CHAPTER IV
RESULTS AND DISCUSSION

4.1 Catalyst Characterization

In this research, the biodiesel production was studied in a batch reactor using heterogeneous basic catalyst. In order to investigate the optimum conditions for this reaction, catalysts were varied with many parameters, such as the amount of K loading, calcination temperature, and amount of catalyst. In addition, the catalysts were characterized by several technique in order to explain the catalytic activity of the prepared catalyst.
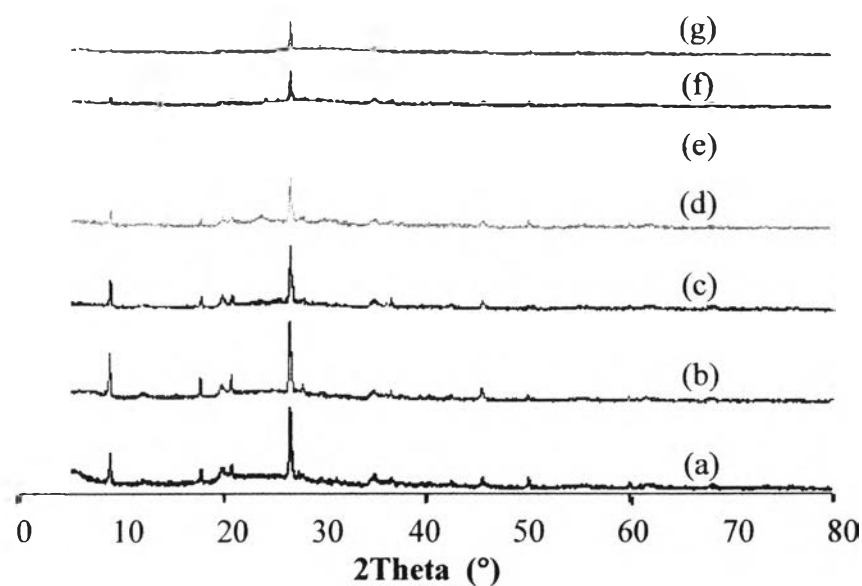
4.1.1 X-ray Diffraction (XRD)

Figure 4.1 XRD patterns of montmorillonite and KOH/montmorillonite catalysts: (a) Montmorillonite, (b) 5% K/montmorillonite, (c) 10% K/montmorillonite, (d) 15% K/montmorillonite, (e) 20% K/montmorillonite, (f) 25% K/montmorillonite, (g) 30% K/montmorillonite.

The XRD patterns of fresh montmorillonite and KOH/ montmorillonite catalysts with different potassium loadings are shown in Figure. 4.1. The XRD pattern of montmorillonite shows diffraction peaks at 2θ = 9, 18, 20, 21, 27, 35, 45, and 48°, which contain quartz and montmorillonite K-10. However, several broad 2θ peaks located at about 7, 20, 35, 54 and 62, attributing to the diffraction of (001), (110), (105), (210), and (300) reflections, are observed. These planes are based on the XRD patterns of the non-acid-treated montmorillonite. As may be seen, the intensities of the (001) and (110) reflection decrease gradually when the increase in potassium content and disappears completely when the amount of potassium reach 30% (curve g). It has been reported that the clay structure loses positive charge (the protons). In addition, the presence of the potassium cations produce a distortion of the clay structure, resulting in a loss of the crystallographic properties of the clay.
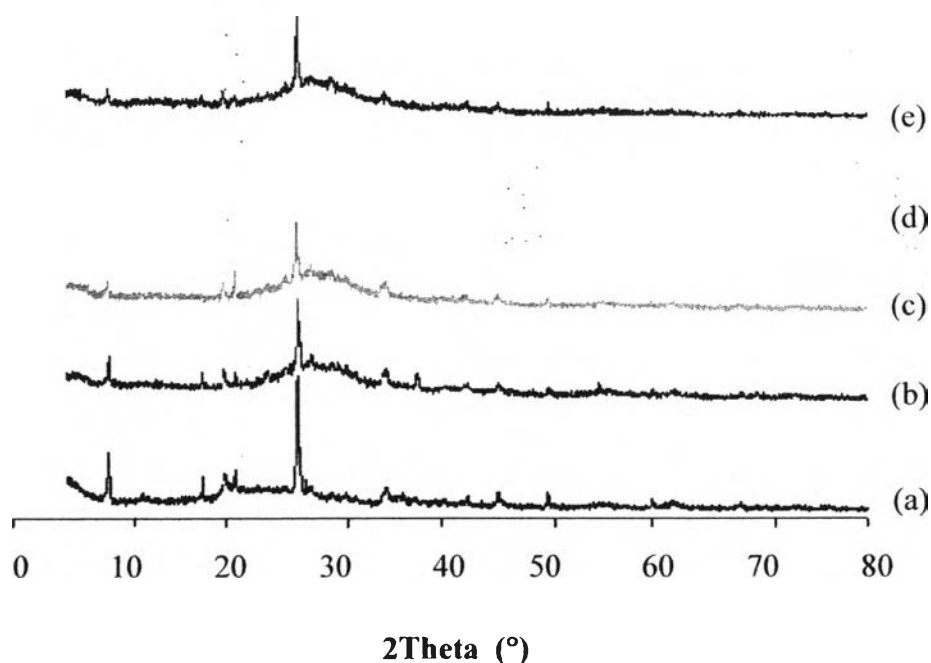

