

CHAPTER IV RESULTS AND DISCUSSION

4.1 Characterization of Vegetable Oils

The vegetable oils used in this study are crude palm kernel oil and crude coconut oil. Some of their properties such as density, kinematic viscosity, free fatty acid, and moisture content are determined and summarized in Table 4.1. According to Thai Industrial Standard (TIS 203-2520), an edible virgin oil has been defined as an oil obtained by mechanical or thermal processes and may have been purified by washing, settling, filtering or centrifuging. They are allowed to have acid value not exceeding 4 mg KOH/g of oil and a maximum moisture content of 0.2%. On the other hand, industrial vegetable oil is not edible and can have the acid value upto 10 mg KOH/ g of oil and moisture content up to 0.5%. With these criteria, as seen in Table 4.1, the crude palm kernel oil and crude coconut oil used in this study can be classified as edible virgin oils.

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

Properties	Crude Palm Kernel Oil (PKO)	Crude Coconut Oil (CCO)
Density at 27°C (g/ml)	0.908	0.909
Kinematic Viscosity (mm ² /s)	28.65	24.85
Free Fatty Acid	1.05 (as lauric acid)	2.25 (as lauric acid)
Moisture Content (%)	0.09	0.17

Both palm kernel oil and coconut oil can be classified as lauric acid oils since these oils contain lauric acid at levels of about 50% (Weiss, 1970). This information was confirmed by analyzing the fatty acid composition of the oils using

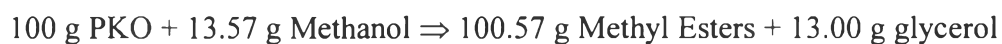
gas chromatography. As shown in Table 4.2, the major fatty acid components for crude palm kernel oil are lauric, myristic and oleic acid, while crude coconut oil containing mainly lauric, myristic and palmitic acid. Based on these compositions, the molecular weight of crude palm kernel oil and crude coconut oil used in this study are 708.22 and 638.36 g/mole respectively.

Table 4.2 Fatty acid compositions of crude palm kernel oil and crude coconut oil

Fatty acid	Crude Palm Kernel Oil (%)	Crude Coconut Oil (%)
Caprylic acid (C8:0)	2.67	6.4
Capric acid (C10:0)	3.46	5.8
Lauric acid (C12:0)	49.45	48.1
Myristic acid (C14:0)	16.08	19.0
Palmitic acid (C16:0)	7.74	8.9
Palmitoleic acid (C16:1)	0.07	0.1
Stearic acid (C18:0)	1.93	2.8
Oleic acid (C18:1)	14.11	5.9
Linoleic acid (C18:2)	2.36	1.4
Linolenic acid (C18:3)	-	-
Arachidic acid (C20:0)	0.09	0.1
Others	2.04	1.5
Total	100	100

4.2 Heterogeneous Catalytic Transesterification of Crude Palm Kernel Oil and Crude Coconut Oil

Base on molecular weight of crude palm kernel oil and crude coconut oil, the mass balance from the transesterification with methanol can be written as following (assume 100% conversion):



Stoichiometrically, 1 mole of vegetable oil requires 3 moles of alcohol to form 1 mole of glycerol and 3 moles of methyl esters. Hence, based on molecular weight of crude palm kernel oil and crude coconut oil, 100 grams of crude palm kernel oil requires 13.57 grams of methanol to complete conversion, while 15.03 grams of methanol is required in case of crude coconut oil transesterification. The calculation of molecular weight of both crude palm kernel oil and crude coconut oil are shown in Table A5 (Appendix A).

Initially, the mixture of vegetable oil, methanol and solid catalyst will separate into three phases. The reaction is controlled by diffusion and poor diffusion of reactants results in a slow rate (Srivastava and Prasad, 2000). Thus, stirring is needed to increase the contact among reactants and catalyst. As methyl esters are formed, they act as a solvent for both vegetable oil and methanol. High temperature and long reaction time are also required because the rate of transesterification increased with increasing temperature and the longer the reaction time results in higher conversion (Suppes *et al.*, 2001). Several studies on heterogeneous catalytic transesterification have shown that, at high temperature, the high conversion of vegetable oils can be obtained (Suppes *et al.*, 2001 and Exconde, 2002). Therefore, this thesis first fixed the reaction temperature and time at 200°C and 4 hours. After the transesterification, the products are the mixtures of esters, glycerol, methanol, mono-, di-, and triglycerides and the spent solid catalyst. The spent catalyst is separated from the products by filtration. After the catalyst removal, the product is left overnight for the phase separation, which will result in the methyl esters phase (top phase) and the glycerol phase (bottom phase). Since the methyl esters phase can be significantly contaminated with glycerol and methanol, it were further purified by washing with warm distilled water at 50°C which was recommended the best refining process (Karaosmanoğlu *et al.*, 1996).

