CHAPTER IV

RESULTS AND DISCUSSION

4.1 Synthesis of biodiesel from crude palm oil

The crude palm oil obtained from Thai Eastern Group CO., Ltd. was used for the synthesis of the biodiesel. The compositions of fatty acids of crude palm oil are also analyzed using AOAC method (AOAC 969.33) and the results indicated that the palm oil contained palmitic acid and oleic acid as major component (Table 4.1).

Table 4.1 Compositions of fatty acids in crude palm oil (See details in Appendix C)

Fatty acid composition	% of total fatty acids
Lauric acid, C12:0	4.9
Myristic acid, C14:0	2.1
Palmitic acid, C16:0	36.6
Stearic acid, C18:0	3.9
Oleic acid, C18:1	41.5
Linoleic acid, C18:2	9.3
Linolenic acid, C18:3	0.2
Others	1.5

Normally, there are two grades of commercial palm oil including high grade palm oil and low grade palm oil. The high grade contains 5% of FFAs while the low grade contains 10-20% of FFAs. Because the FFAs content of the palm oil analyzed by ASTM D-5555 prior to use was 7.782%, the palm oil was low grade palm oil. The biodiesel was prepared by transesterification of palm oil and methanol using sodium hydroxide as a catalyst. During the transesterification process the conversion of palm oil was monitored by Thin Layer Chromatography (TLC). The fatty acid methyl esters were monitored by iodine vapor and vanillin/H_2SO_4 as a spot at R_f value of 0.40. The transesterification process was carried out at five different ratios as shown

in Table 4.2. It found that the transesterification at 50°C for 1.5 h gave high yield (94.22%) when the ratio of oil:methanol was 1:16.

Table 4.2 Molar ratio converts crude palm oil as palm oil methyl ester via base-catalyzed process (adsorption time = 1.5 h and temperature = 50°C)

Molar ratio (Oil : CH₃OH)	Result	% biodiesel
1 : 3	Incomplete reaction	0
1 : 6	Incomplete reaction	0
1 : 10	Incomplete reaction	0
1 : 16*	Complete reaction	94.22
1 : 19	Complete reaction	80.14

Note: (*) is the condition to produce methyl ester.

Incomplete reaction produced soap.
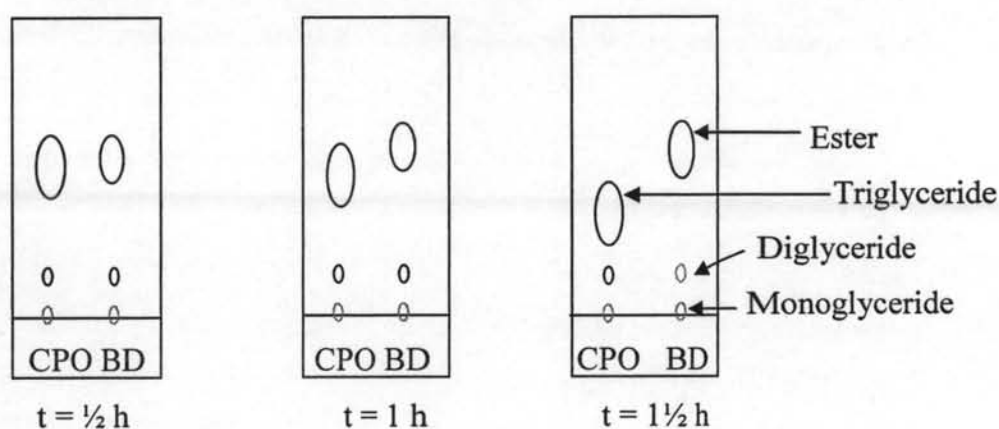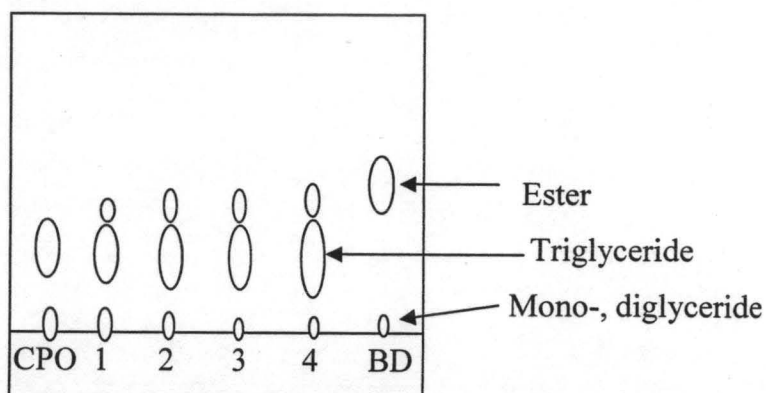

CPO: Crude palm oil

BD: Biodiesel (Methyl ester)

Mobile phase: a mixture of hexane, ethyl acetate and acetic acid (90:10:1 v/v)

Stationary phase: TLC aluminium sheet, silica gel 60 F_{254}

Figure 4.1 Reproductive TLC of methyl ester which synthesized with base-catalyzed process

Due to high FFAs in palm oil, the production of biodiesel was tested using 2-step process, acid catalyzed process and then base catalyzed process. The TLC results were showed in Figure 4.2. In initial process was esterification to reduce FFAs reaction before to produce biodiesel, but the reaction was slow. Then, the second process was transesterification to produce biodiesel.

Where CPO: Crude palm oil

    BD: Biodiesel (Methyl ester)

      1: Adsorption time of methyl ester via acid-catalyzed process 1 h.

      2: Adsorption time of methyl ester via acid-catalyzed process 2 h.

      3: Adsorption time of methyl ester via acid-catalyzed process 3 h.

      4: Adsorption time of methyl ester via acid-catalyzed process 4 h.

Mobile phase: a mixture of hexane, ethyl acetate and acetic acid (90:10:1 v/v)

Stationary phase: TLC aluminium sheet, silica gel 60 F_{254}

Figure 4.2 Reproductive TLC of methyl ester which synthesized with 2-step catalyzed process

The results of synthesized methyl ester both base-catalyzed process and 2-step process were showed in Table 4.3. The base-catalyzed process was required a large excess of methanol although the yield of product is rather high and short adsorption time. It was observed that when molar ratio of crude palm oil:methanol is 1:19, %yield was decreased. This might be due to the excess methanol which dissolved methyl ester. This was washed out with water. In comparison of one step process and the 2-step process the methyl ester obtained from the 2-step process contained less FFAs.