2Theta (°)

Figure 4.2 XRD patterns of 25 %K/montmorillonite uncalcined catalyst and calcined catalyst at different temperatures: (a) uncalcined 25%K/montmorillonite, (b) 25% K/montmorillonite calcined at 300 °C, (c) 25% K/montmorillonite calcined at 400 °C,

(d) 25% K/montmorillonite calcined at 500 °C, (e) 25% K/montmorillonite calcined at 600 °C.

Figure 4.2 illustrates the XRD patterns of 25 %K/montmorillonite at different calcination temperatures 300, 400, 500, and 600 °C. It was found that when the catalysts were calcined at high temperatures (300 to 600 °C), the XRD patterns show the slight reduction of crystallinity due to the collapse of layer.

4.1.2 Surface Area Analyzer

**Table 4.1** Surface area, pore volume and Si/Al ratio of the catalysts

| Catalyst	Surface Area (m^2/g)	Pore volume (cm^3/g)	Si/Al ratio	Potassium* leaching (%)
Montmorillonite	58.51	0.392	7.11	-
Fresh 25%K/ Mont	4.09	0.125	5.97	-
Spent 1st 25%K/ Mont	-	-	5.86	19.53
Spent 2nd 25%K/ Mont	-	-	5.96	31.19
Spent 3rd 25%K/ Mont	-	-	5.84	40.09

* determined by XRF

Table 4.1 shows surface area of montmorillonite, fresh 25%K/montmorillonite, and Spent 25%K/montmorillonite. It can be seen that fresh 25% K/montmorillonite had much lower surface area of 4.09 m^2/g, as compared to 58.51 m^2/g of montmorillonite. The different Si/Al ratios have no significant difference were observed for the fresh and spent catalysts. The leaching of potassium

was determined by XRF. Leaching was potassium loss when the spent catalyst was retested and it was found that reaction rate was decreased. It could be suggested that potassium was dissolved in reaction mixture and leached out.
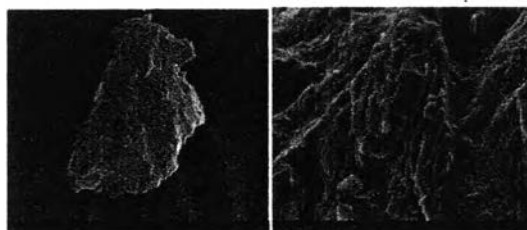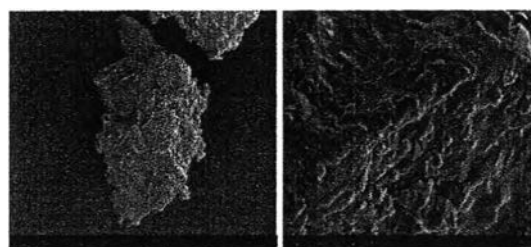
4.1.3 Scanning Electron Microscope (SEM)
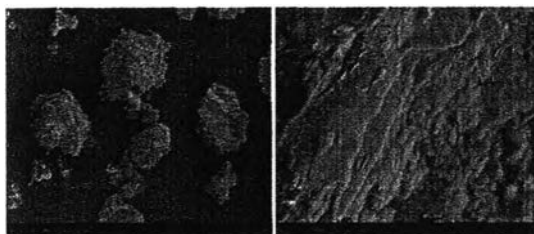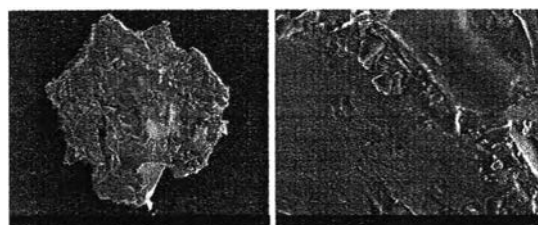

