (g)

x_i = weight fraction of fatty acid

Calculation weight of each methyl ester

$$W_{ME} = \left(\frac{C \times V_{TD}}{V_S} \right) \times V_P \qquad \text{……….. B-5.2}$$

Where

W_{ME} = weight of methyl ester (g)

C = concentration of each methyl ester from calibration curve (g/ml)

V_{TD} = total volume dilute (ml)

V_S = volume product dilute (ml)

V_P = total volume of product (ml)

The weight of methyl esters for each fatty acid can be determined from GC data with corresponding calibration equation. Methyl heptadecanoate was used as internal standard. Below are standard calibration curves for the key methyl esters (Figure B-5.2-B-5.5). Then apply in the equation B-5.2

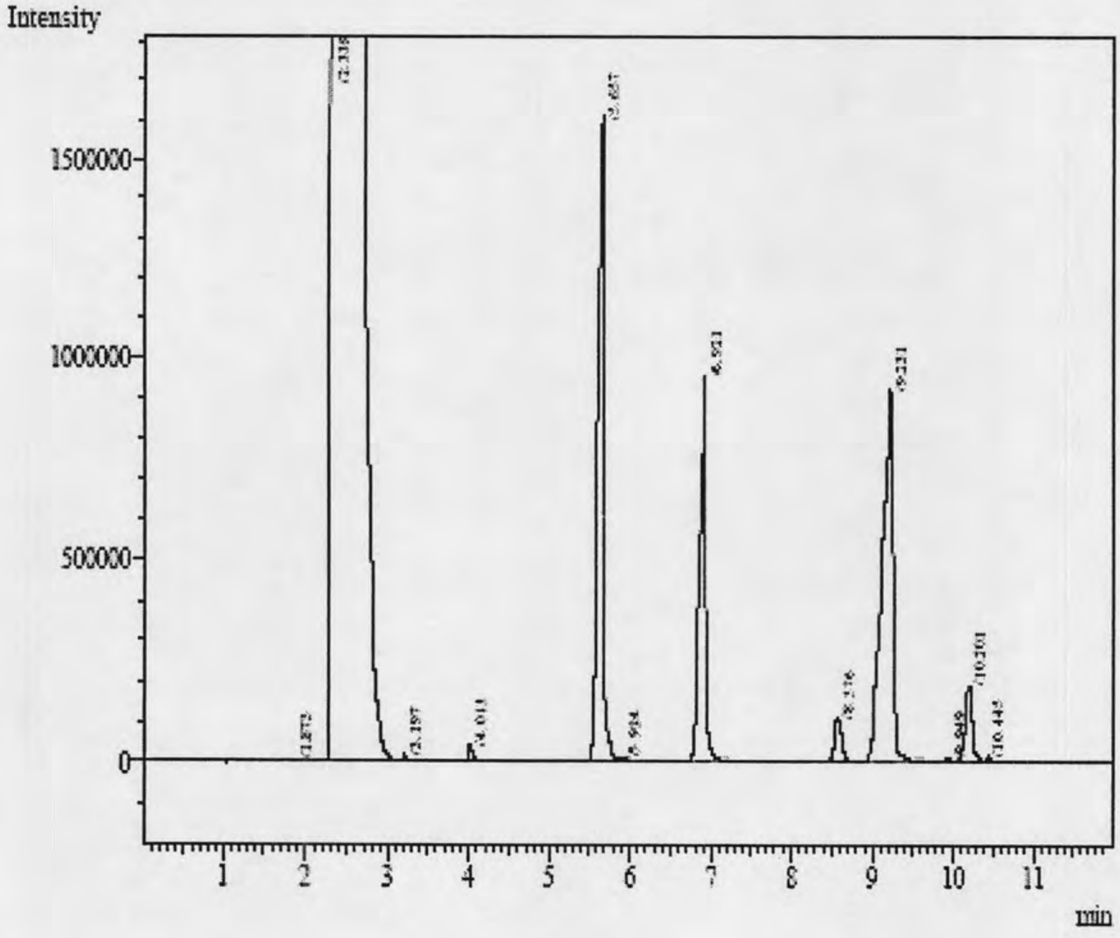


Figure B-5.1 Profile of component of each purified palm oil from GC. At mole fraction of methanol and purified palm oil (42:1), mass fraction of catalyst and oil (0.5 wt %)