The purity of biodiesel products (methyl esters) is then determined by HPLC. The methyl esters studied by the HPLC appear at the retention time less than

8 min in chromatogram, while the peaks at the longer retention time are mono-, di-, and triglycerides. To confirm this, the chromatograms of crude palm kernel oil, crude coconut oil and its methyl esters are shown in Appendix B. The chromatograms from HPLC show that the triglycerides peaks of both crude palm kernel oil and crude coconut oil appear at the retention time longer than that for the methyl esters. Therefore the HPLC is suitable for both qualitative and quantitative analysis of the methyl esters from transesterification of crude palm kernel oil and crude coconut oil.

The methyl esters content and the methyl esters yield are defined as respectively shown in Equation (3.1) and (3.2).

$$\text{Methyl Esters content (wt\%)} = \frac{\text{Weight of methyl esters (determined by HPLC)}}{\text{Weight of methyl esters phase (top phase)}} \times 100 \quad (3.1)$$

$$\text{Methyl Esters Yield (wt\%)} = \frac{\text{Weight of methyl esters (determined by HPLC)}}{\text{Weight of vegetable oil used}} \times 100 \quad (3.2)$$

4.3 Investigation of Heterogeneous Catalysts for Transesterification

In this study, based on their acidity and basicity, six solid catalysts (ZrO_2 , ZnO , $\text{SO}_4^{2-}/\text{SnO}_2$, $\text{SO}_4^{2-}/\text{ZrO}_2$, KNO_3/KL zeolite, and $\text{KNO}_3/\text{ZrO}_2$) are first studies as heterogeneous catalysts for transesterification. To evaluate for their catalytic activity, they have been tested for the transesterification of crude palm kernel oil and crude coconut oil. The experimental conditions are set at methanol:oil molar ratio of 6:1, 3% by weight of catalysts (based on weight of vegetable oil), pressure at 50 bars under nitrogen atmosphere, temperature at 200°C , and the 350 rpm stirrer. The HPLC chromatograms of the methyl esters products obtained from these experiments are shown in Appendix B.

4.3.1 Crude Palm Kernel Oil Transesterification

The transesterification of crude palm kernel oil with methanol by using heterogeneous catalyst was carried out by following the procedure as described in section 3.3.2. The results are reported in Table 4.3.

Table 4.3 Crude palm kernel oil transesterification by solid catalysts

Condition: 200 °C, 50 bars, 350 rpm, 6:1 methanol:oil

No.	Catalyst	M.E. Content (wt%)	M.E. Yield (wt%)
1	-	32.3	30.4
2	ZrO ₂	69.0	64.5
3	ZnO	98.9	86.1
4	SO ₄ ²⁻ /SnO ₂	95.4	90.3
5	SO ₄ ²⁻ /ZrO ₂	95.8	90.3
6	KNO ₃ /KL zeolite	77.8	71.4
7	KNO ₃ /ZrO ₂	78.3	74.4

Table 4.3 shows that, in the blank test or no catalysts present (run no. 1), the amount and purity of methyl esters are relatively very low even it is performed at high temperature (200°C) and sufficient reaction time (4 hours). However, when the solid catalysts are added, the methyl esters content and yield in the product are significantly increased. This indicates that the solid catalysts considerably increase the rate of the transesterification of vegetable oils.

Among the investigated catalysts, of SO₄²⁻/SnO₂ and SO₄²⁻/ZrO₂ superacid solid catalysts render the highest yield of methyl esters at 90.3 wt% based on crude palm kernel oil. Moreover, the purities of methyl esters (or esters content) from these two catalysts are relatively high as well (95.4 wt% and 95.8 wt% for SO₄²⁻/SnO₂ and SO₄²⁻/ZrO₂ respectively). However, the esters content if uses ZnO is the highest (98.9 wt%). For the solid superbase catalysts (KNO₃/ZrO₂, KNO₃/KL zeolite), they are moderately active. The methyl esters content of 78.3 wt% is

obtained if $\text{KNO}_3/\text{ZrO}_2$ is used as the catalyst, whereas methyl esters content of 77.8 wt% is obtained when $\text{KNO}_3/\text{KLzeolite}$ is used. Both of them give the methyl esters yield higher than 70 wt%. Among the tested catalysts, ZrO_2 gives the lowest amount of methyl esters content and yield.