Raw Montmorillonite
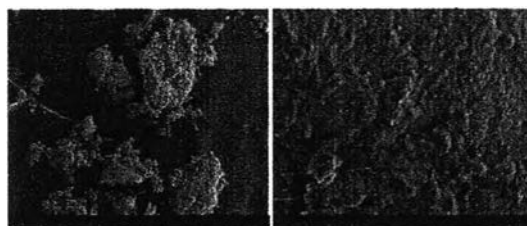
15%K Montmorillonite

25%K Montmorillonite uncalcined

25%K Montmorillonite Calcined at 300 °C

|← x3.0k →| ← x20.0k →|

25%K Montmorillonite Calcined at 500 °C

|◄——— x3.0k ———►| ◄—— x20.0k ———►|

Figure 4.3 SEM micrographs of montmorillonite and modified montmorillonite clay.

Scanning electron microscope has extensively been used to examine the morphology of catalysts and particle size of the prepared catalyst. Figure 4.3 shows the SEM micrographs of the loaded catalysts. A comparison of the SEM images proves that the adsorption of the potassium cause an increase of the degree of agglomeration of montmorillonite particle. The particle size of the catalyst was increased when increasing the percent loading of K. This is because the potassium species were highly distributed upon the surface and aggregated to form the higher particle size. This result corresponded to the potassium content measured by EDS.