Table B-5.1 Data of time and area in Figure B-5.1

Peak of saample	Retention time (min)	Area
Hexane	2.338	3619104354
Methyl palmitate	5.657	7821533
Methyl heptadecanoate	6.921	5066550
Methyl stearate	8.576	692129
Methyl oleate	9.231	8531761
Methyl linoleate	10.201	1142115

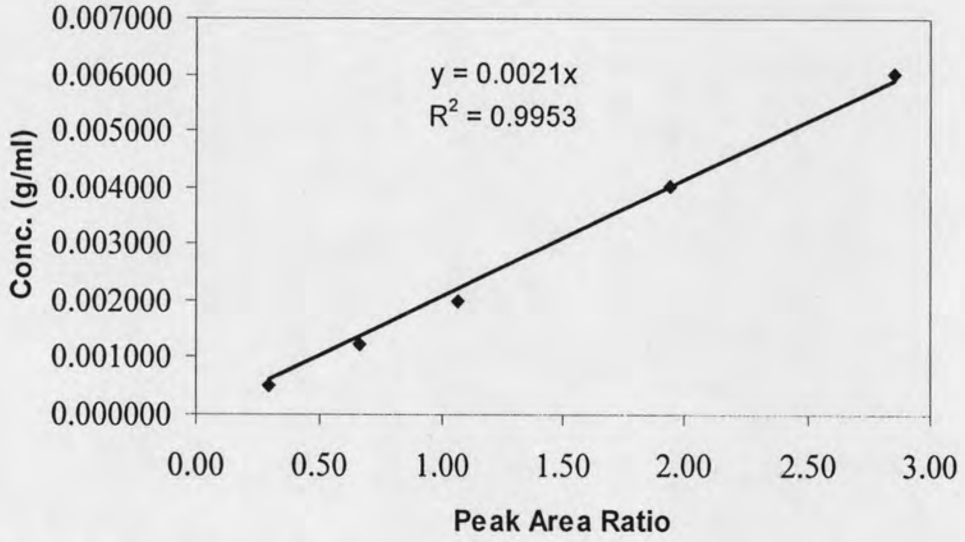


Figure B-5.2 Standard calibration curve for methyl plamitate (corrected with use of methyl heptadecanoate as an internal standard)

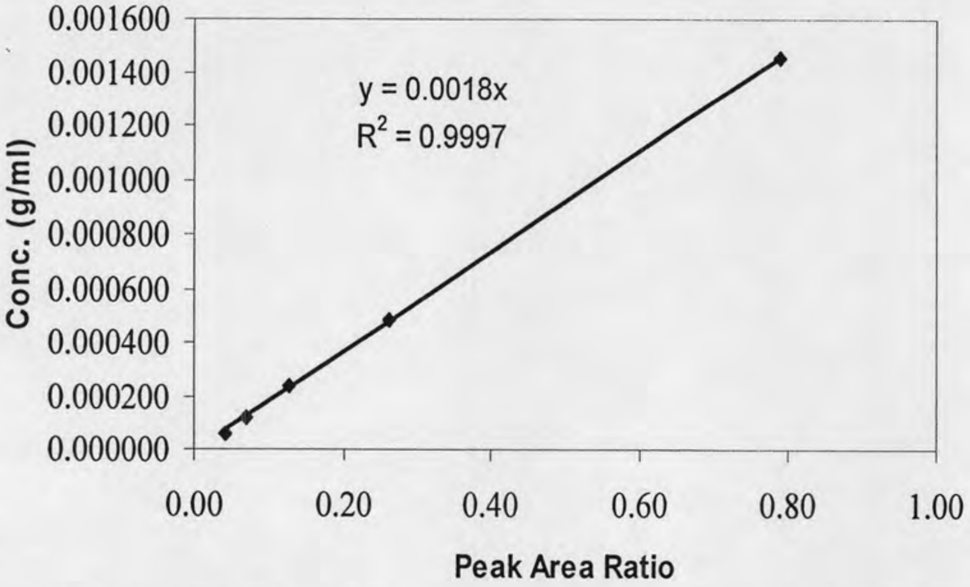


Figure B-5.3 Standard calibration curve for methyl stearate (corrected with use of methyl heptadecanoate as an internal standard)