Table 4.3 Yields (%) of the synthetic methyl ester from palm oil by base–catalyzed process and two-step process

Exp	Temp(°C)	CPO:MeOH	Catalyst	Time (h)	Yield (%)	% FFAs
1	50	1 : 3	NaOH	1.5	0	0
2	50	1 : 6	NaOH	1.5	0	0
3	50	1 : 16	NaOH	1.5	94.22	0.184 ± 0.002
4	50	1 : 19	NaOH	1.5	80.14	0.184 ± 0.004
5	80	1 : 10	H_2SO_4	4	86.69	0.060 ± 0.003
(2 steps)	50	1 : 6	NaOH	1		

Additionally the methyl ester was confirmed by analysis of ^1H and ^{13}C NMR. ^1H and ^{13}C NMR of the palm oil and the palm oil methyl esters were showed in Figures 4.3a, 4.3b, 4.3c and 4.3d.
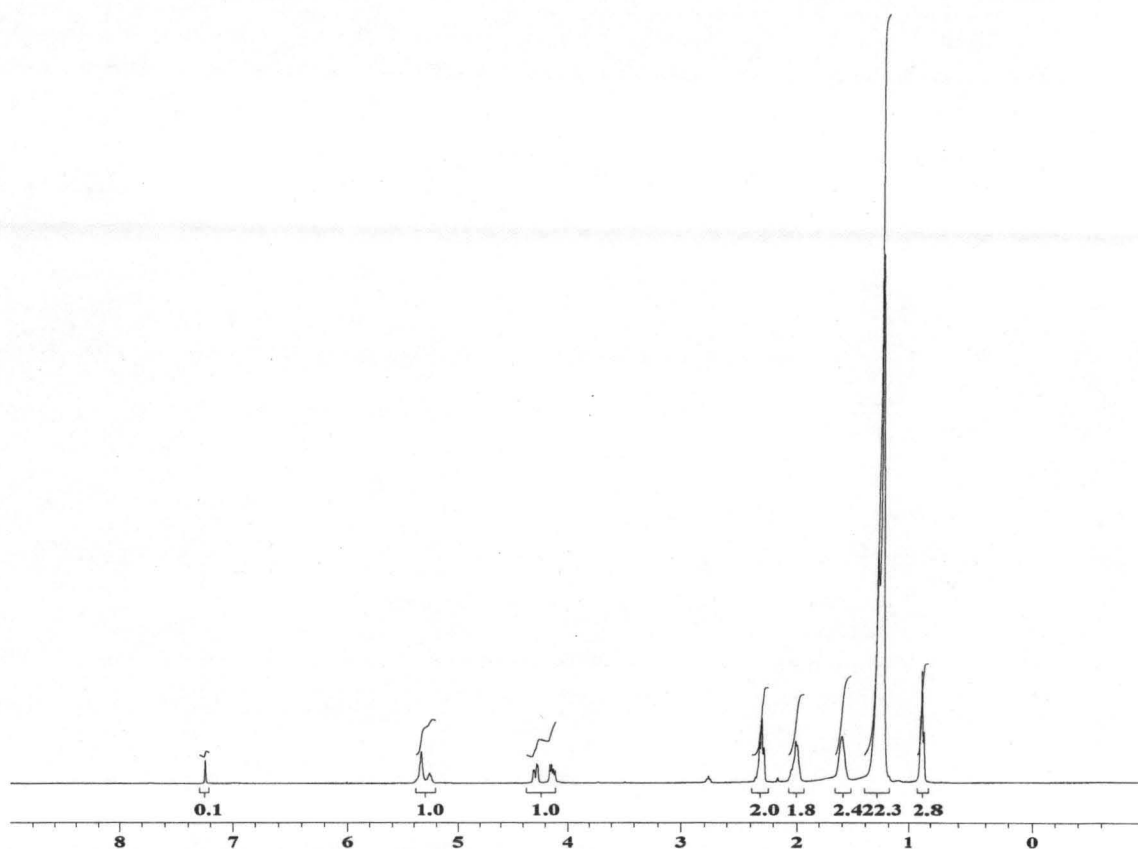
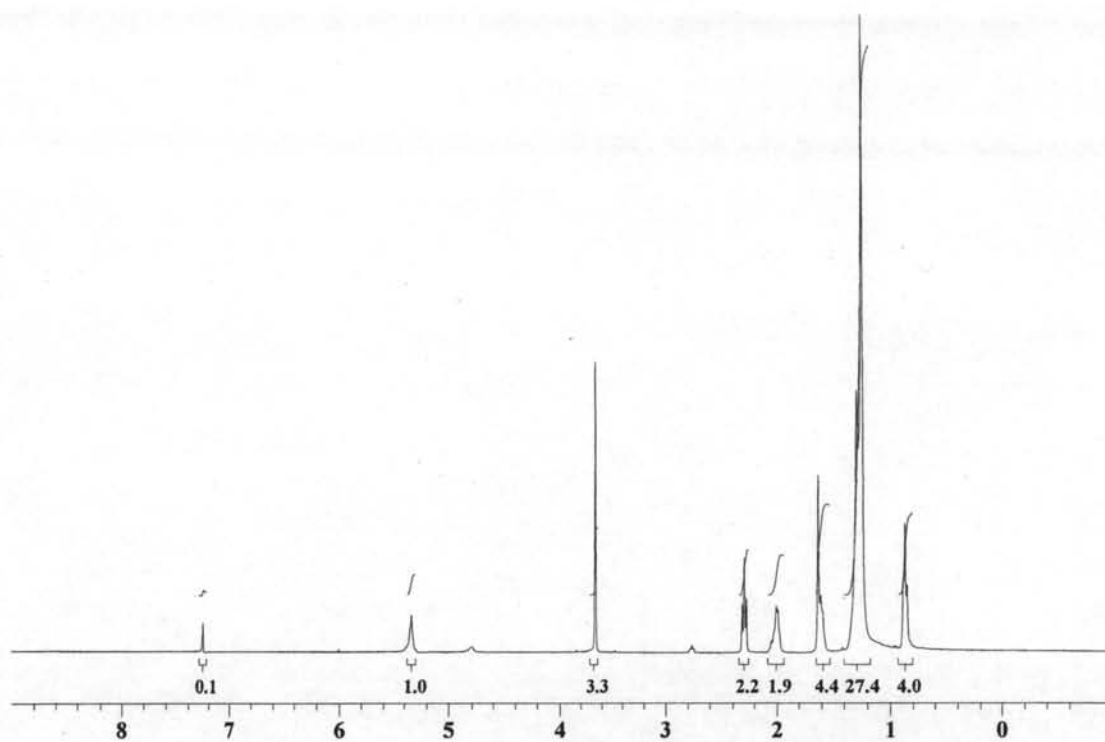**Figure 4.3a** ^1H NMR spectrum of the palm oil in $CDCl_3$