From the results, all of investigated catalysts have shown potential to be used as heterogeneous catalysts for the transesterification of crude palm kernel oil with methanol. Moreover, soap formation was not observed when the solid catalysts were used. In addition, from the methyl esters yield, the order of solid catalysts which provide the amount of esters from highest to lowest is: $\text{SO}_4^{2-}/\text{ZrO}_2$ and $\text{SO}_4^{2-}/\text{SnO}_2 > \text{ZnO} > \text{KNO}_3/\text{ZrO}_2 > \text{KNO}_3/\text{KL-zeolite} > \text{ZrO}_2$.

4.3.2 Crude Coconut Oil Transesterification

The catalytic activities of six solid catalysts were also investigated for transesterification of crude coconut oil. The reaction conditions are set as in the case of crude palm kernel oil transesterification. The results of the transesterification of crude coconut oil are reported in Table 4.4.

Table 4.4 Crude coconut oil transesterification by solid catalysts

Condition: 200 °C, 50 bars, 350 rpm, 6:1 methanol:oil

Experiment No.	Catalyst	M.E. Content (wt%)	M.E. Yield (wt%)
1	-	42.9	41.0
2	ZrO_2	54.3	49.3
3	ZnO	83.2	77.5
4	$\text{SO}_4^{2-}/\text{SnO}_2$	88.3	80.6
5	$\text{SO}_4^{2-}/\text{ZrO}_2$	93.0	86.3
6	$\text{KNO}_3/\text{KL zeolite}$	82.3	77.2
7	$\text{KNO}_3/\text{ZrO}_2$	70.7	65.5

As shown in Table 4.4, $\text{SO}_4^{2-}/\text{ZrO}_2$ provides highest methylester content and yield at 93.0% and 86.3% respectively, followed by $\text{SO}_4^{2-}/\text{SnO}_2$, ZnO, $\text{KNO}_3/\text{KL-zeolite}$, $\text{KNO}_3/\text{ZrO}_2$ and ZrO_2 . It is interesting to note that the blank test (no added catalyst) of crude coconut oil transesterification gives higher methyl esters content and yield than the blank test from crude palm kernel oil.

4.3.3 Zirconia and Zinc Oxide

Zirconia (ZrO_2) catalyst possesses both acidic and basic properties. It has been used in several chemical reactions, such as hydrogenation, esterification, and etc. In this study, ZrO_2 exhibits the lowest catalytic activity because it gives the lowest methyl esters content and yield when compare to the other studied catalysts. It can catalyze the transesterification of crude palm kernel oil and crude coconut oil to yield only 64.5 wt% and 49.3 wt% of methyl esters, respectively.

On the other hand, ZnO has shown the potential to catalyze the transesterification of both crude palm kernel oil and crude coconut oil. Stern *et al.*(1999) patented ZnO and mixture of ZnO as the heterogeneous catalysts for the production of alkyl esters from vegetable oils or animal oils with alcohols. In this study, ZnO can give high methyl esters content upto 98.9 wt% for crude palm kernel oil transesterification and 83.2 wt% for crude coconut oil transesterification. Moreover, ZnO also give the highest amount of methyl esters yield for both crude palm kernel oil and crude coconut oil transesterification.

4.3.4 Sulfated Zirconia and Sulfated Stannous Oxide

Both of sulfated zirconia ($\text{SO}_4^{2-}/\text{ZrO}_2$) and sulfated stannous oxide ($\text{SO}_4^{2-}/\text{SnO}_2$) are considered as solid superacid, which have high acid strength. They can be prepared easily from methods described in other studies (Miao and Gao, 1997, and Chavan *et al.*, 1996). As expected, both of them show high catalytic activity for both types of oil. The amount of methyl esters produced from crude palm kernel oil is slightly greater than that from crude coconut oil. This may be due to the higher amount of free fatty acid and water content of coconut oil which may have an effect on the reaction.

Sulfated zirconia can be used as a heterogeneous catalyst for the transesterification to yield high methyl esters content and yield. When compare to the transesterification of crude palm kernel oil and crude coconut oil catalyzed by ZrO_2 , the methyl esters produced from SO_4^{2-}/ZrO_2 is much higher than that from unsulfated ZrO_2 .

Sulfated stannous oxide is another solid superacid which can be used as catalyst for transesterification. It was first develop by Chavan *et al.* (1996) for use in the transesterification of ketoesters. In this study, to evaluate its catalytic activity, it was applied to catalyze the crude palm kernel oil and crude coconut oil transesterification. From the results, SO_4^{2-}/SnO_2 shows relatively high activity. Methyl esters content and yield of about 95.4 wt% and 90.3 wt% are obtained in case of crude palm kernel oil and 88.3 wt% and 80.6 wt% are received in case of crude coconut oil, respectively. This demonstrates that SO_4^{2-}/SnO_2 can be used as a heterogeneous catalyst for crude palm kernel oil and crude coconut oil transesterification.

