CHAPTER IV
RESULTS AND DISCUSSION

4.1 Characterization of Vegetable Oils

The vegetable oils used in this study were characterized by measuring some of its properties. The results are shown in Table 4.1. According to Thai Industrial Standard (TIS 203-2520), an edible virgin oil is defined as oil obtained by mechanical processes or application of heat only, which may have been purified by washing, setting, filtering or centrifuging only. It has acid value of 4 mg KOH/g of oil and a maximum moisture content of 0.2%. While industrial vegetable oil is oil which is not edible with acid value of 10 mg KOH/ g of oil and moisture content greater than 0.5%. With these criteria, the palm kernel oil and coconut oil used in this experiment can be classified as edible virgin oils.

Table 4.1 Properties of crude palm kernel oil and crude coconut oil

	Palm Kernel Oil (PKO)	Coconut Oil (CCO)
Density at 27°C, g/ml	0.8915	0.8889
Kinematic Viscosity, mm^2/s	29.023	28.249
FFA (% Lauric acid)	4.23	6.09
Moisture Content, %	1.19	1.57

Palm kernel oil and coconut oil are categorized as lauric acid oils. These are oils that contains short-chained acids like lauric acid at levels of about 50% (Weiss, 1970). This general information was confirmed by analyzing the fatty acid composition of the oils using gas chromatography. The results are shown in Table 4.2. It show that the major fatty acid components for PKO are lauric, myristic and oleic acid while lauric, myristic and palmitic acid for coconut oil. The molecular weight of PKO and CCO were calculated based on the fatty acid composition. The values for PKO and CCO were 715.3 and 693.9 g/mole, respectively.

Table 4.2 Fatty acid composition of PKO and CCO (Analysis done at Thailand Institute of Scientific and Technological Research)

Fatty acid	Crude palm kernel oil	Crude coconut oil
Caprylic acid (C8:0)	2.87	5.68
Capric acid (C10:0)	3.11	5.2
Lauric acid (C12:0)	47.49	46.23
Myristic acid (C14:0)	16.27	19.74
Palmitic acid (C16:0)	8.66	10.31
Palmitoleic acid (C16:1)	-	-
Stearic acid (C18:0)	2.16	2.77
Oleic acid (C18:1)	16.25	7.72
Linoleic acid (C18:2)	2.57	2.14
Linolenic acid (C18:3)	-	-
Arachidic acid (C20:0)	0.16	0.08
Others	0.46	0.13
Total	100.00	100.00
Molecular Weight, g/mole	715.3	693.9

4.2 Transesterification Reaction

Initially the methanol-NaOH mixture and the vegetable oil will form a two-phase system. Stirring is needed to have contact of the reactants. Srivastava (2000) noted that the reaction is conducted close to the boiling point of methanol (60 to 70° C) at atmospheric pressure and a 1-hour reaction time is necessary for a high ester conversion. Therefore, the reaction temperature and time used in the experiment was fixed to 65°C and 1 hour. After transesterification of triglycerides, the products are mixtures of esters, glycerol, methanol, catalyst and mono-, di-, and triglycerides. An overnight was needed to allow the complete separation of the methyl ester layer and the glycerol layer. The bottom phase of the mixture would consist of glycerol and the top phase as the methyl ester layer. The CCO and PKO, and its transesterified products can be seen in Figure 4.1 and 4.2. Since the methyl ester is our interest in the study, it was further purified by washing with hot distilled water at 50°C which was recommended the best refining process by Karaosmanoglu *et al.* (1996).
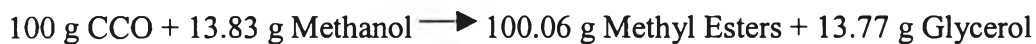
Figure 4.1 Picture of CCO (left), CCO methyl esters (middle) and glycerol
(right).

Figure 4.2 Picture of PKO (left), PKO methyl esters (middle) and glycerol
(right).

Based on stoichiometry, the chemical reaction between PKO or CCO and methanol to produce esters are as follows:

100 g PKO + 13.40 g Methanol ⟶ 100.09 g Methyl Esters + 13.31 g Glycerol

100 g CCO + 13.83 g Methanol ⟶ 100.06 g Methyl Esters + 13.77 g Glycerol

However, unavoidable and undesirable reactions would occur to form soap. These reactions are shown in Figure 4.3. It was observed from the characterization of vegetable oil that the moisture contents of crude oils are high. The presence of water will drive the formation of soap thereby affecting the amount of vegetable oil to be used in the transesterification. In order to see the effect of the side reaction, the production yield was calculated using equation 4.1.
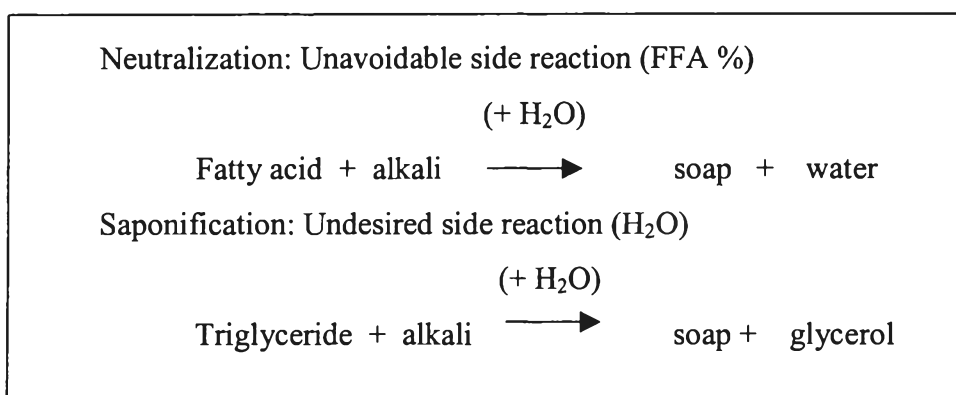
Figure 4.3 Saponification and neutralization reaction.

$$\text{Production yield, \%} = \frac{\text{mass of washed and dried methyl ester layer}}{\text{Theoretical mass of methyl ester from mass balance}} \times 100 \quad (4.1)$$

The quality of biodiesel was determined using HPLC. Chromatograms of vegetable oils and its methyl esters are shown in Appendix A. The methyl esters studied by the HPLC appear in the retention time less than 10 min, while the peaks at the longer retention times are believed to be partially methylated esters such as mono- and diglycerides. Comparison of the chromatograms of vegetable oil and its methyl esters showed the peak intensities of methyl esters are apparently increased with a decrease in those partially methylated esters as transesterification proceeds.

The methyl ester content was calculated using the normalization method and is shown in equation 4.2.

$$\text{M.E. Content \%} = \frac{\text{Area of Methyl Esters}}{\text{Total Area} - \text{Area of Solvent}} \times 100 \tag{4.2}$$

The conversion was calculated using equation 4.3.

$$\text{Conversion, \%} = \frac{\text{M.E. Content (\%) x Production Yield (\%)}}{\text{Weight of Vegetable Oil used}} \tag{4.3}$$

4.3 Effect of the Amount of Sodium Hydroxide

One important variable affecting the ester conversion is the amount of catalyst. A lot of research has confirmed that NaOH is one of the effective catalysts for this reaction. In the characterization of vegetable oil, it showed that crude oils contain a high percentage of free fatty acid so that NaOH catalyst can be used in the neutralization. The amount of NaOH needed to neutralize crude oils were determined using AOCS Cd 3a-63. The values needed to neutralize 100 g of PKO and CCO were 0.85 g and 1.22 g NaOH, respectively. The free fatty acid of crude vegetable oil depends on the source and the season of harvesting the plant crop (Weiss, 1970), so in order to account this effect the amount of NaOH used was corrected by adding the amount needed for the neutralization plus the amount of NaOH as catalyst.

The effect of the amount of NaOH in the transesterification of crude PKO is shown in Figure 4.4. The 0.5% NaOH as catalyst was chosen to be appropriate in the reaction. It was observed that increasing the catalyst would enhance the saponification as noticed in the low production yield of 1% NaOH. It was also mentioned by Noureddini *et al.* (1998) that higher catalyst concentrations increase the solubility of methyl esters in the glycerol phase of the final product. As a result, a significant amount of methyl esters remains in the glycerol phase after the phase separation.