4.1.4 Energy Dispersive Spectrometer (EDS)
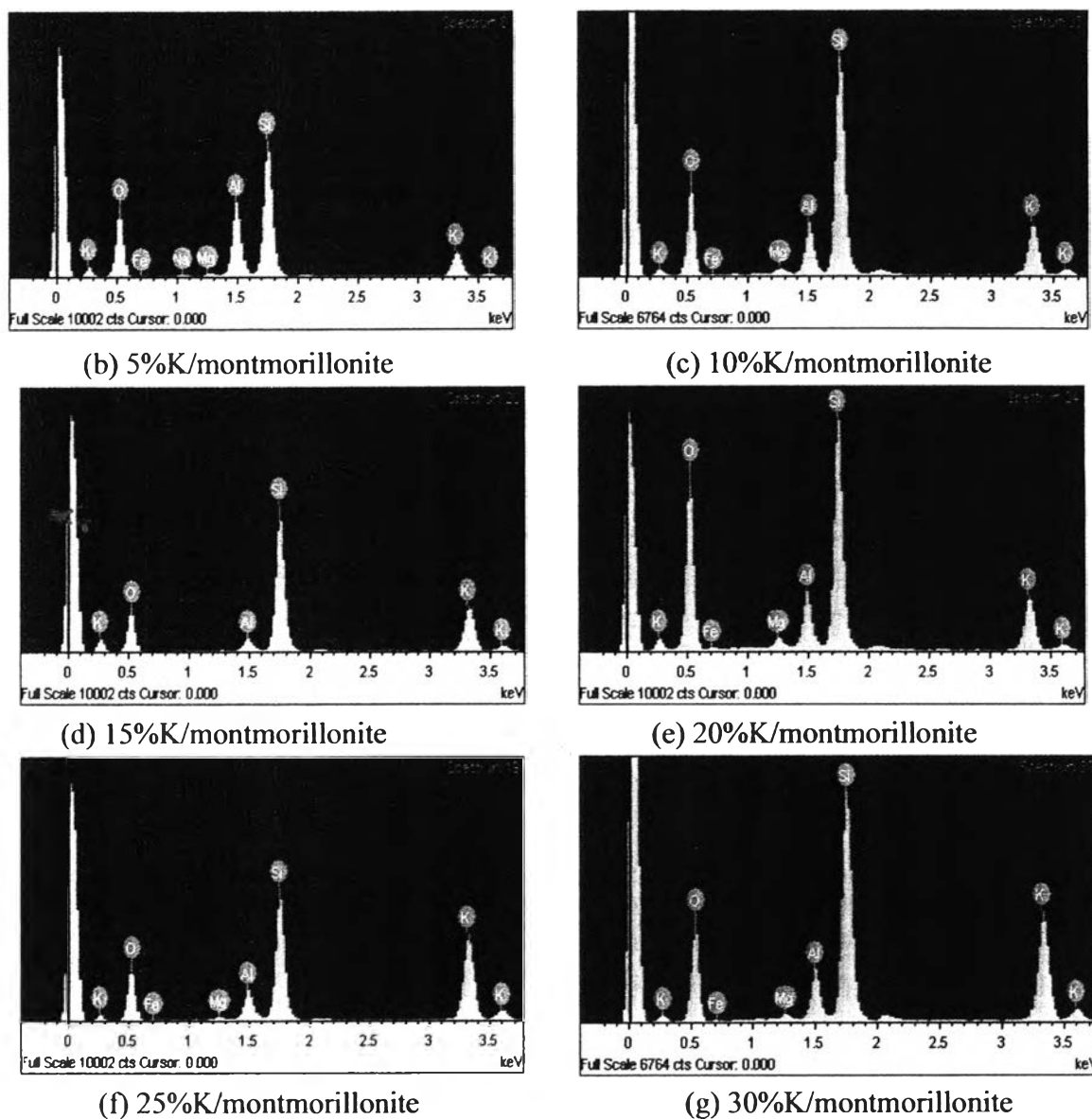

(a) Montmorillonite

(b) 5%K/montmorillonite

(c) 10%K/montmorillonite

(d) 15%K/montmorillonite

(e) 20%K/montmorillonite

(f) 25%K/montmorillonite
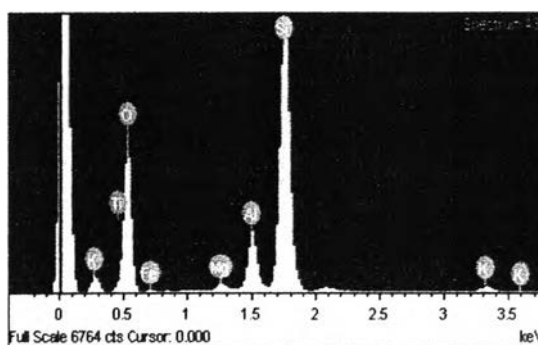
(g) 30%K/montmorillonite

Figure 4.4 EDS analysis of pure supports and loading catalysts.

EDS analysis on the composition of montmorillonite and 5%K/montmorillonite, 10%K/montmorillonite, 15%K/montmorillonite, 20%K/montmorillonite, 25%K/montmorillonite, and 30%K/montmorillonite are shown in Figure 4.5. Table 4.2 indicates the major composition of montmorillonite. The potassium content was partially identified by the Energy Dispersive

Spectrometer (EDS). Raw montmorillonite contain K 1.34%. This result confirmed that the %K that loaded on montmorillonite were appropriate amount. When loading more potassium the other composition were decreased due to %wt relative.

Table 4.2 Composition of montmorillonite and KOH/montmorillonite from EDS

Element (%)	Montmorillonite	5%K/mont	15%K/mont	25%K/mont
O	53.65	50.59	49.95	45.01
Mg	0.73	0.74	0.53	0.37
Al	6.43	6.88	7.54	3.87
Si	34.3	31.86	25.76	23.10
K	1.34	6.87	14.07	26.00
Fe	3.12	2.62	2.07	1.80
Total	100	100	100	100

Table 4.2 also shows the potassium contents of pure montmorillonite and potassium loaded catalysts and montmorillonite composition. From the table, Raw montmorillonite contain K 1.34%. This result confirmed that the %K that loaded on montmorillonite were appropriate amount.

4.1.5 Hammett Indicator

Table 4.3 Basic strength of difference K loading catalysts

Catalyst	Basic strength $(H\_)$	Basicity (mmol/g)
Montmorillonite	$7.2 < H\_ < 9.8$	0.038
5%K/montmorillonite	$9.8 < H\_ < 11.0$	1.09
10%K/montmorillonite	$9.8 < H\_ < 11.0$	1.17
15%K/montmorillonite	$9.8 < H\_ < 11.0$	1.48
20%K/montmorillonite	$9.8 < H\_ < 11.0$	2.74
25%K/montmorillonite	$13.0 < H\_ < 15.0$	4.27
30%K/montmorillonite	$13.0 < H\_ < 15.0$	4.23

Table 4.3 illustrates the basic strength of the prepared catalysts and as-received montmorillonite. Basic strength of the catalysts $(H\_)$ was determined by using the following Hammett indicators: bromthymol Blue ($H\_=7.2$), phenolphthalein ($H\_=9.8$), Tropaeolin ($H\_=11$), 2,4-dinitroaniline ($H\_=15$), and 4-nitroaniline ($H\_=18.4$). Montmorilonite possessed the weak basic strength in a range of ($7.2 < H\_ < 9.8$). After loading potassium from 5 to 20 wt%, the modified catalyst gave a higher basic strength in the range of ($9.8 < H\_ <11$). Further loading potassium higher than 20%K, all the prepared catalysts exhibited higher basic strength in a range of ($13 < H\_ < 15.0$). Nevertheless, it required other titration methods for distinguishing the difference of basicity of them. Table 4.3 also shows the basicity from acid titration technique of as-received montmorillonite and KOH/montmorillonite catalysts with various potassium loadings. The results revealed that the basicity of prepared catalysts are higher than that of the as-received montmorillonite clay, and the highest of basicity of catalyst was obtained at 25% potassium. Therefore, it indicated that the