4.3.5 KL-zeolite impregnated by Potassium Nitrate and Zirconia-supported Potassium Nitrate

KNO_3 /KL zeolite used in the experiments was prepared by impregnating 21 wt% (base on weight of KL zeolite) of KNO_3 onto KL zeolite, which was found to exhibit the highest basic strength (Wang *et al.*, 2000). Because of its high basic strength, it can catalyze the reaction and gives high methyl esters content and yield for both crude palm kernel oil and crude coconut oil.

Zirconia-supported potassium nitrate is another catalyst which has high basic strength (Zhu *et al.*, 1996). From the transesterification results, it can be used as a heterogeneous catalyst for the transesterification of crude palm kernel oil and crude coconut oil since it can catalyze the reactions effectively to yield 78.3 wt% and 70.7 wt% of methyl esters content in case of crude palm kernel oil and crude coconut oil, respectively.

Many of the investigated solid catalysts show high potential to be used as the heterogeneous catalysts for the vegetable oils transesterification. Although they give a little lower amount of methyl esters when compare to

homogeneous catalyst, catalyst separation step will be simplified when heterogeneous catalyst is used. They could replace the homogeneous catalyst in the vegetable oils transesterification with methanol. Among them, $\text{SO}_4^{2-}/\text{ZrO}_2$ and $\text{SO}_4^{2-}/\text{SnO}_2$ exhibit the highest catalytic activity to catalyze the crude palm kernel oil and coconut oil transesterification. High methyl esters content and yield can be obtained when $\text{SO}_4^{2-}/\text{ZrO}_2$ and $\text{SO}_4^{2-}/\text{SnO}_2$ are used as the heterogeneous catalysts. It is interesting to investigate the parameters affecting the vegetable oils transesterification catalyzed by $\text{SO}_4^{2-}/\text{ZrO}_2$ and $\text{SO}_4^{2-}/\text{SnO}_2$ solid superacids. Since $\text{SO}_4^{2-}/\text{ZrO}_2$ shows better catalytic effect than $\text{SO}_4^{2-}/\text{SnO}_2$, therefore, $\text{SO}_4^{2-}/\text{ZrO}_2$ is selected for further investigation.

4.4 Vegetable Oils Transesterification Catalyzed by $\text{SO}_4^{2-}/\text{ZrO}_2$

Sulfated zirconia ($\text{SO}_4^{2-}/\text{ZrO}_2$) is then studied for transesterification of crude palm kernel oil and crude coconut oil. First, the reaction time is varied in order to find the optimized reaction time for transesterification. Second, the amount of $\text{SO}_4^{2-}/\text{ZrO}_2$ is varied to find the optimum amount of solid catalysts. Finally, the preliminary study of re-used catalysts is reported.

4.4.1 Effect of reaction time on transesterification catalyzed by $\text{SO}_4^{2-}/\text{ZrO}_2$

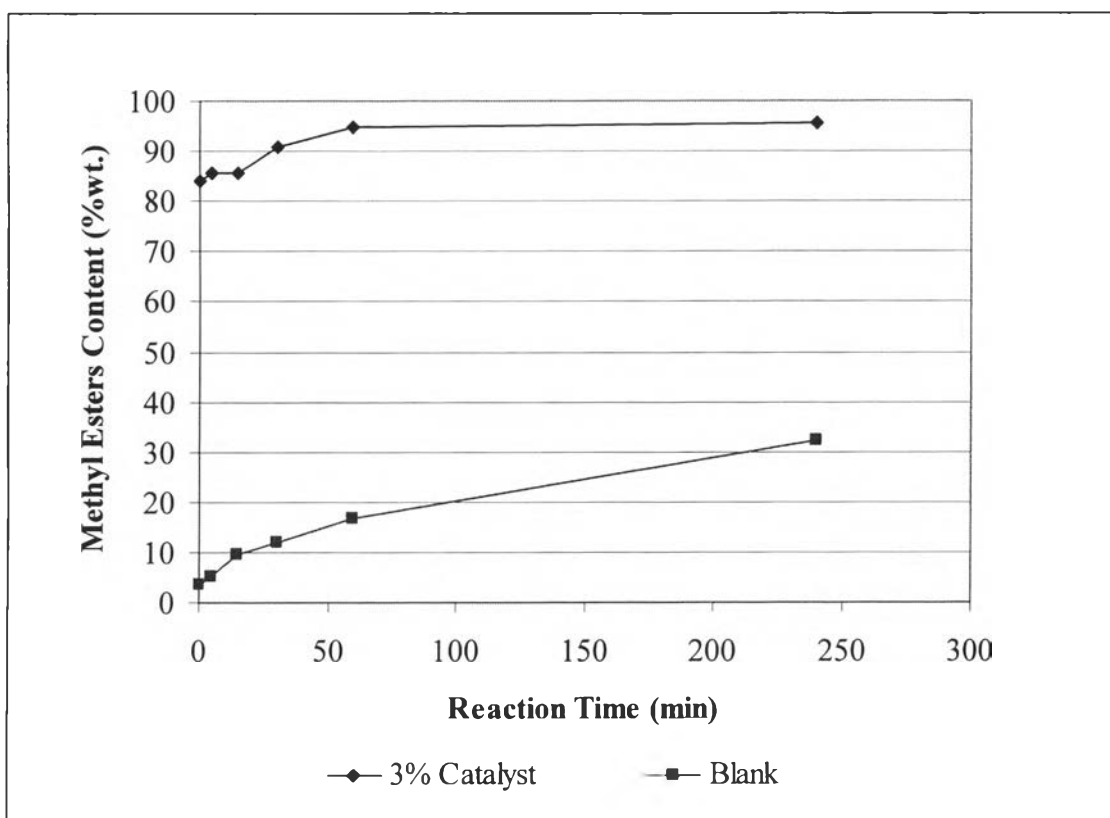
The results of catalytic and non-catalytic crude palm kernel oil transesterification are shown in Table 4.5 and Figure 4.1, which the methyl esters content is plotted as a function of reaction time.