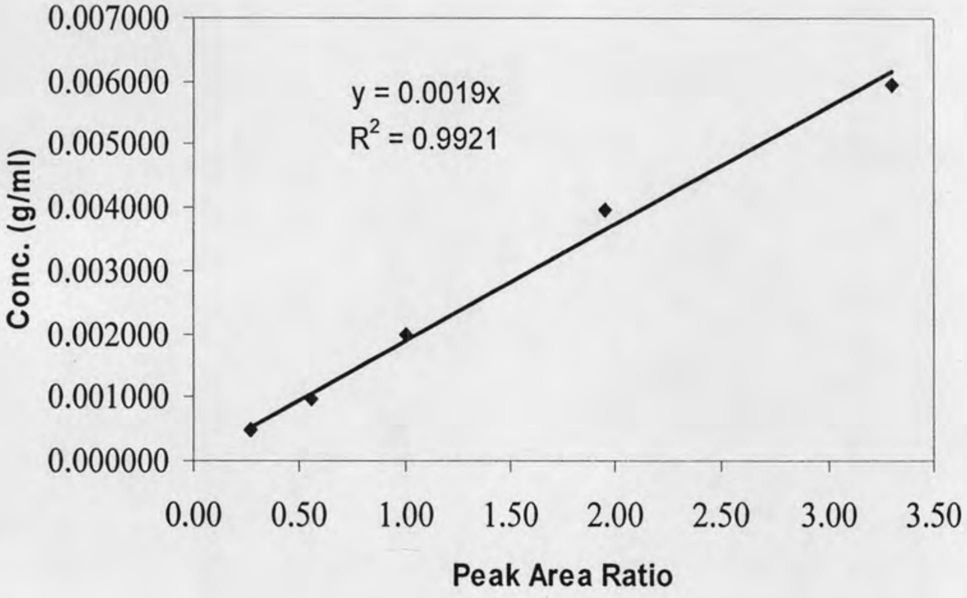


Figure B-5.4 Standard calibration curve for methyl oleate (corrected with use of methyl heptadecanoate as an internal standard)

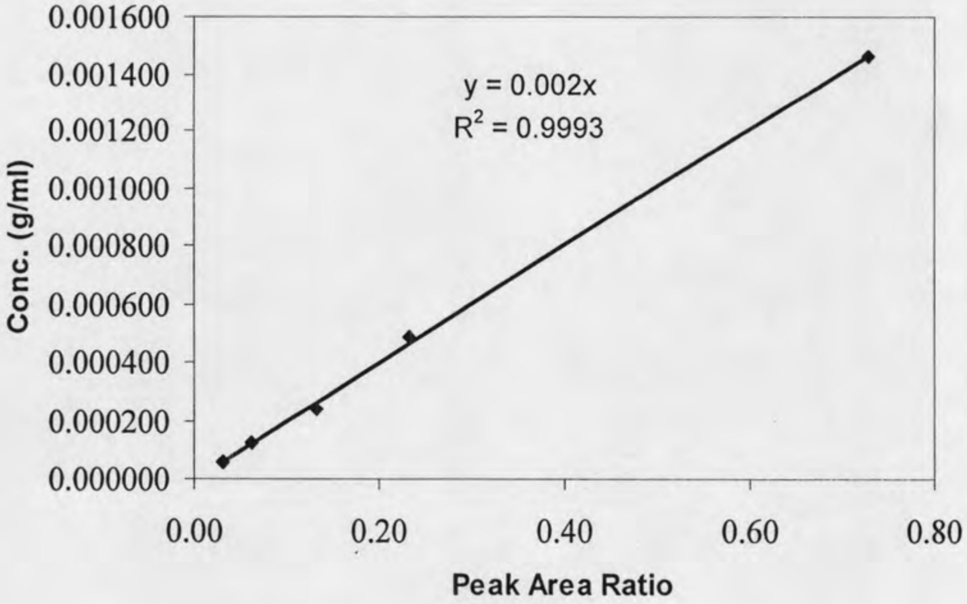


Figure B-5.5 Standard calibration curve for methyl linoleate (corrected with use of methyl heptadecanoate as an internal standard)