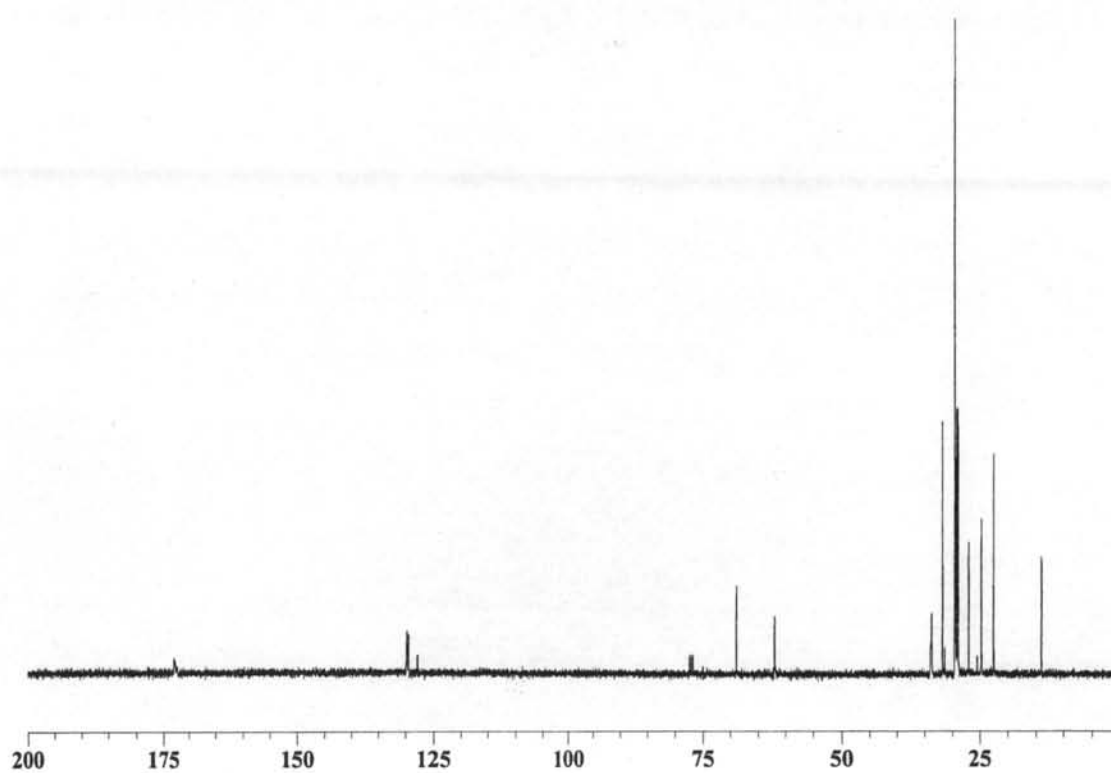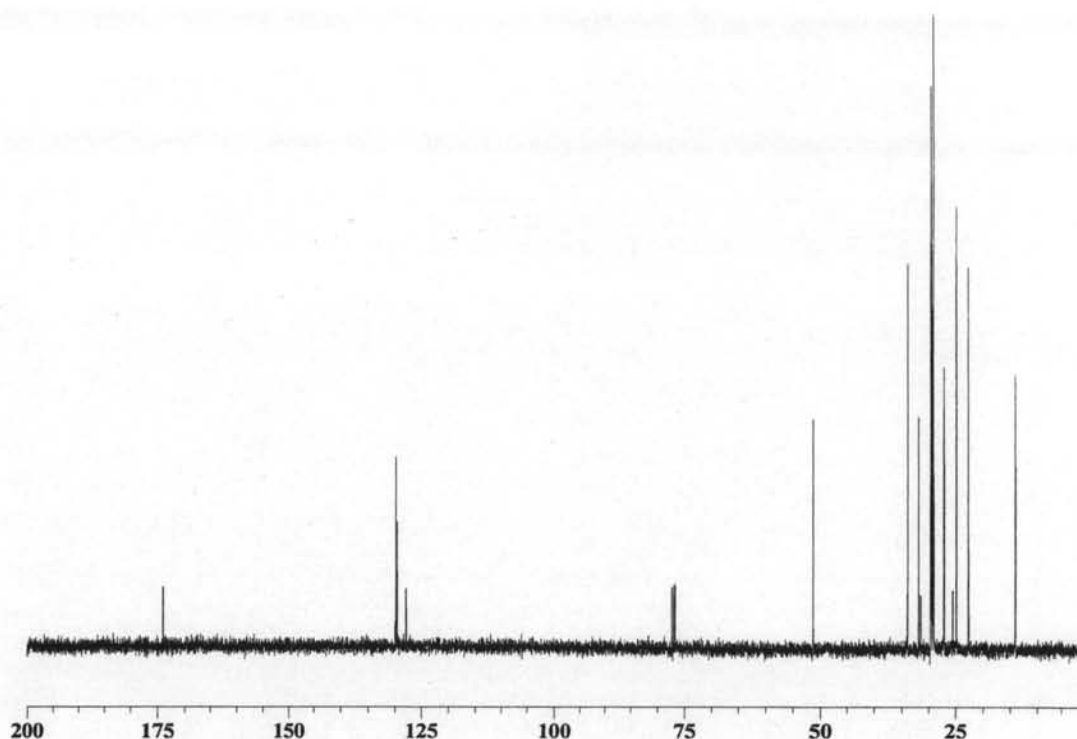**Figure 4.3b** ^{1}H NMR spectrum of the palm oil methyl ester in CDCl$_3$

Figure 4.3c ^{13}C-NMR spectrum of the palm oil in CDCl$_3$

Figure 4.3d ^{13}C-NMR spectrum of the palm oil methyl ester in CDCl$_3$

In comparison of the ^{1}H-NMR spectra of the palm oil methyl esters (Figure 4.3b) and the palm oil (Figure 4.3a), a presence of the methoxy protons at δ_H 3.66 in the ^{1}H NMR spectrum of the palm oil methyl ester indicated that the biodiesel comprised most of the FAMEs.

From the ^{13}C-NMR spectrum of palm oil methyl ester (Figure 4.3d) the signals of the carbon of glycerol moiety at δ_C 62.0 and δ_C 68.9 were absented, and those signals were replaced by a signal of the carbon of methoxy group at δ_C 51.4.

The methyl ester content of palm oil methyl ester was also analyzed using the integration of the methoxy protons at δ_H 3.66 and the methylene protons adjacent to carbonyl at δ_H 2.29 in the ^{1}H NMR spectrum. It was found that the ester content was 96.40%.

Moreover, the fatty acid composition of the methyl ester was analyzed using GC-MS. The GC chromatogram was presented in Appendix D and the fatty acid compositions of the methyl ester were summarized in Table 4.4.