The methanol to oil molar ratio was kept constant at 6 to 1. Initially, the mixture of reactants and solid catalyst was at room temperature and it was then heated to desired reaction temperature at 200°C. The heating period is 15 minutes.

Table 4.5 Catalytic and non-catalytic transesterification of crude palm kernel oil

Condition: 200 °C, 50 bars, 350 rpm, 6:1 methanol:oil

Time	Methyl Ester Content (%wt.)	
	3% SO ₄ ²⁻ /ZrO ₂	Blank
0	84.1	3.7
5	85.5	5.3
15	85.7	9.5
30	91.0	11.9
60	95.0	16.7
240	95.8	32.3

**Figure 4.1** Effect of reaction time on catalytic and non-catalytic transesterification of crude palm kernel oil.

Interestingly, 84.1 wt% of methyl esters is already observed after heating the mixture from room temperature to 200°C in the test that contains $\text{SO}_4^{2-}/\text{ZrO}_2$. However, for the blank run, only 3.7 wt% of methyl esters is observed. These results indicate that the presence of the $\text{SO}_4^{2-}/\text{ZrO}_2$ catalyst significantly increases the rate of the transesterification.

After the reactor's temperature reaches the desired temperature, the methyl esters content increases slowly with increasing reaction time for both catalytic and non-catalytic reaction. At 60 min, 95.0 wt% of methyl esters is produced from catalytic reaction, while non-catalytic reaction has methyl esters content only 16.7 wt%.

After 60 min, the amount of methyl esters produced from catalytic reaction seems to be constant at around 95 wt%. This may be explained by the fact that the reaction has reached the equilibrium or the catalyst has deactivated. Another possible reason is that the rate constants for the conversion of di- and monoglycerides to monoglycerides and glycerol is very low when compare to the rate constants for conversion of triglycerides to diglycerides (Boocock *et al.*, 1998). Therefore, further investigations are needed to examine the reason for that phenomenon. In case of non-catalytic reaction, however, methyl esters content still increases slowly with increasing reaction time.

The crude coconut oil transesterification catalyzed by $\text{SO}_4^{2-}/\text{ZrO}_2$ was also performed to study the effect of the reaction time on the methyl esters content. The results are reported in Table 4.6 and Figure 4.2.

Table 4.6 Crude palm kernel oil and crude coconut oil transesterification catalyzed by $\text{SO}_4^{2-}/\text{ZrO}_2$

Condition: 200 °C, 50 bars, 350 rpm, 6:1 methanol:oil

Time	Methyl Ester Content (%wt.)	
	Crude palm kernel oil	Coconut Oil
0	84.1	82.9
5	85.5	86.9
15	85.7	88.0
30	91.0	89.0
60	95.0	92.8
240	95.8	93.0