The effect of this parameter in the transesterification of crude CCO is shown in Figure 4.5. It also shows that 0.5% NaOH as catalyst was also sufficient for the reaction. Increasing the catalyst would then affect the production yield.
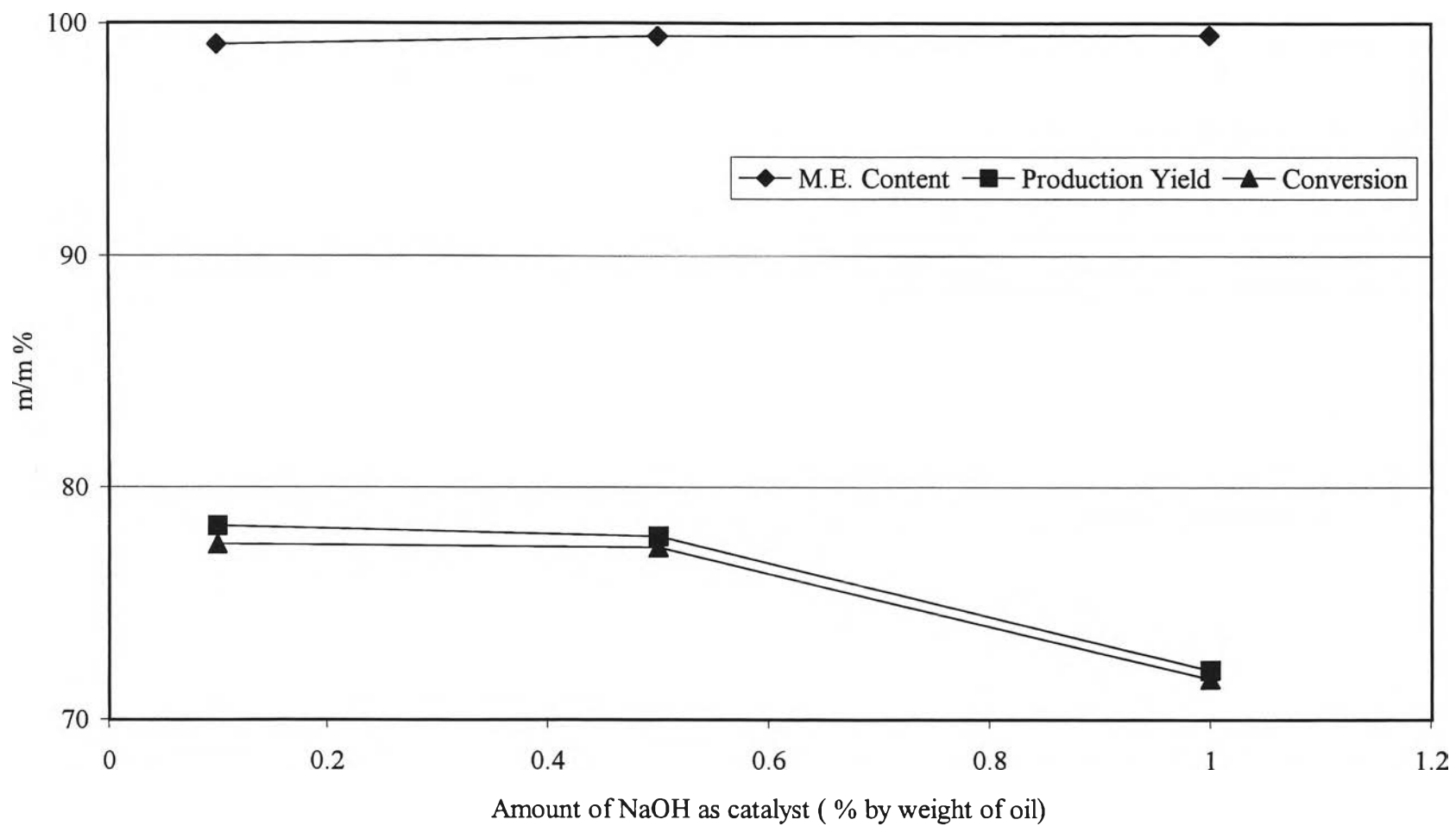
Figure 4.4 Effect of the amount of NaOH in the transesterification of Palm Kernel Oil.
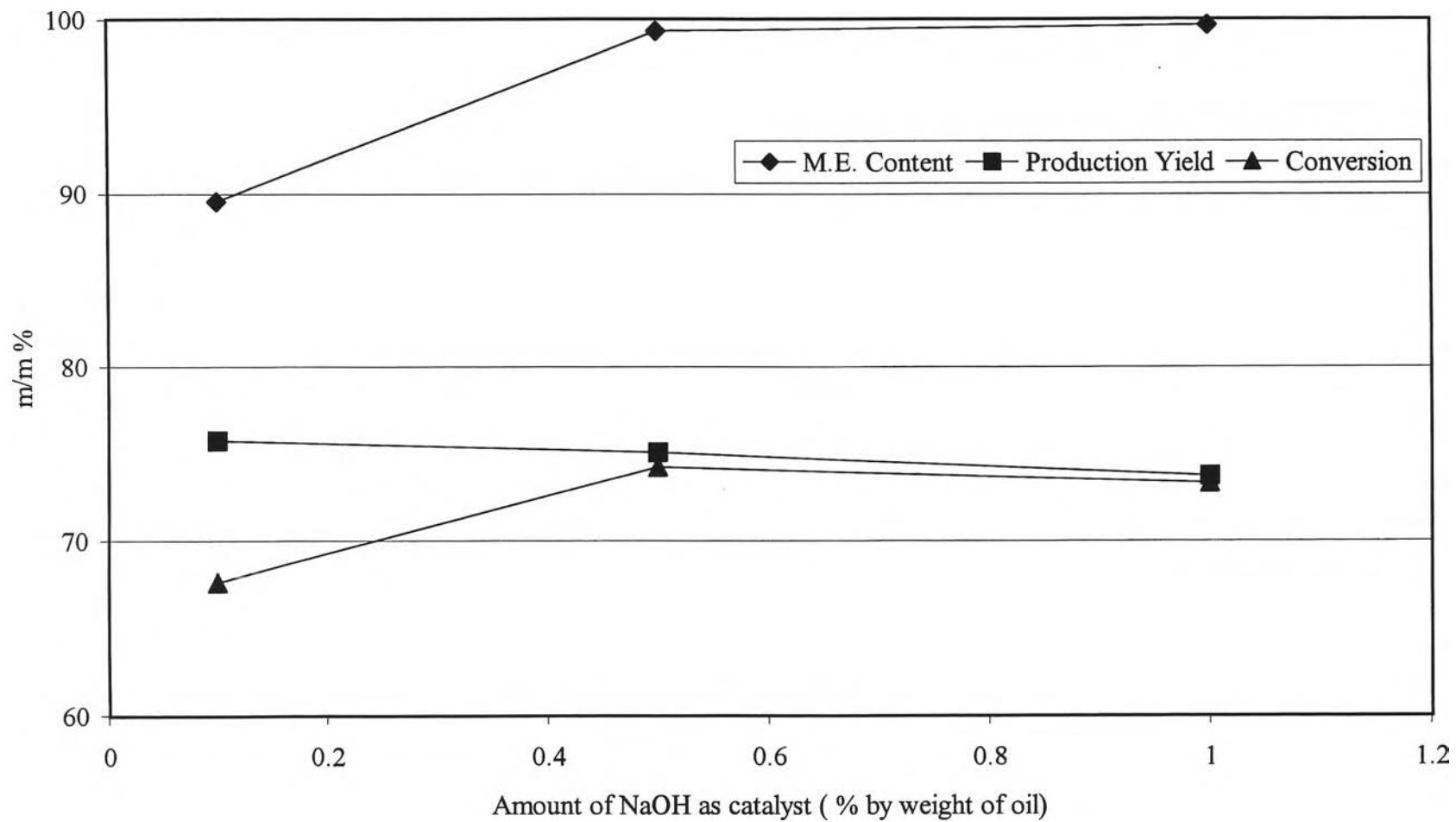
Figure 4.5 Effect of the amount of NaOH in the transesterification of Coconut Oil.