Example finds percent yield of methyl ester based on the data from the chromatogram in Figure B-5.1 and the standard calibration curves for different methyl esters figure B-5.2-B-5.5. From the data of peak GC, it can convert to weight of each methyl ester and then apply in equation B-5.2. Volume of product 1.9 ml, volume product dilutes 0.05 ml, total volume dilute = 5 ml

Concentration of each of methyl ester (g/ml) = peak area ratio x calibration constant

Concentration of methyl palmitate = peak area ration of palmitate x 0.0021

$$= \frac{7821533}{5066550} \times 0.0021$$

$$= 0.00324189 \text{ g/ml}$$

Thus, weight of methyl palmitate $= \frac{0.00324189 \times 1.9 \times 5}{0.05} = 0.615959g$

Concentration of methyl stearate = peak area ration of stearate x 0.0018

$$= \frac{692129}{5066550} \times 0.0018$$

$$= 0.00024589 \text{ g/ml}$$

Thus, weight of methyl stearate $= \frac{0.00024589 \times 1.9 \times 5}{0.05} = 0.046719g$

Concentration of methyl oleate = peak area ration of oleate x 0.0019

$$= \frac{8531761}{5066550} \times 0.0019$$

$$= 0.00319948 \text{ g/ml}$$

Thus, weight of methyl oleate $= \frac{0.00319948 \times 1.9 \times 5}{0.05} = 0.607901g$

Concentration of methyl linoleate = peak area ration of palmitate x 0.002

$$= \frac{1142115}{5066550} \times 0.002$$

$$= 0.00045085 \text{ g/ml}$$

Thus, weight of methyl linoleate $= \frac{0.00045085 \times 1.9 \times 5}{0.05} = 0.085662g$

Sum of weight of methyl ester (W_{ME}) = 0.615959+0.046719+0.607901+0.085662

= 1.356241 g

Weight of fatty acid (W_{Fa}) = Volume of purified palm oil x density

= 1.92 x 0.92

= 1.7664 g

Then apply in equation B-5.1

$$\%\text{Yield of methyl ester} = \frac{1.356241}{1.7664 \times 0.979} \times 100$$

$$= 78.47\ \%$$

APPENDIX C

The 17 th Thai Chemical Engineering and Applied Chemistry Conference

(TiCHE 17 th)

29-30 October 2007, Chiangmai, Thailand

Production Methyl Esters from Palm Fatty Acids in Supercritical Methanol

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EFP3_1

Production Methyl Esters from Palm Fatty Acids in Supercritical Methanol

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1. Introduction

The decrease of world petroleum reserves and the atmospheric pollution that 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's usually produced by the tranesterification of vegetable oil or animal fat with short chain alcohol. 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 FFA and moisture in the reaction mixture produces soap (Zullaikah et al., 2005). Acid catalyzed process does not produce soap, however it requires a long time for the reaction to complete. Alternatively, transesterification using enzyme catalyst such as lipase can also convert oils and fats into methyl esters (Fukuda et al., 2006). Although the method is more environmentally friendly, the high cost of enzymes makes the process unattractive for industrial scale.

Saka and Kusdiana (2000) proposed a method of biodiesel production via non-catalytic transesterification of vegetable oils in supercritical methanol. Compared with the catalytic processes, the reaction was found to be complete in a very short time and purification of products is much simpler and more environmentally friendly. However, the reaction requires temperatures of 350–400 °C and pressures of 45–65 MPa, thus resulting in high production cost. Therefore, use of inexpensive raw material would decrease production cost of biodiesel considerably. Alternatively, palm fatty acids, a by product of palm oil industry, is a potential raw material for the production of biodiesel. In 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 stop 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. Analysis of methyl ester in products was carried out by using gas chromatography (GC).