Table 4.4 Summarized GC-MS of palm oil methyl ester via base-catalyzed process

Peak no.	Name of fatty acid	Retention time (min.)	Area (%)
2	Lauric acid, C12:0	5.62	4.92
3	Myristic acid, C14:0	9.79	2.47
4	Palmitic acid, C16:0	14.52	37.87
5	Linoleic acid, C18:2	18.36	8.77
6	Oleic acid, C18:1	18.53	41.37
8	Stearic acid, C18:0	19.10	4.60

The physical properties of synthesized methyl ester obtained from the base-catalyzed process were analyzed and the results were showed in Table 4.5.

Table 4.5 Physical properties of the methyl ester obtained from the base-catalyzed process

Properties	Methyl ester	Limits	Method
% Methyl ester, %wt	92.6	96.5	EN 14103
Viscosity at 40 °C, mm^2/s	4.3	3.5-5.0	ASTM D445
Flash Point, °C	142	>120	ASTM D93
Carbon residue, %wt	0.0004	<0.30	ASTM D4530
Total moisture, %wt	0.1081	<0.050	ASTM D5530
Group I metals (Na+K), mg/kg	2.4	<5.0	ASTM D5185
Group II metals (Ca+Mg), mg/kg	3.73	<5.0	ASTM D5185
Phosphorus, mg/L	2.68	<10.0	ASTM D5185

4.2 Determination of FFAs content in me
thyl ester

The FFAs content of the synthesized biodiesel was analyzed according to ASTM D5555 after it was adsorbed with basic alumina, at temperature 30°C with various weights of basic alumina and adsorption time. The results were showed in Table 4.6 and Figure 4.4.

Table 4.6 Content of FFAs in methyl ester after adsorbed with basic alumina (at 30°C)

Time (min.)	Weight of alumina	%FFAs remaining
	0% wt	0.184
set 1 10 min	1% wt	0.062
	2% wt	0.047
	3% wt	0.035
	4% wt	0.025
set 2 20 min	1% wt	0.055
	2% wt	0.042
	3% wt	0.030
	4% wt	0.022
set 3 30 min	1% wt	0.055
	2% wt	0.040
	3% wt	0.025
	4% wt	0.020
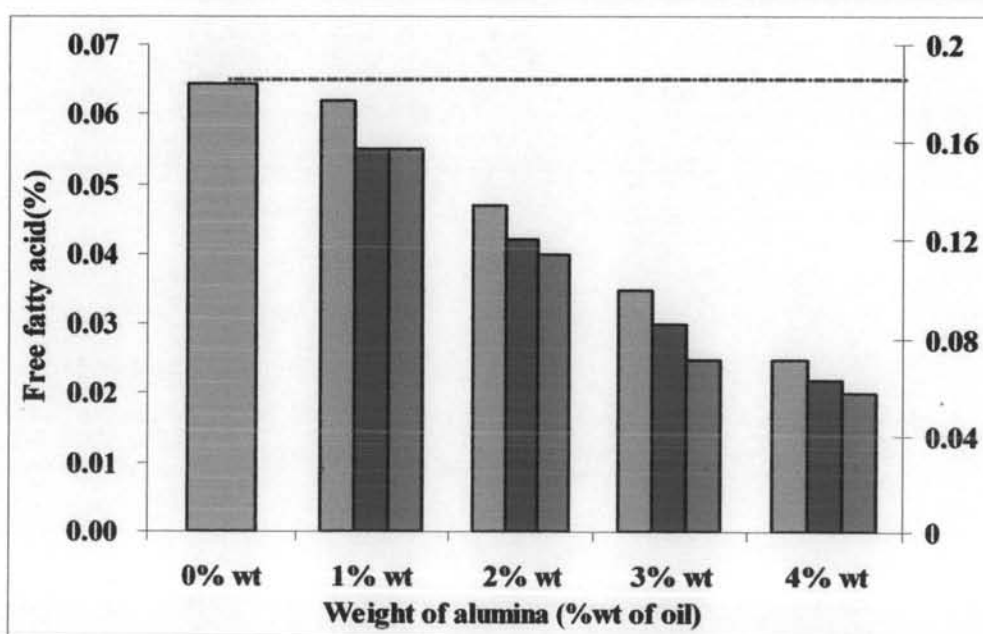
Figure 4.4 Diagram of FFAs in methyl ester after adsorbed with basic alumina

From Table 4.6 it was found that the FFAs content of the palm oil methyl ester was reduced to 0.020% when basic alumina 4.0% weight of oil was used as adsorbent at 30°C for 30 min. The higher amount of alumina was increased, the FFAs remaining was increased more, when magnesol, activated carbon (powder), activated carbon (granule), molecular sieve, bentonite and NaOH treated bentonite (4.0% wt/wt of oil) were used as adsorbents at 30°C for 30 min. The results were shown in Table 4.7 and Figure 4.5.

From Table 4.7 it was found that FFAs content of the palm oil methyl ester adsorbed by activated charcoal (powder form), magnesol and basic alumina were about 0.02%. However, this investigation was showed the compared results of activated charcoal and magnesol. Also, effect of temperatures was studied as shown in Table 4.8 and Figure 4.6. It was found that the temperature effected the adsorption. The FFAs content was decreased when the temperature was increased. The adsorption was exothermic reaction; the rate of adsorption was increased, although adsorption capacity was decreased with increasing temperature. In contrary, if decreasing temperature was gave decreasing the rate of adsorption and adsorption capacity was increased [54]. Furthermore, color of the palm oil methyl ester adsorbed by the activated charcoal (powder) was pale yellow while color of the palm oil methyl ester adsorbed by others were the same as before adsorption.

Table 4.7 Results of treatments with different adsorbents on the FFAs of methyl ester. (At 30°C, 4.0% weight of adsorbent and adsorption time 30 min)

Adsorbent	% Weight of oil remaining	%FFA ASTM D5555	%Methyl ester (from ^{1}H NMR)**	Appearance
None	-	0.184 ± 0.002	93.66	orange-red liquid
Magnesol	91.07	0.021 ± 0.001	93.79	orange-red liquid
Alumina	95.91	0.028 ± 0.002	92.28	orange-red liquid
Activated charcoal (powder)	92.66	0.023 ± 0.004	95.24	yellow liquid
Activated charcoal (granule)	95.64	0.088 ± 0.004	94.39	lightly orange-red liquid
Molecular sieves	96.18	0.086 ± 0.006	94.29	orange-red liquid
Bentonite standard (std.)	95.26	0.088 ± 0.004	95.93	orange-red liquid
Bentonite standard (NaOH)	95.33	0.091 ± 0.001	92.50	orange-red liquid

Note: The ^{1}H-NMR spectra of each adsorbent are showed in Appendix D.