The results showed that the optimum amount of NaOH to be added in the transesterification of PKO and CCO is 0.5% (based on the weight of oil) plus the amount needed to neutralize the oil.
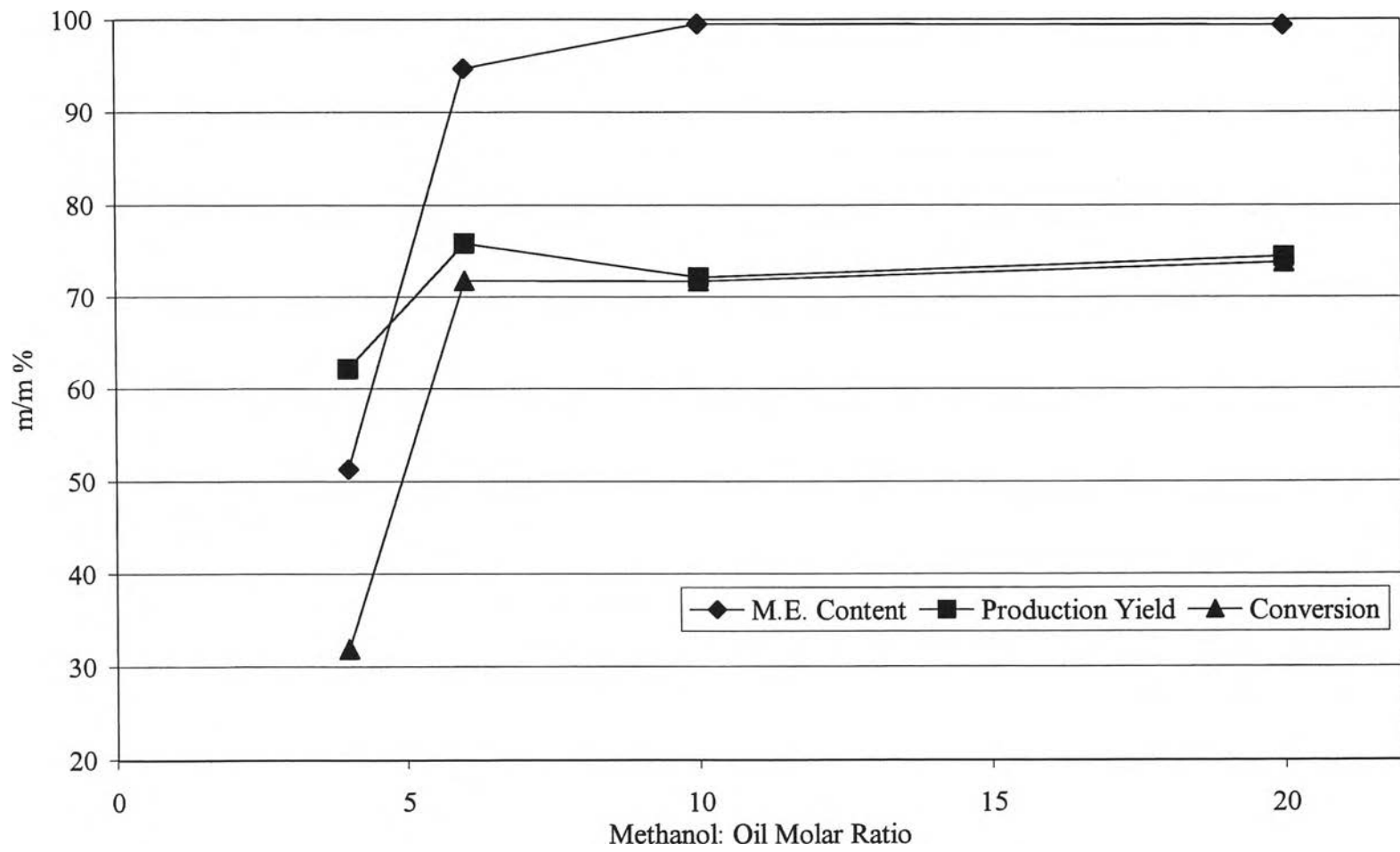
4.4 Effect of Methanol to Oil Molar Ratio