3. Results and Discussions

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 the results on the percent yields are shown in the figure 1 in which the reaction was carried out for 30 min. 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.

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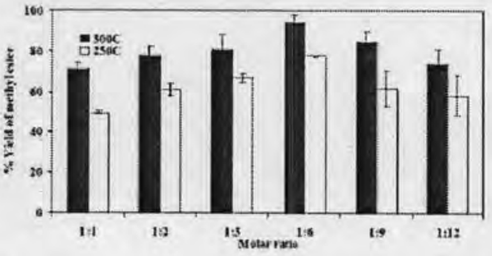

Figure 1 Effects of molar ratios on methyl esterification of palm fatty acids at 250 and 300 °C, reaction time 30 minutes.

3.2 Effect of 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 2. At higher temperature, the percent yield increased further to 94 %, which was obtained at 300 °C.

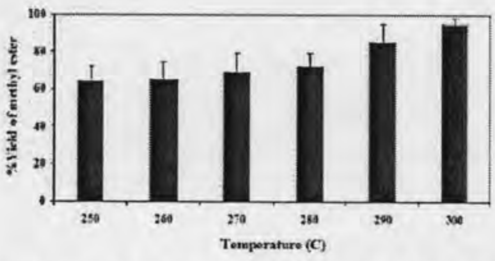

Figure 2 Effect of temperature on methyl esterification of palm fatty acids at 240-300 °C, reaction time 30 minutes and molar ratio of fatty acid to methanol of 1:6.

3.3 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 palm fatty acids to methanol of 1:6 at 250 and 300 °C. As shown in Figure 3. 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 reaction time required to reach the maximum yield of methyl ester of 92% was 70 min.

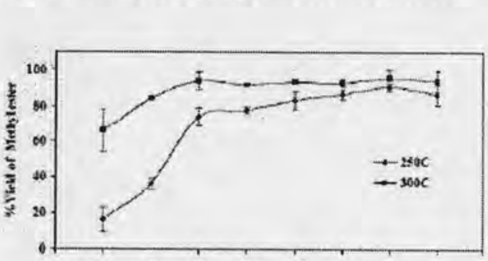

Figure 3 Effect of reaction time on methyl esterification of palm fatty acids at 250 and 300 °C, reaction time 30 minutes and molar ratio of fatty acid to methanol of 1:6.

3.4 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 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 shows that the presence of water indeed lowered the percent yield of methyl ester. Water between 5-25 vol% of water to fatty acid 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%.

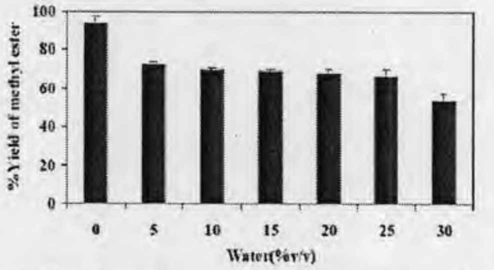

Figure 4 Effect of water on percent yield of methyl ester of palm fatty acids at 300 ° C, 30 minutes

4. Conclusions

The production of biodiesel from palm fatty acids is feasible by supercritical methanol esterification reaction. The most suitable conditions are 300 °C, 30 min and molar ratio of palm fatty acids to methanol of 1:6. Percent methyl ester yield is 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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Contributed Paper

Production Methyl Esters from Palm Fatty Acids in Supercritical Methanol

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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 tranesterification 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 inexpensive 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.

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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 litters 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.