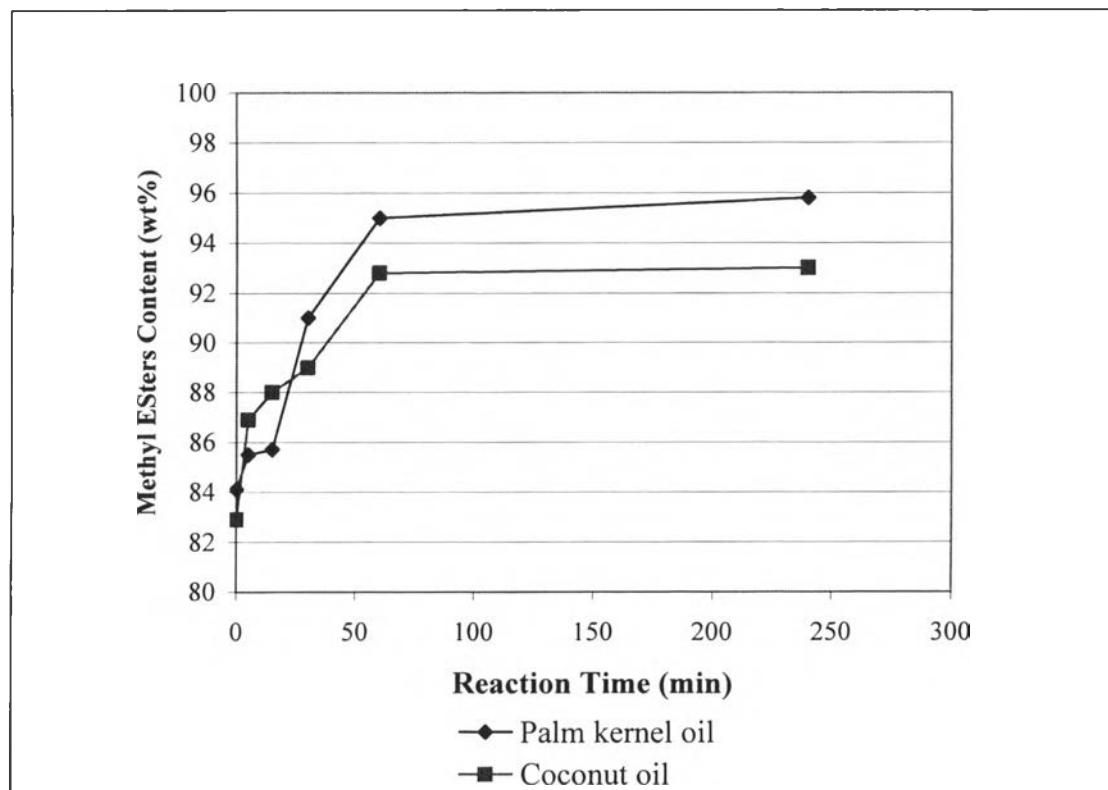


Figure 4.2 Effect of reaction time on transesterification of crude palm kernel oil and crude coconut oil.

As shown in Figure 4.2, the transesterification of crude coconut oil catalyzed by $\text{SO}_4^{2-}/\text{ZrO}_2$ shows the similar trend as in case of crude palm kernel oil transesterification. After the temperature reaches 200 °C, up to 82.9 wt% of methyl esters is achieved when $\text{SO}_4^{2-}/\text{ZrO}_2$ is used as the catalyst. This indicates that high amount of coconut methyl esters is also produced during the heating period, which is absolutely due to the high activity for transesterification of $\text{SO}_4^{2-}/\text{ZrO}_2$. The methyl esters content reaches 92.8 wt% at reaction time 60 minutes and the methyl esters content is relatively constant after this reaction period. This may be explained by the fact that the reaction has reached the equilibrium or the catalyst has deactivated. However, the methyl esters produced from crude palm kernel oil was slightly higher than that from crude coconut oil. This is probably due to the higher amount of free fatty acid and water content of coconut oil which may have an effect on the reaction.

It has been shown that $\text{SO}_4^{2-}/\text{ZrO}_2$ can be used as an effective heterogeneous catalyst for transesterification of both crude palm kernel oil and crude coconut oil. This solid can catalyze the reaction to yield methyl esters more than 90 wt% after a sufficient time (about 1 hour) and amount of added solid catalyst of 3% by wt. Therefore, it is interesting to further investigate the effect of the amount of added catalyst and the possibility to reuse the spent catalyst.