** Calculation of the yield of transesterification as shown in Appendix B.
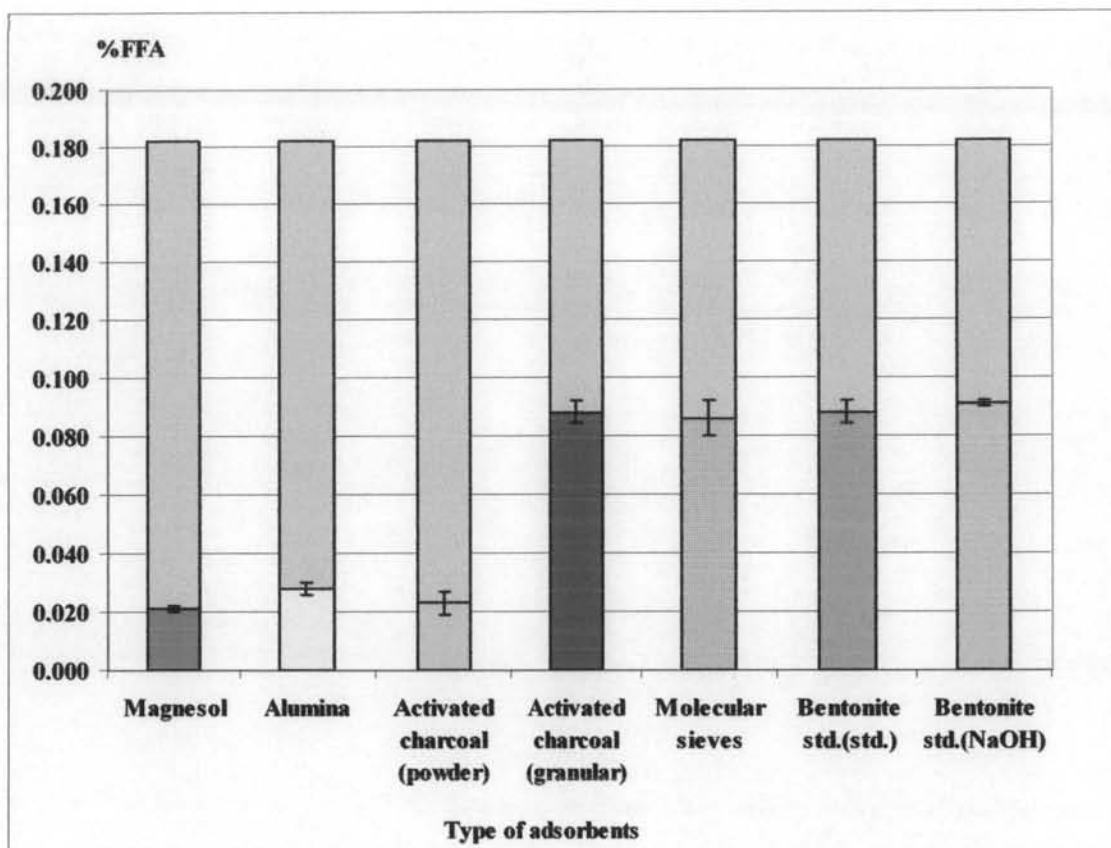
Figure 4.5 Diagram of FFAs after adsorbed with different adsorbents

Table 4.8 Effect of temperature on the FFAs adsorption of activated charcoal
(powder form)

Temperature (^{o}C)	%FFAs
30	0.023 ± 0.004
40	0.019 ± 0.002
50	0.015 ± 0.000
60	0.014 ± 0.002
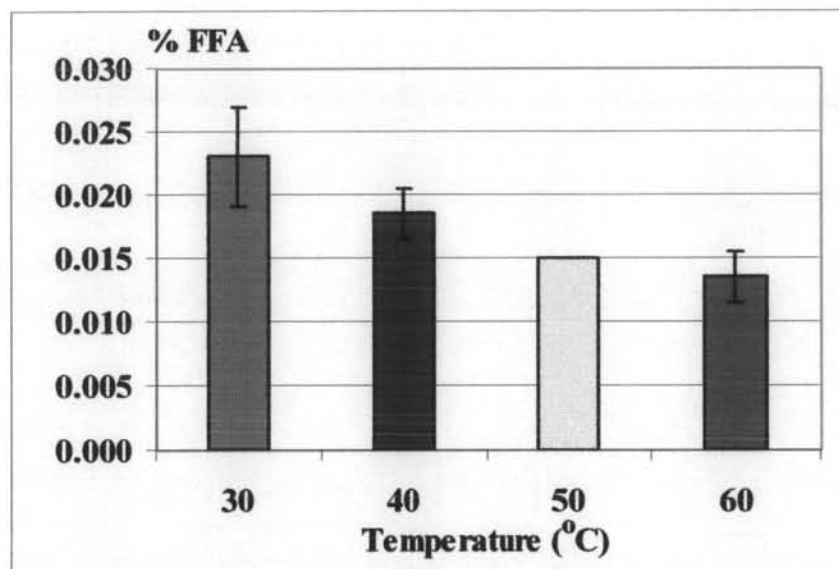
Figure 4.6 % FFAs after the treatment with activated charcoal (powder form) at various temperatures

The activated charcoal (powder form) can adsorb phospholipids, color bodies, metal ions associated with FFAs in micellar or other complex forms) [56], levels of other contaminants including metal group IA and IIA, color and moisture were also determined.

4.3 Determination of metal contents in methyl ester

The metal content in methyl ester was found to be metal group IA and IIA in periodic chart of the elements such as potassium (K), magnesium (Mg), calcium (Ca) and sodium (Na) as well as phosphorus. The inductively Coupled Plasma Emission Spectrometer (ICP-AES spectrometer) was use for analysis of metal content according to ASTM D5185. The result of magnesol and activated charcoal treated methyl ester were shown in Table 4.9.

Table 4.9 The metal contents were adsorbed activated charcoal (powder form) in methyl ester via base-catalyzed process

Metal Sample	Ca	P	Na	Mg	K
Methyl ester, mg/L	2.21	2.68	2.40	1.52	Nil
Methyl ester adsorbed with magnesol, mg/L	Nil	Nil	Nil	Nil	Nil
Methyl ester adsorbed with activated charcoal (powder), mg/L	Nil	Nil	Nil	Nil	Nil

From Table 4.9, all of metals were adsorbed by magnesol and activated charcoal. Therefore, activated charcoal could be used efficiently as compared with magnesol.

4.4 Determination of total moisture content in methyl ester

The determination of total moisture in methyl ester by Karl Fischer Coulometer with HYDRANAL® - Coulomat AG-H as reagent (ASTM D5530) was shown in Table 4.10.