amount of potassium which could dratically increase both basic strength and basicity of the prepared catalyst.
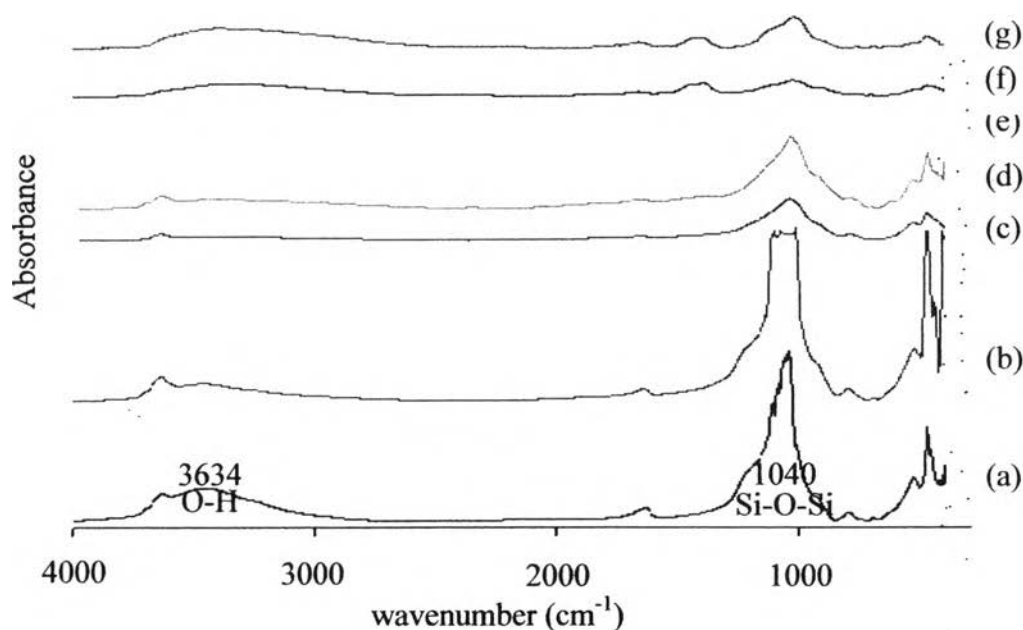
4.1.6 FTIR

Figure 4.5 FTIR spectra of montmorillonite and KOH/montmorillonite: (a) montmorillonite, (b) 5%K/montmorillonite, (c) 10%K/montmorillonite, (d) 15%K/montmorillonite, (e) 20%K/montmorillonite, (f) 25%K/montmorillonite, (g) 30%K/montmorillonite.

The raw montmorillonite and K/montmorillonite catalysts were compressed onto disk using KBr and scanned through infraredspectometer from 4000 cm^{-1} to 400 cm^{-1} to obtain infrared absorption spectra, as shown in Figure 4.5. The peak at 1040 cm^{-1} attributed to Si-O-Si stretching and peak at 3634 attributed to 0-H stretching due to potassium hydroxide loaded on montmorillonite can be observed.

4.1.7 CO₂–TPD

For measuring the basic properties of catalyst, the temperature-programmed desorption of CO_2 (CO_2-TPD) was used. The patterns of unstitute a main CO_2 desorption at 170 °C, 400 °C, and at a high temperature above 600. The desorption peak at 170 °C is attributed to the interaction of CO_2 with weak basic site. The peak appeared at 400 °C and 600 °C can be attributed to moderate weak, moderate, and strong strength basic site respectively.
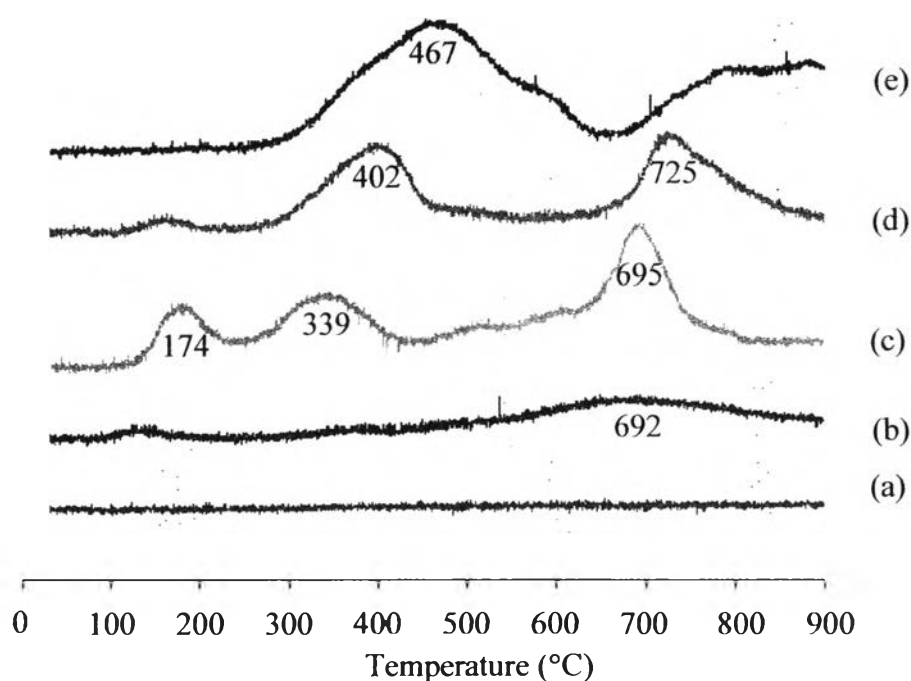