4.4.2 Effect of the amount of added $\text{SO}_4^{2-}/\text{ZrO}_2$ on transesterification

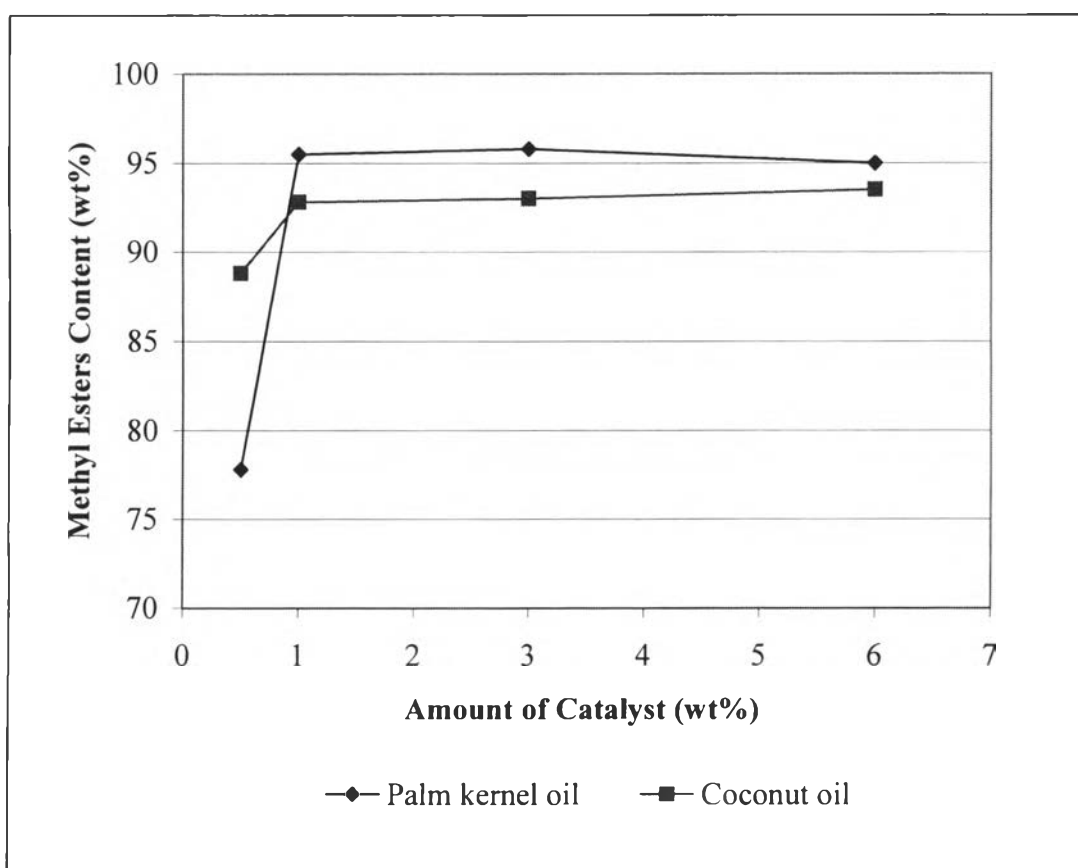
For homogeneous catalysts, it has been revealed that the amount of catalyst has a strong influence on the conversion of vegetable oil to ester (Freedman *et al.*, 1984, Fangrui, 1999, and Srivastava and Prasad, 2000). Therefore, the effect of the amount of $\text{SO}_4^{2-}/\text{ZrO}_2$ on transesterification of crude palm kernel oil and crude coconut oil is studied. The reaction was carried out with a methanol:oil molar ratio of 6:1, under nitrogen atmosphere at pressure of 50 bars, at temperature 200°C and the stirrer speed of 350 rpm.

The effect of the amount of $\text{SO}_4^{2-}/\text{ZrO}_2$ on the methyl esters content are shown Table 4.7 and plotted in Figure 4.3.

Table 4.7 Effect of amount of $\text{SO}_4^{2-}/\text{ZrO}_2$ on methyl esters content

Condition: 200 °C, 50 bars, 350 rpm, 6:1 methanol:oil

Amount of Catalyst (wt%)	Methyl Ester Content (%wt)	
	Crude palm kernel oil	Coconut Oil
0.5	77.8	88.8
1	95.5	92.8
3	95.8	93.0
6	95.0	93.5

**Figure 4.3** Effect of amount of $\text{SO}_4^{2-}/\text{ZrO}_2$ on methyl esters content.

In case of crude palm kernel oil, after 4 hours, 77.8 wt% of methyl esters are obtained when only 0.5 wt% of $\text{SO}_4^{2-}/\text{ZrO}_2$ is used. However, when 1 wt% of $\text{SO}_4^{2-}/\text{ZrO}_2$ is added, much higher methyl esters content (95.5 wt%) can be achieved. Moreover, the methyl esters content produced by 3 wt% and 6 wt% of $\text{SO}_4^{2-}/\text{ZrO}_2$ are 95.8 wt% and 95.0 wt%, respectively. It is interesting to note that the amount of ester is significantly increased when the amount of catalysts is increased from 0.5 wt% to 1 wt%. However, if the amount of $\text{SO}_4^{2-}/\text{ZrO}_2$ is added beyond 1 wt%, the methyl esters content is relatively constant.

For crude coconut oil, the results are strikingly similar as the results from crude palm kernel oil. The amount of methyl esters (88.8 wt%) is obtained when 0.5 wt% of catalyst is added. When 1 wt% of catalysts is used, the methyl esters content is increased to 92.8 %, and when 3 wt% and 5 wt% of $\text{SO}_4^{2-}/\text{ZrO}_2$ are added, the methyl esters respectively are 93.0% and 93.5%.