The molar ratio of methanol to oil is also considered as one of the most important variables affecting the ester yield. In the transesterification, 3 moles of methanol for every mole of oil is needed to form 3 moles of methyl esters and one mole of glycerol. Freedman et al. (1984) studied this effect in the transesterification of refined sunflower oil. They noted that at 6:1 molar ratio, a 98% conversion of the ester was obtained. While as the molar ratio decreased to the theoretical ratio of 3:1, the percentage of ester decreased to 82%.

The results of the effect of methanol: oil ratio for crude palm kernel oil is shown in Figure 4.6. The molar ratio 3:1 was studied but a wax /gel formation was observed which indicates that at this amount, the reaction favored was the saponification reaction. At a 4:1 molar ratio, the conversion and production yield was low due to interference of soap formation. At a 6:1 molar ratio, there was quick separation of methyl ester and glycerol layer and it showed that the conversion and yield was maximal. While at a 10:1 and 20:1 molar ratio, the reaction mixture was homogeneous so there was a need for evaporation to remove excess methanol to allow the separation of the two layers. The production yield and conversion were comparable to that obtained by using 6:1 molar ratio.

Figure 4.6 Effect of Methanol: Oil Molar Ratio in the transesterification of Palm Kernel Oil.

The effect of this parameter in the transesterification of crude CCO is shown in Figure 4.7. The observations and trends of the results were similar to the transesterification of crude PKO.

The results showed that the ideal methanol: oil ratio for the transesterification of crude PKO and CCO is at 6:1 molar ratio, the same as has been reported earlier.

4.5 Effect of Moisture Content

Fangrui (1999) mentioned that for an alkali-catalyzed transesterification, the vegetable oil and alcohol must be substantially anhydrous because water makes the reaction partially change to saponification, which produces soap. The soap lowers the yield of esters and renders the separation of ester and glycerol, and the water washing more difficult. Freedman *et al.* (1984) has stressed the importance of nearly dry oil and substantially free from fatty acids. He stated that when the reaction conditions do not meet the requirements, ester yields are significantly reduced.

The crude PKO and CCO were dried with anhydrous Na_2SO_4 (20% based on the weight of oil). They were then compared with undried crude vegetable oils. These were done to see the effect of moisture content in the ester yield. The results are shown in Figure 4.8. It can be noted that the effect of moisture content is insignificant. On the other hand, the presence of free fatty acid is crucial in the ester conversion.