Table 4.10 Comparative total moisture content in methyl ester obtained from the base-catalyzed process after the treatment with activated charcoal (powder form) at 60°C and 30 min

Sample	Weight of sample injected (g)		Total moisture content (%wt)		Avg. total moisture content (%wt)
	Rep. 1	Rep. 2	Rep. 1	Rep. 2	
Base-catalyzed methyl ester	0.7786	0.7877	0.1230	0.0931	0.1081 ± 0.0211
Base-catalyzed methyl ester after the treatment with magnesol	0.8220	0.7335	0.0814	0.0625	0.0720 ± 0.0137
Base-catalyzed methyl ester after the treatment with activated charcoal	0.7791	0.7872	0.0500	0.0455	0.0478 ± 0.0032

According to total moisture content in Table 4.10, it could be concluded that magnesol and activated charcoal can adsorb moisture in methyl ester. As the results, the moisture content was reduced up to 66.60% by magnesol and 44.22% by activated charcoal (powder form).

4.5 BET Surface Analysis

From the activated charcoal was determined with BET surface area analyzer, the results of surface area was shown in Table 4.11.

Table 4.11 Comparison of surface area from magnesol and activated charcoal (powder form) by BET Surface Area Analyzer

Adsorbents	Before	After
Magnesol		
- BET Surface Area, sq.m/g	26.263 *	14.138
- T-Plot Surface area, sq.m/g	37.017	21.150
- BJH Total, ml/g	0.19838	0.13548
Activated charcoal (powder)		
- BET Surface Area, sq.m/g	887.11	9.691
- T-Plot Surface area, sq.m/g	331.554	18.336
- BJH Total, ml/g	0.21613	0.05014

(*) See in Appendix F

Normally, the surface area of activated charcoal typically ranges from 500-1400 m^2/g, this work found that surface area of charcoal was 887.11 m^2/g. Table 4.11, it was found that surface area of activated charcoal had about 35 times of magnesol. The specific surface area, pore volumes and pore size distribution of activated carbons were determined from the N_2 adsorption isotherms at 77 K. Micropore volume and micropore area were derived from t-plot method. Pore size distribution was obtained using Barrett, Joyner and Halenda (BJH) method [56]. Figure 4.7 was showed that adsorption isotherm of magnesol and activated charcoal before and after treatments in methyl ester. The nitrogen adsorption isotherm at 77 K on activated charcoal was Type I, which is indicative of microporous materials. All adsorption isotherms had a finite uptake as the relative pressure approached unity. The isotherm of activated charcoal have decreased amount of adsorbed that it meaned something already exist inside the pore of its. The pore size distribution and micropore volume for magnesol and activated charcoal were gave in Figure 4.8 and 4.9, respectively.
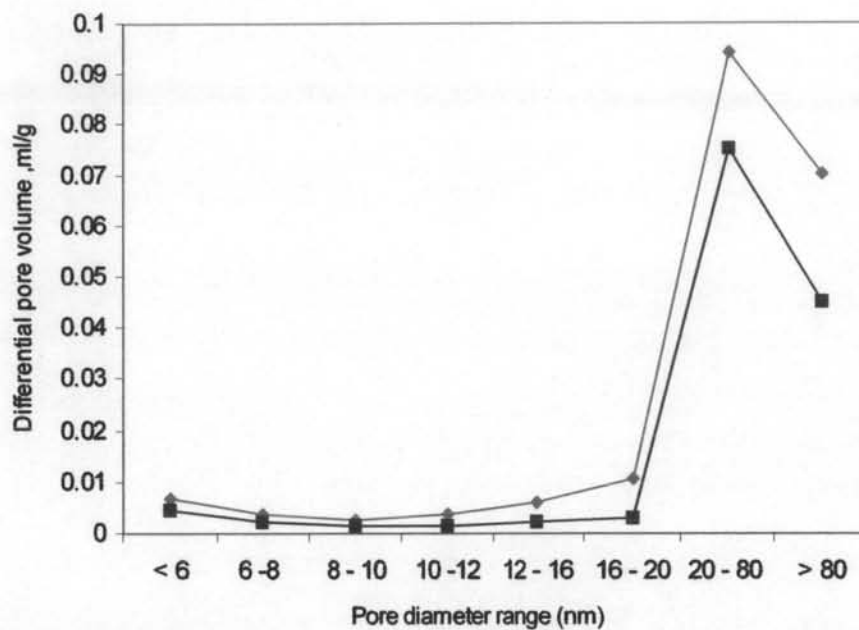
(a)