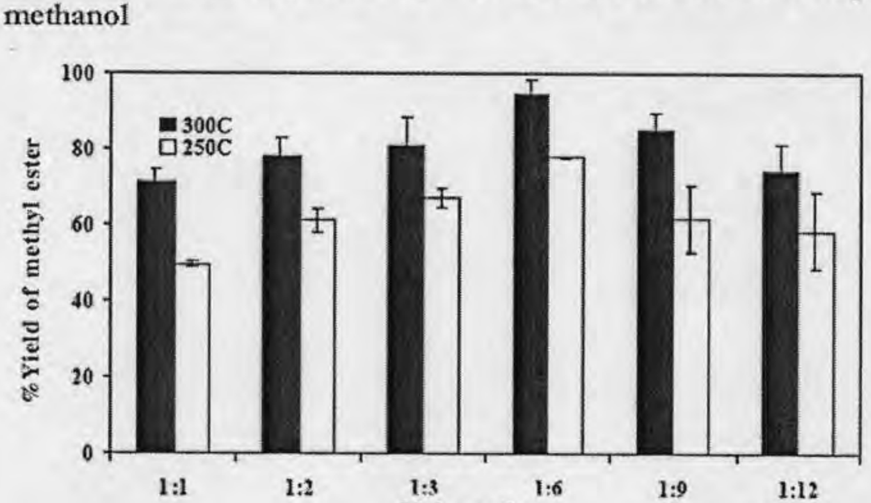

Figure 1. Effects of molar ratios on methyl esterification of palm fatty acids at 250 and 300 °C, reaction time 30 minutes.

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.

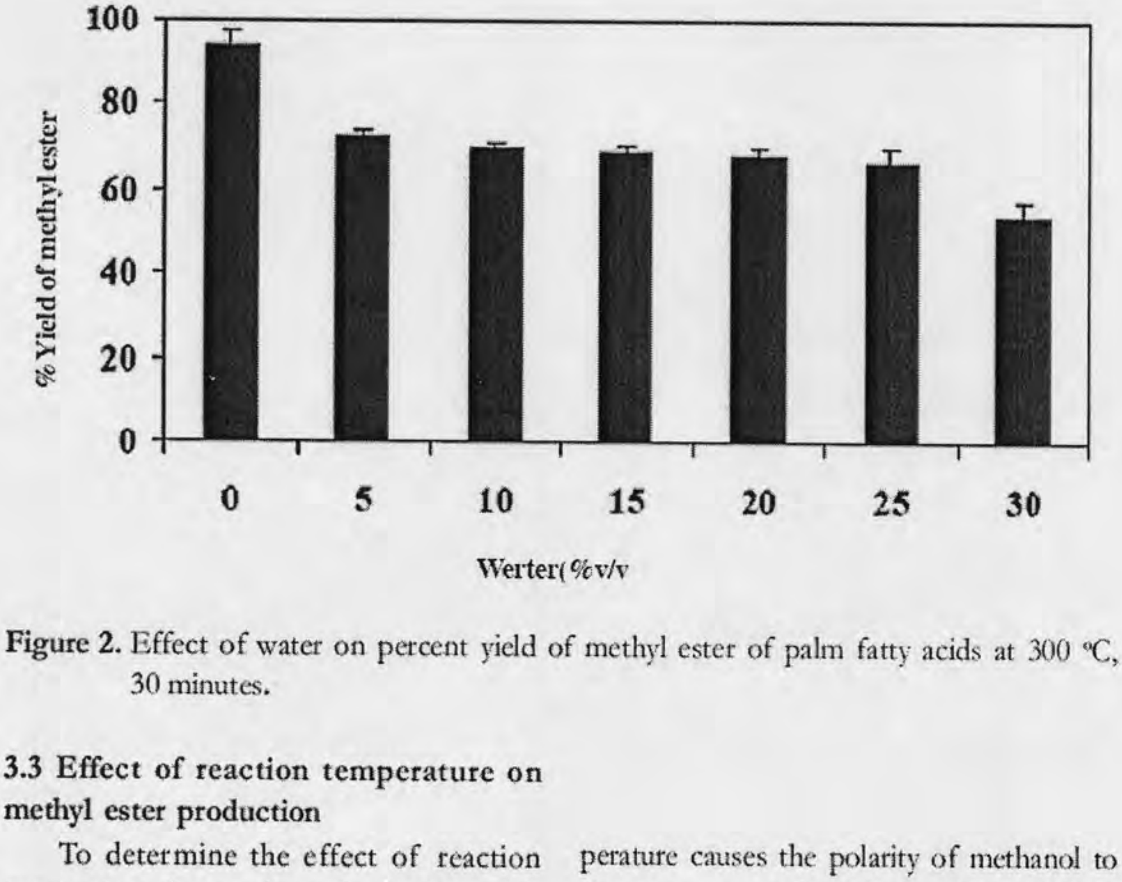

Figure 2. Effect of water on percent yield of methyl ester of palm fatty acids at 300 °C, 30 minutes.