4.6 Investigation of Possible Heterogeneous Catalysts

Screening of the heterogeneous catalysts is necessary to identify the appropriate catalyst for the transesterification of vegetable oil. It would allow several advantages such as lower production cost, environmental friendly and ease of separation of the product mixture that would lead to the simplicity of the downstream process.
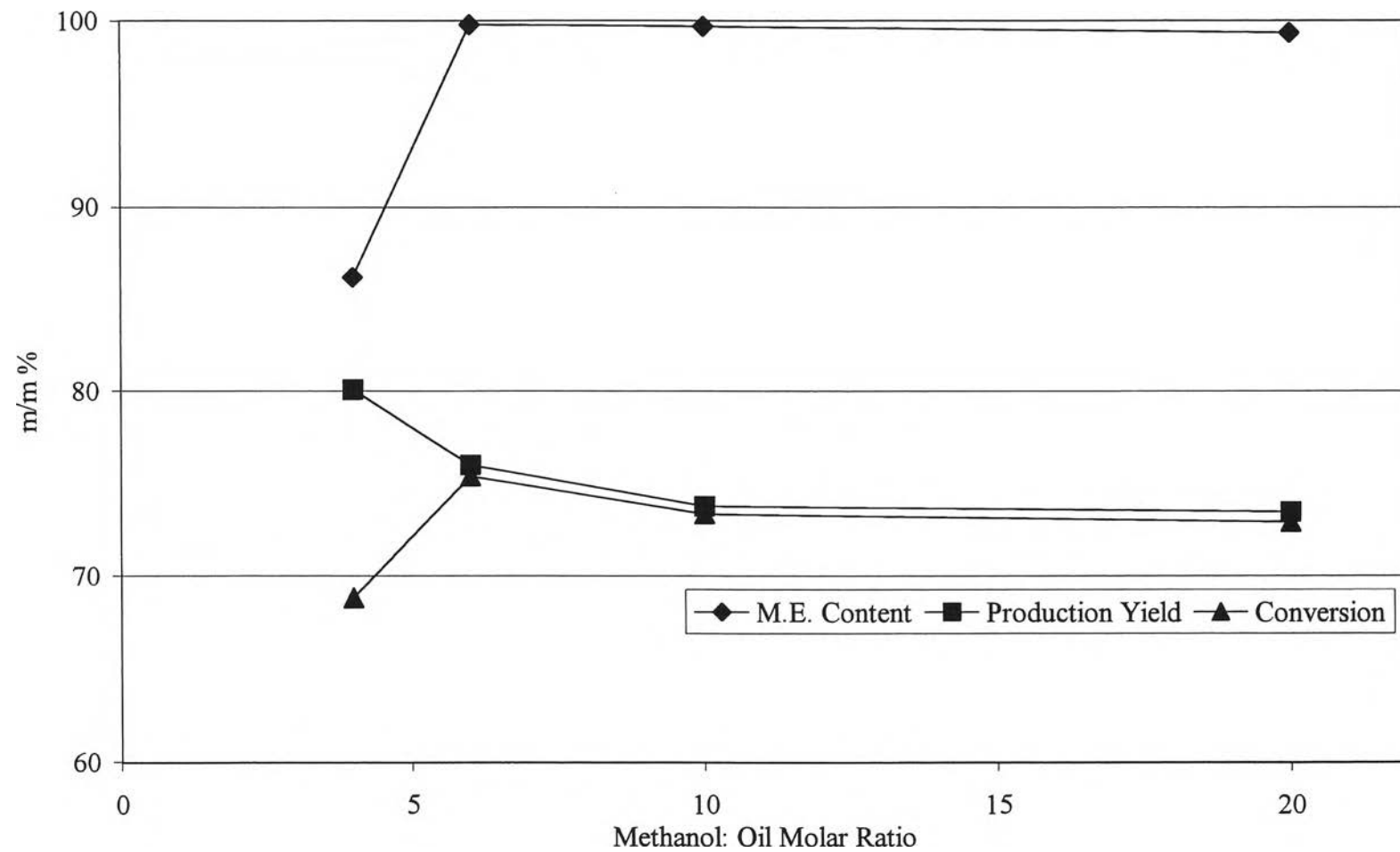
Figure 4.7 Effect of Methanol: Oil Molar Ratio in the transesterification of Coconut Oil.
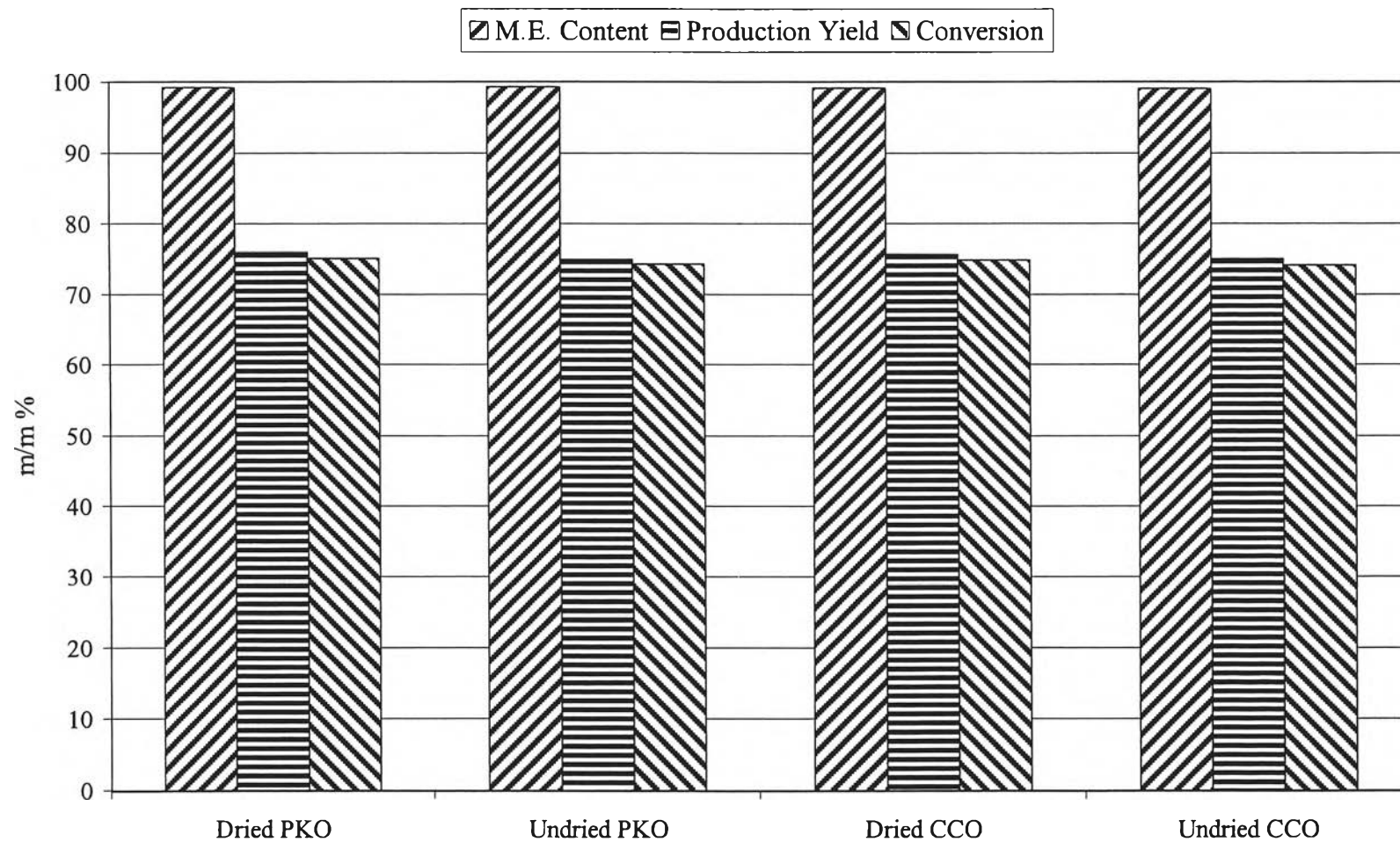
Figure 4.8 Effect of moisture in the transesterification of vegetable oil.