Figure 4.6 CO₂–TPD profiles the prepared catalysts: (a) Raw montmorillonite, (b) 10% K/montmorillonite, (c) 20% K/montmorillonite, (d) 25% K/montmorillonite, (e) 30% K/montmorillonite.

Figure 4.6 illustrate the CO₂–TPD profiles of montmorillonite and K/montmorillonite For montmorillonite, no CO_2 desorption was observed from TPD profile (curve a). This fact would confirm the negligible presence of strong basic sites

in this sample and it agree with the result in Table 4.3. Only two desorption peaks at 120 °C and 692 °C with low intensity emerged in the CO_2–TPD profiles of 10%K/montmorillonite (curve b). When loading potassium increase, absorp of CO_2 is increase. It can be conclude that potassium hydroxide can increase basic strength and basicity of catalysts as shown in the figure. Moreover, basic strength has the same trend compare to Hammett indicator.
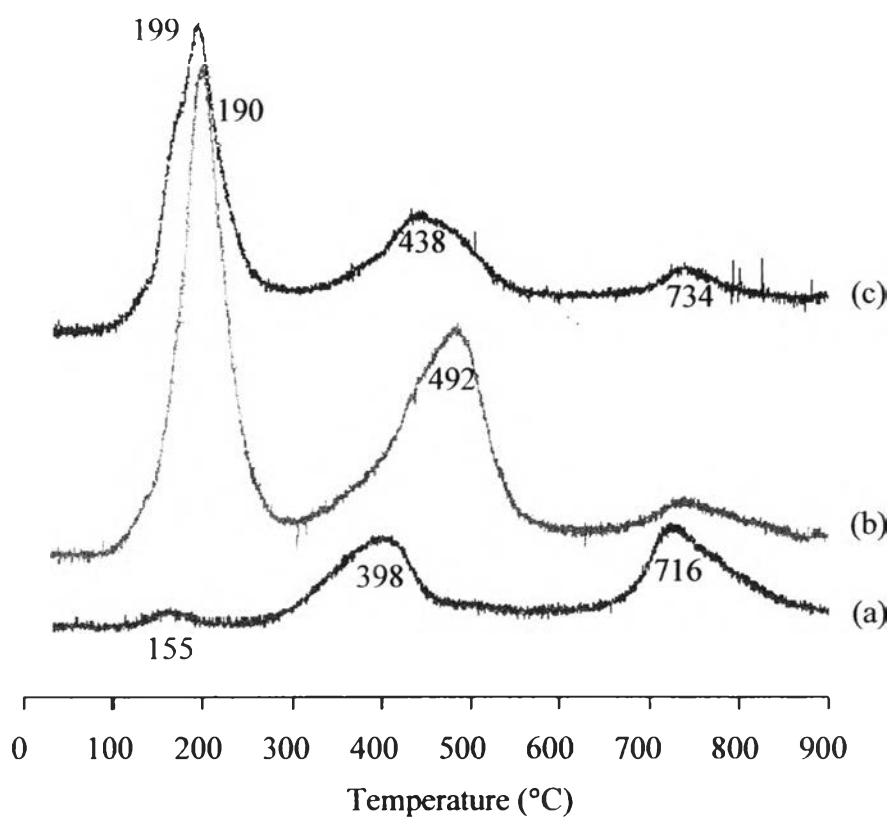

Figure 4.7 CO_2–TPD profiles of calcined catalyst and uncalcined catalyst: (a) 25%K uncalcined /montmorillonite, (b) 25%K/montmorillonite calcined at 400 °C, (c) 25%K/ montmorillonite calcined 600 °C.