It can be concluded that 1 wt% of $\text{SO}_4^{2-}/\text{ZrO}_2$ (based on weight of vegetable oil) is sufficient enough to catalyze the transesterification of crude palm kernel oil and crude coconut oil. It is probable that, when more than 1 wt% of $\text{SO}_4^{2-}/\text{ZrO}_2$ is used, the maximum methyl ester content is probably limited by the equilibrium of transesterification, since the amount of ester is relatively constant after more than 1 wt% of $\text{SO}_4^{2-}/\text{ZrO}_2$ is added.

4.4.3 Re-use of $\text{SO}_4^{2-}/\text{ZrO}_2$ catalyst

The spent $\text{SO}_4^{2-}/\text{ZrO}_2$ catalyst obtained from transesterification of crude palm kernel oil with 3 wt% catalyst and 4 hours reaction time is tested to determine whether $\text{SO}_4^{2-}/\text{ZrO}_2$ catalyst obtained by filtering is fully deactivated. The used $\text{SO}_4^{2-}/\text{ZrO}_2$ catalyst is recovered by filtering the product mixture with nylon membrane filter. The recovered catalyst is then dried at 100°C and directly added to the reactor to test for crude palm kernel oil transesterification.

As shown in Table 4.8, the reaction catalyzed by spent $\text{SO}_4^{2-}/\text{ZrO}_2$ yields only 27.7 wt% of methyl esters content, which is close to methyl esters content produced by non-catalytic reaction and is much lower than methyl esters produced by fresh $\text{SO}_4^{2-}/\text{ZrO}_2$. This indicates that the spent $\text{SO}_4^{2-}/\text{ZrO}_2$ is fully

deactivated and cannot be directly reused for transesterification without further treatment.

Table 4.8 Comparison between fresh catalyst and spent catalyst

Condition: 200 °C, 50 bars, 350 rpm, 6:1 methanol:oil

Experiment No.	Catalyst	Methyl Esters Content (wt%)
1	-	32.3
2	Fresh $\text{SO}_4^{2-}/\text{ZrO}_2$	95.8
3	spent $\text{SO}_4^{2-}/\text{ZrO}_2^*$	27.7
4	spent $\text{SO}_4^{2-}/\text{ZrO}_2^{**}$	95.9

* Spent $\text{SO}_4^{2-}/\text{ZrO}_2$ catalyst from crude palm kernel oil transesterification.

** Spent $\text{SO}_4^{2-}/\text{ZrO}_2$ catalyst from crude palm kernel oil transesterification with catalyst regeneration.

However, if the spent $\text{SO}_4^{2-}/\text{ZrO}_2$ is regenerated by immersion the spent catalyst in a 0.5 M H_2SO_4 solution for 30 min, filtered, and dried at 110°C for 24 hours to form the sulfated sample ($\text{SO}_4^{2-}/\text{ZrO}_2$) again. The regenerated catalyst is calcined at 500°C for 2 hours prior to use. As expected, the regenerated $\text{SO}_4^{2-}/\text{ZrO}_2$ give high amount of methyl esters content (95.9 wt%) as in the case of freshly prepared $\text{SO}_4^{2-}/\text{ZrO}_2$ catalyst (95.9 wt%). This shows that the spent $\text{SO}_4^{2-}/\text{ZrO}_2$ from transesterification can be easily regenerated and results in the same activity as in fresh catalyst.

4.5 Effect of Nitrogen

In previous sections, all experiments are carried out under nitrogen atmosphere at pressure of 50 bars. In order to investigate whether the nitrogen has any effect on the transesterification, the reaction is carried out under its own generated pressure. From previous section, it is known that 1% of $\text{SO}_4^{2-}/\text{ZrO}_2$

catalyst is efficient to catalyze the reaction, so only 1% of catalyst was used. The results are shown in Table 4.9.

Table 4.9 Effect of nitrogen gas on the transesterification

Condition: 200 °C, 50 bars, 350 rpm, 6:1 methanol:oil

Condition	Methyl Esters Content (wt%)	
	Crude palm kernel oil	Coconut Oil
Presence of N ₂ (50bars)	95.5	92.0
Absence of N ₂	89.0	92.0

As reported in Table 4.9, the methyl esters produced from crude palm kernel oil transesterification under nitrogen atmosphere is slightly greater than that in the absence of nitrogen gas. In case of coconut oil, however, the amount of methyl esters produced is similar for both in the presence and absence of nitrogen.

From the results, it can be concluded that nitrogen has no effect on the methyl esters content because the amount of methyl esters produced from the reaction in the presence of nitrogen is not significantly different from the results from the absence of nitrogen.