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 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. At higher temperature, the percent yield increased further to 94 %, which was obtained at 300 °C.

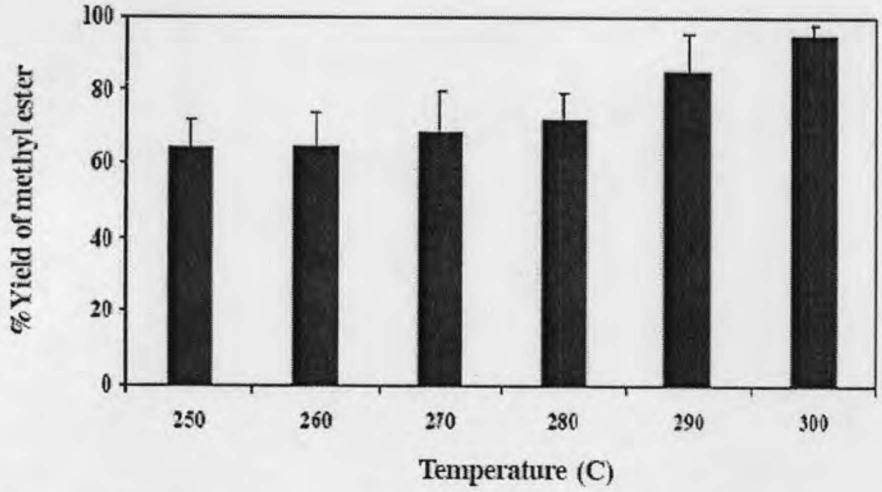

Figure 3. Effect of temperature on methyl esterification of palm fatty acids at 250-300 °C, reaction time 30 minutes and molar ratio of fatty acid to methanol of 1:6.

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.

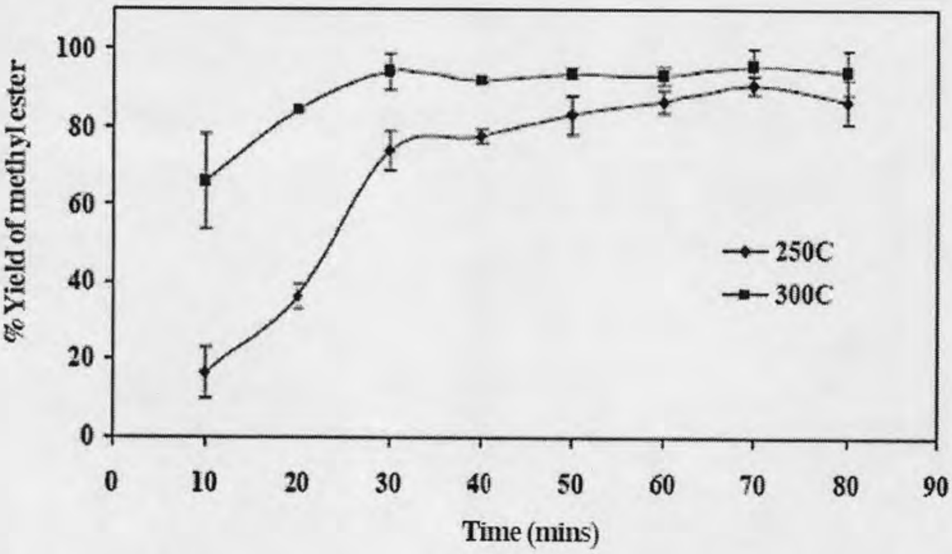

Figure 4. Effect of reaction time on methyl esterification of palm fatty acids at 250 and 300 °C, reaction time 30 minutes and molar ratio of fatty acid to methanol of 1:6.

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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VITA

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