This figure shows basic strength and basic strength of calcined and uncalcined catalysts. It is clearly seen that when the calcination temperature was increase, the basic strength decreased. It could be suggested that calcination process reduce basic strength of catalyst. However calcination increase basicity of weak basic strength.

4.2 Transesterification Reaction

Transesterification reaction was performed by using palm oil and methanol as reactant over the prepared catalyst. Transesterification reaction occurred in a batch reactor with these initial conditions: 6wt% of catalyst (based on weight of vegetable oil), 60°C of reaction temperature, 300 rpm of stirring rate, and 15:1 molar ratio of methanol to oil. The catalysts used in this work were prepared by impregnation technique to find the optimum condition for transesterification of palm oil by investigating these parameters: influence of K loading, calcination temperature, amount of catalyst, and reusability of catalyst.

4.2.1 Influence of K Loading on Biodiesel Yield

To investigate the effect of KOH loading on biodiesel yield, the catalysts were prepared with different potassium loadings in the range of 5–30%wt of K on montmorillonite support. These catalyst were sieved in 20–40 mesh before further testing their activity with these initial conditions: 6wt% of catalyst (based on weight of vegetable oil), 60°C of reaction temperature, 300 rpm of stirring rate, and 15:1 molar ratio of methanol to oil. %FAME (fatty acid methyl ester) of mixture was investigated by a gas chomatograph every hour until 10 hour of reaction time. Biodiesel yield was reported by %FAME every hour until the 10 hours of reaction time to reach the equilibrium.
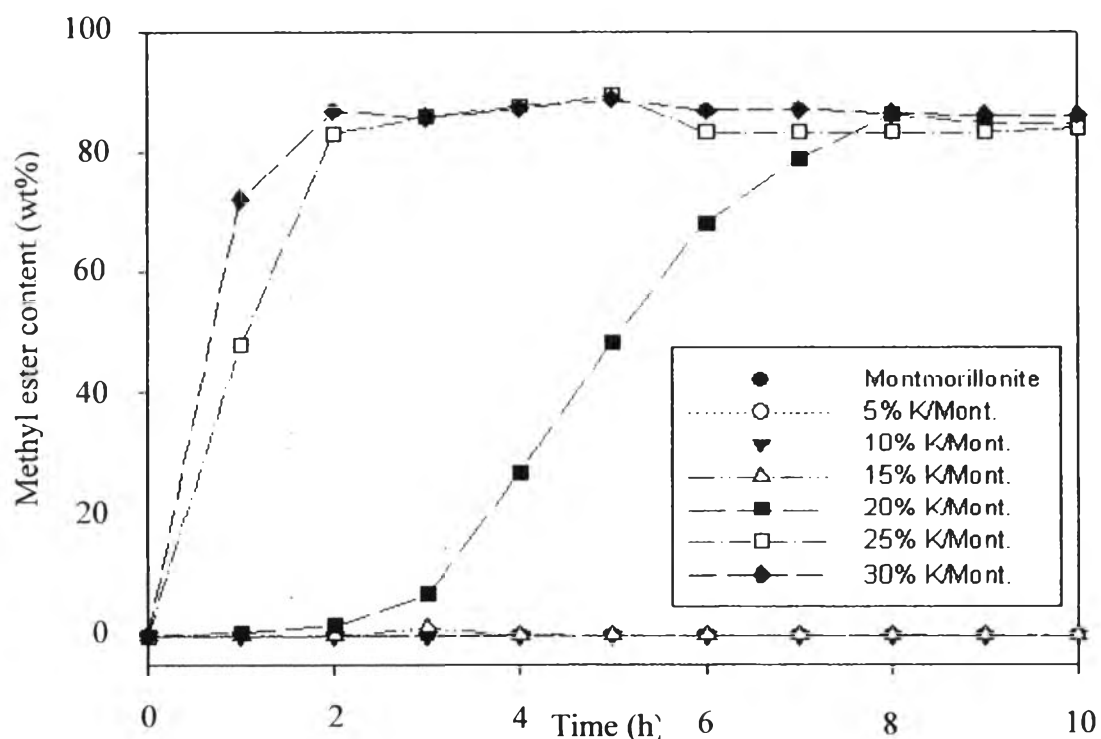
Figure 4.8 Influence of KOH loading on biodiesel yield.