Some heterogeneous catalysts that are used in the transesterification of other ester group were examined. The heterogeneous catalysts were evaluated based on the M.E. content. The results and conditions used are summarized in Table 4.3.

Table 4.3 Heterogeneous Catalysts Screening in the Transesterification of Coconut Oil

Expt. No.	Catalyst	MeOH: Oil Ratio	Temp. °C	Time, hr	M.E. Content, %
1	Na_2CO_3	20:1	65-70	10	28.56
2	K_2CO_3	20:1	65-70	10	99.34
3	$CaCO_3$	20:1	65-70	10	10.48
4	ZrO_2	20:1	65-70	10	38.75
5	ZnO	20:1	65-70	10	54.27
6	Beta	20:1	65-70	10	21.52
7	NaX	20:1	65-70	10	14.58
8	NaY	20:1	65-70	10	21.90
9	Al_2O_3	20:1	65-70	10	22.73
10	$SO_4 \cdot SnO_2$	20:1	65-70	10	26.49
11	K_2CO_3	20:1	30	6	99.37
12	Blank	10:1	200 [50 bar]	4	51.39
13	K_2CO_3	10:1	200 [50 bar]	4	97.24
14	$CaCO_3$	10:1	200 [50 bar]	4	94.46
15	ZrO_2	10:1	200 [50 bar]	4	94.78
16	ZnO	10:1	200 [50 bar]	4	99.01
17	Beta	10:1	200 [50 bar]	4	83.78
18	NaX	10:1	200 [50 bar]	4	85.46
19	NaY	10:1	200 [50 bar]	4	81.08
20	Al_2O_3	10:1	200 [50 bar]	4	58.84
21	$SO_4 \cdot SnO_2$	10:1	200 [50 bar]	4	97.00