(b)
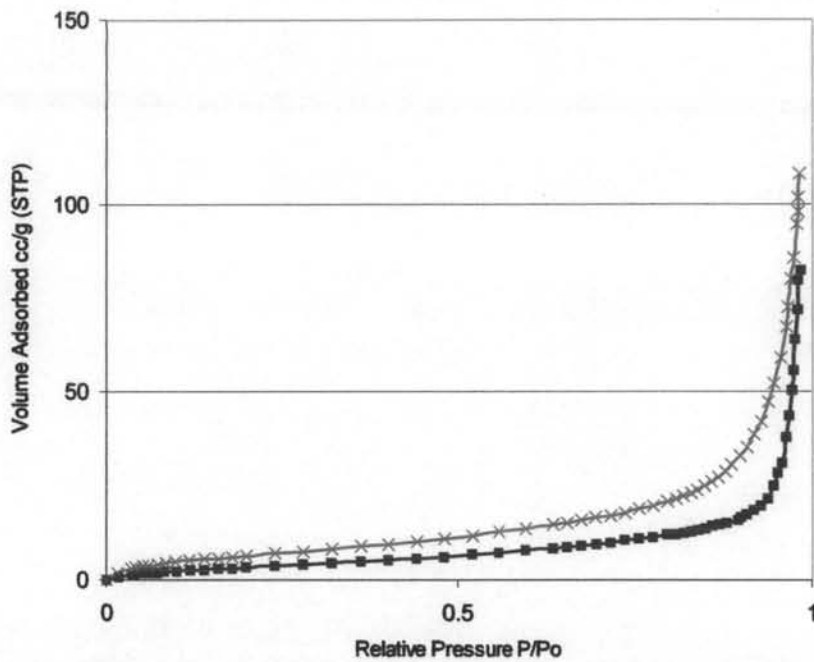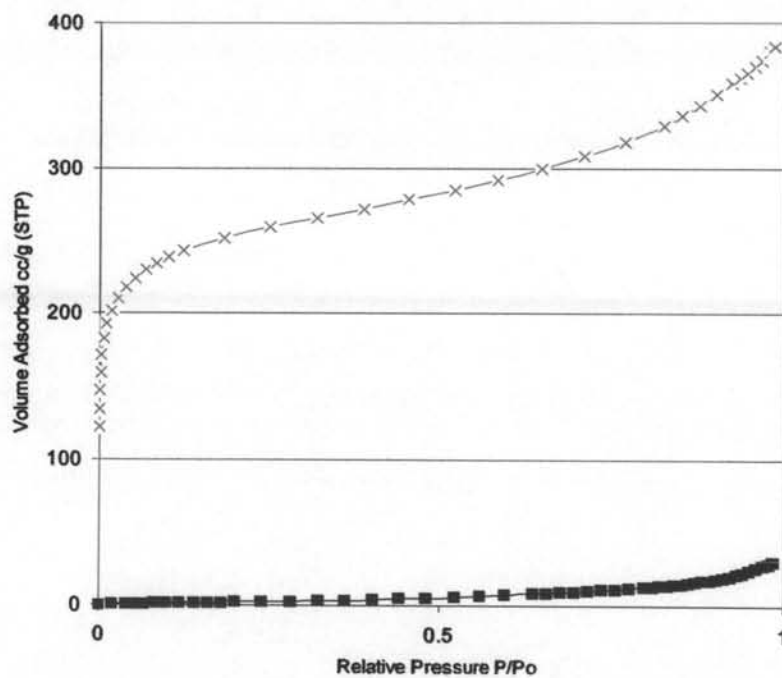
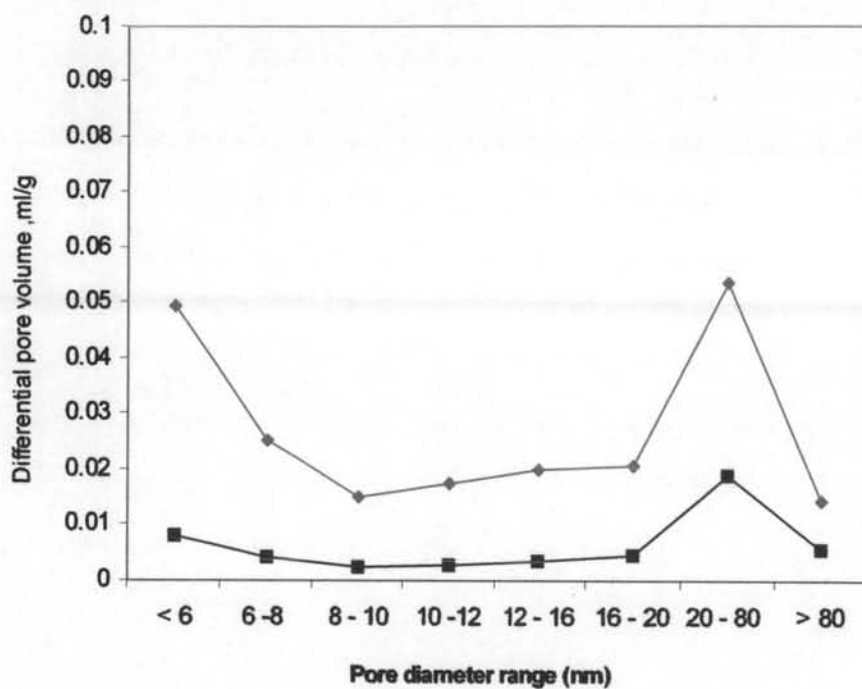———✕——— before methyl ester adsorption ———■——— after methyl ester adsorption

P: Pressure, P_0: Pressure saturated

Figure 4.7 Adsorption isotherm of (a) magnesol and (b) activated charcoal after and before methyl ester adsorption
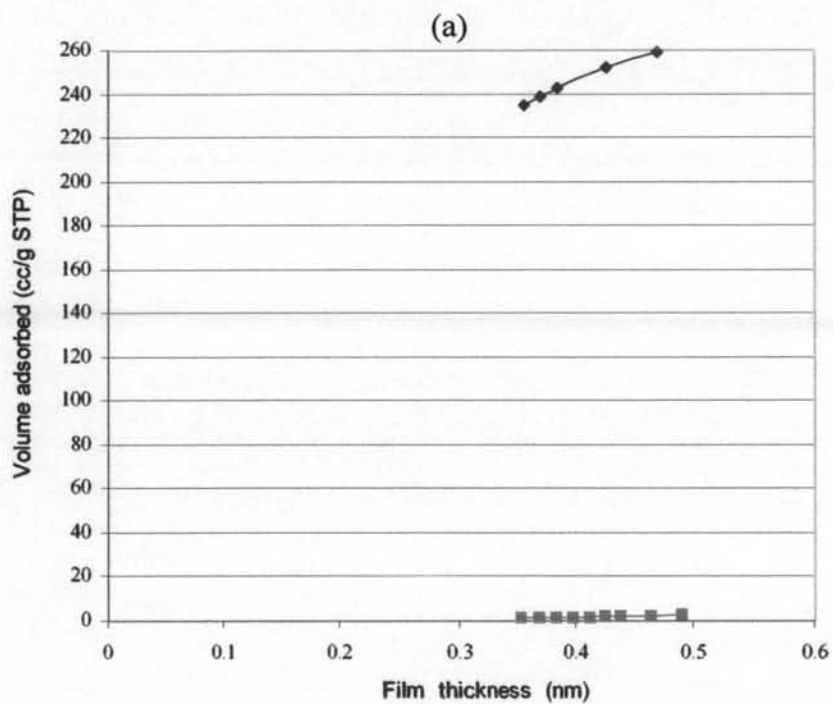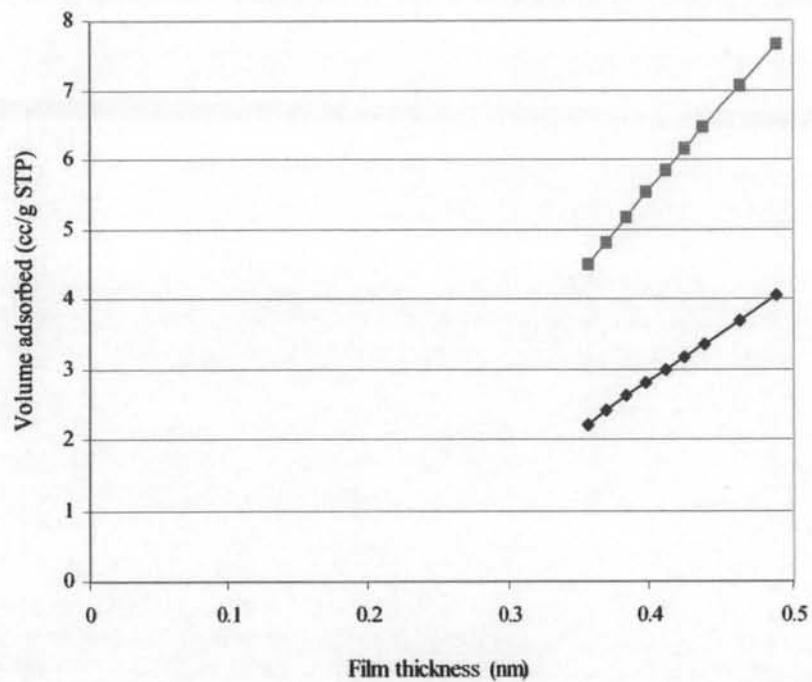
(a)