Certain carbonate systems are known to promote glycerolysis of triglycerides (Khan, 2002). Na_2CO_3, K_2CO_3 and $CaCO_3$ were tested. The Na_2CO_3 was considered ineffective in catalyzing the reaction. Results showed that K_2CO_3 can catalyze the transesterification of vegetable oil and has a good ester yield even at 30° C. However, the potassium carbonate is soluble in the mixture.

CaCO₃ was identified by Suppes (2001) to be an effective catalyst for reactions between simple alcohols and soybean oil. Results showed that the solubility of $CaCO_3$ is low as compared to the other carbonate group studied. The CaCO3 has a 94.46 % methyl esters content and now verified as a possible catalyst for the production of biodiesel.

Stern (1999) patented ZnO as one of the heterogeneous catalyst for the production of esters from vegetable oils or animal oils alcohols. It was confirmed in this study that ZnO has the potential to catalyze the reaction having the highest methyl esters content (99.01%) when compared to the other catalysts.

ZrO_2 is reported as a good catalyst for various esterification reactions (Yu, 1990). It was investigated for the transesterification of coconut oil and it showed a possibility of catalyzing the reaction with a M.E. content of 94.78 %.

Zeolites are accounted for by Zajdlewicz (2001) to catalyze the transesterification of vegetable oil. NaX, NaY, and Beta zeolite were tested for this reaction. It showed that all the zeolites could be used as a catalyst when high temperature and pressure is applied.

Acidic Alumina was tested for this reaction but the result showed that the weight loss is very high (~ 67%) implying the possible dissolution of the catalyst in the mixture. Moreover, it has also a low M.E. content even at high temperature so it is not suitable as heterogeneous catalyst for the transesterification of vegetable oil.

Sulfated Stannous Oxide ($SO_4 \cdot SnO_2$) is reported as an efficient catalyst in the transesterification of keto-esters (Chavan, 1995). Results showed that $SO_4 \cdot SnO_2$ to be a promising heterogeneous catalyst for the transesterification of vegetable oil having a methyl ester yield of 97 %.

Since $CaCO_3$, ZrO_2 and $SO_4 \cdot SnO_2$ were capable of catalyzing the reaction, they were further investigated by varying the reaction temperature. The results are shown in Table 4.4. It showed that all the catalysts investigated are effective in the production of biodiesel when operated at high temperature (200°C) and pressure (50 bar).

$SO_4 \cdot SnO_2$ showed to be the most promising of the catalyst investigated because it can catalyze the reaction even at a temperature of about 130°C. When operated at 200°C, $SO_4 \cdot SnO_2$ would give a high methyl ester content even when 2 hr reaction time was employed.

Table 4.4 Investigation of suitable catalyst for the transesterification of CCO Condition: 10:1 Methanol: CCO Ratio and 6% Weight Catalyst

Catalyst	65°C	130°C [10 bar]	200°C [50 bar]	
	4 hr	4 hr	2 hr	4hr
$CaCO_3$	23.02	36.84	85.50	94.46
ZrO_2	23.48	33.42	75.05	94.78
$SO_4 \cdot SnO_2$	23.87	65.24	92.79	97.00

The possible heterogeneous catalysts for the transesterification of CCO were compared with NaOH and are summarized in Table 4.5. Results showed that ZnO and $SO_4 \cdot SnO_2$ have the same efficiency with NaOH to catalyze the reaction. It was observed in the experiment that the washing step when using heterogeneous catalyst was minimal when compared when using NaOH. This implies one benefit when using heterogeneous catalyst. From this, the ZnO and $SO_4 \cdot SnO_2$ are considered as the most promising heterogeneous catalysts for transesterification of vegetable oil.

Table 4.5   Heterogeneous catalyst transesterification versus NaOH-catalyzed transesterification

Catalyst	Production Yield, %	M.E. Content, %	Conversion, %
NaOH*	75.77	99.12	74.97
CaCO$_3$**	57.74	94.46	54.55
ZrO$_2$**	74.44	94.78	70.56
SO$_4$·SnO$_2$**	72.53	97.00	70.36
ZnO**	68.99	99.01	68.31

*Conducted using 6:1 methanol: CCO molar ratio, 0.5 % catalyst at 65°C for 1 hour.

** Conducted using 10:1 methanol: CCO molar ratio, 6 % catalyst at 200°C and 50 bar for 4 hr.