(b)

before methyl ester adsorption ——■—— after methyl ester adsorption

Figure 4.8 The pore volume distribution for (a) magnesol and (b) activated charcoal after and before methyl ester adsorption

(a)

(b)

before methyl ester adsorption   · after methyl ester adsorption

Figure 4.9 The t-plot of (a) magnesol and (b) activated charcoal after and before methyl ester adsorption obtained from the adsorption isotherm

4.6 Recovering adsorbent

The activated charcoal (powder form) is the adsorbent of adsorption FFAs in methyl ester. Because of the FFA content of the palm oil methyl ester after adsorption with magnesol (commercial grade) and activated charcoal (powder) were similar, both were evaluated their reusability and the results were shown in Table 4.12.

Table 4.12 Number of times of activated charcoal and magnesol reused adsorption by analyzed FFAs content in methyl ester (at $60^{\circ}C$ and 30 min)

No.	% FFAs after using magnesol	% FFAs after using activated charcoal (wash with hexane)	% FFAs after using activated charcoal (wash with methanol)
	None = 0.184 ± 0.000		
1	0.092 ± 0.002	0.046 ± 0.003	0.046 ± 0.002
2	0.138 ± 0.003	0.092 ± 0.000	0.092 ± 0.003
3	0.184 ± 0.000	0.138 ± 0.002	0.138 ± 0.000
4	0.184 ± 0.002	0.138 ± 0.002	0.138 ± 0.003
5	0.184 ± 0.003	0.184 ± 0.002	0.138 ± 0.002
6	0.184 ± 0.002	0.184 ± 0.000	0.138 ± 0.000
7	0.184 ± 0.000	0.184 ± 0.003	0.138 ± 0.002
8	-	-	0.138 ± 0.003

The adsorbents were washed with solvent and dried before they were reused each time. From Table 4.12, it could be concluded that the number of the activated charcoal (powder) is reused more than magnesol and the adsorption efficiency of the activated charcoal (powder) was constant after the second use. The SEM analysis of the activated charcoal (powder) before and after adsorption in Figure 4.8 suggested that the fatty acids or soap probably filled in the pore of the activated charcoal (powder) and then resulted in the constant adsorption at the outer surface. When it was washed with hexane, it can be used only 5 times. When the activated charcoal (powder) was washed with methanol, it can be used more than 8 times. Methanol will be a good solvent for recovering the activated charcoal (powder) because methanol can be used in the transesterification process.

(a)

(b)

(c)
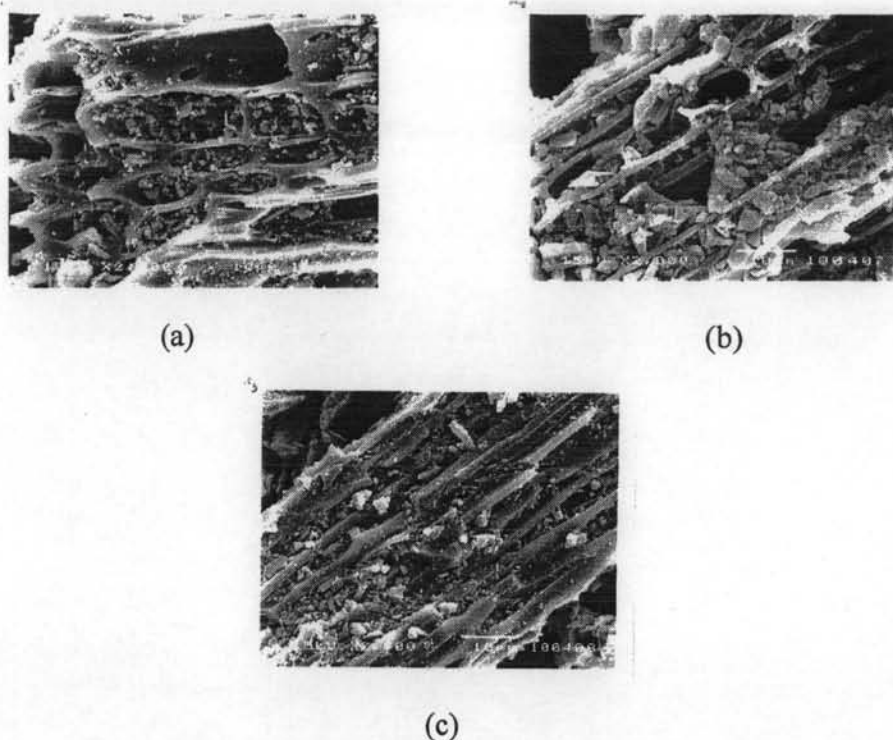
Figure 4.10 Photographs of activated charcoal by SEM; (a) before methyl ester
adsorption (b) after methyl ester adsorption and (c) inactive adsorption.
Resolution × 3000

4.7 The value of adsorbents in Thailand

Several adsorbents were used to adsorb impurities for increasing efficiency of
methyl ester. For magnesol which is commercial grade from USA, has the moderate
cost. Nevertheless, it was reused for few times. In this research, the activated charcoal
in powder form can be reused several times, however the activated charcoal is more
expensive than magnesol. The comparison of several adsorbents including value and
properties, were summarized in Table 4.13 and 4.14, respectively.

Table 4.13 The value of several adsorbents which used in this investigation (As of April/2007)

Type of adsorbents	Value of kg. unit (baht)	Value of biodiesel (bath/litre/time)
Magnesol	70	3
Activated charcoal (powder)	100	4.5
Activated charcoal (granule)	20-60	1-3
Molecular sieve (4Å)	300	13
Alumina (Aluminium oxide)	990	44
Bentonite clay	7	0.50

Table 4.14 General properties of adsorbents which presented in this investigation

Adsorbent \ Properties	Magnesol	Alumina	Activated charcoal	Molecular sieve (4Å)	Bentonite clay
Appearance	White solid (powder)	White solid (powder)	Black solid (powder, granule)	Tan pellet	Tan solid (powder)
MW, g/mol	NA	101.96	12.01	NA	NA
Odor	Odorless	Odorless	Odorless	Odorless	Mild
Solubility (water)	None	None	None	ND	Negligible
Boiling point, °C	NA	2,980	NA	NA	NA
Melting point, °C	1,910	2,072	3,500	NA	NA
Density, g/cm^3	3.95	3.97	15-35 (powder) 21-25 (granule)	NA	NA

NA – Not applicable

ND – Not determined