In this work, the content of KOH loaded on montmorillonite was varied within a range of 5–30%wt. The influence of KOH loading on the biodiesel yield is illustrated in Figure 4.8. It indicated that montmorillonite and K/montmorillonite at low K loading: (5%K, 10%K, and 15%K), the catalysts exhibited no activity or showed insignificant effect on biodiesel yield. After loading amount of K was increased 20%K, the maximum biodiesel yield of 86.0% was obtained at 8 hours and remained constantly until 10 hours. It could be suggested that the reaction reached equilibrium after 8 hours. Further increasing K loading to 25%K/montmorillonite and 30%K/montmorillonite, it could dramatically increase the reaction rate which reached the equilibrium within 5 hours with the maximum biodiesel yield of 89.3 and 88.6%, respectively. In the present study, the result show that basic strength (Table4.3)

facilitate the catalytic activity and strong basic sites react with reactant yielding higher methyl ester yield.

4.2.2 Influence of Calcination Temperature on Biodiesel Yield

From the previous section, 25%K loading was selected as an appropriate catalyst due to its high % FAME and lower amount of potassium loaded compared to 30%K. 25 %K/montmorillonite was further studied on the calcination effect.
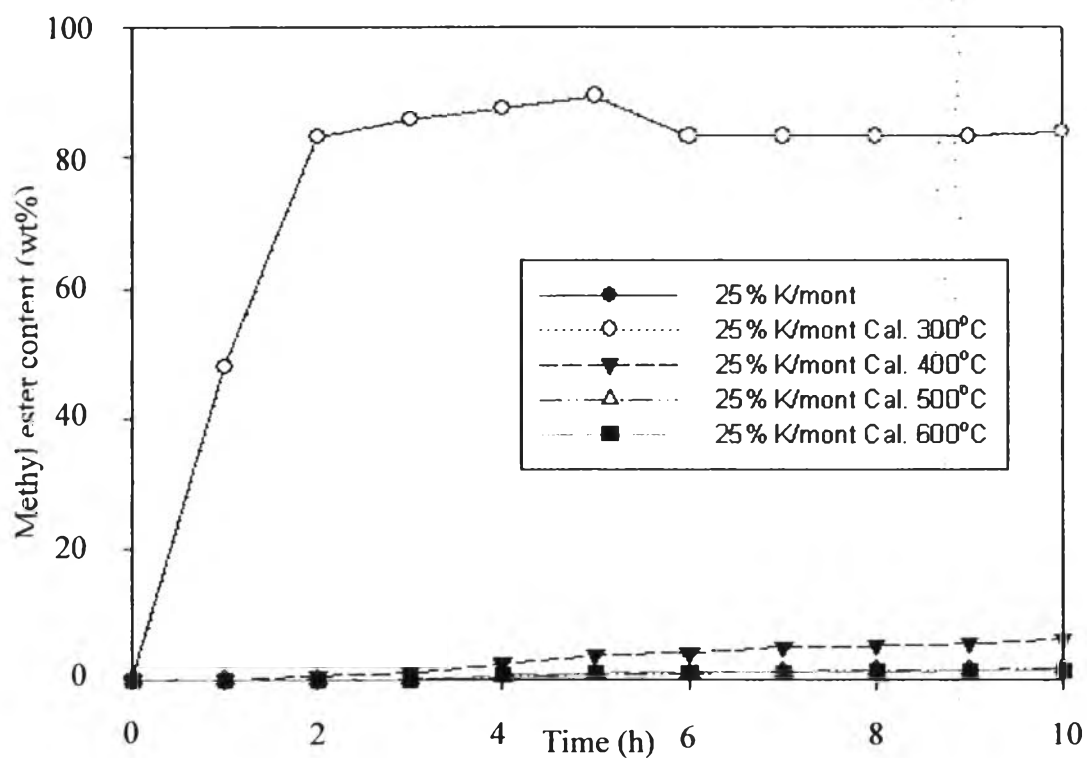

Figure 4.9 Influence of calcination temperature on biodiesel yield.

The catalysts 25%K/montmorillonite were calcined at different temperatures: 300 °C, 400 °C, and 500 °C to investigate the effect of calcinations temperature on biodiesel yield. From Figure 4.9, it was found that the

The non calcined catalyst showed the highest activity with had optimum at 5 hour. It could be concluded that calcination is not gave higher activity than the calcined catalyst and the methyl ester content of the calcined catalysts were in the following order: 300 °C > 400 °C > 500 °C. From Figures 4.6–4.7, it revealed that basicity not only change with the amount of potassium but also calcinations temperature.

The influence of amount of catalyst on biodiesel yield was investigated by selecting 25%K loading and non calcine due to the high performance as previous result. To increase amount of catalyst can reduce the reaction time to reach equilibrium.

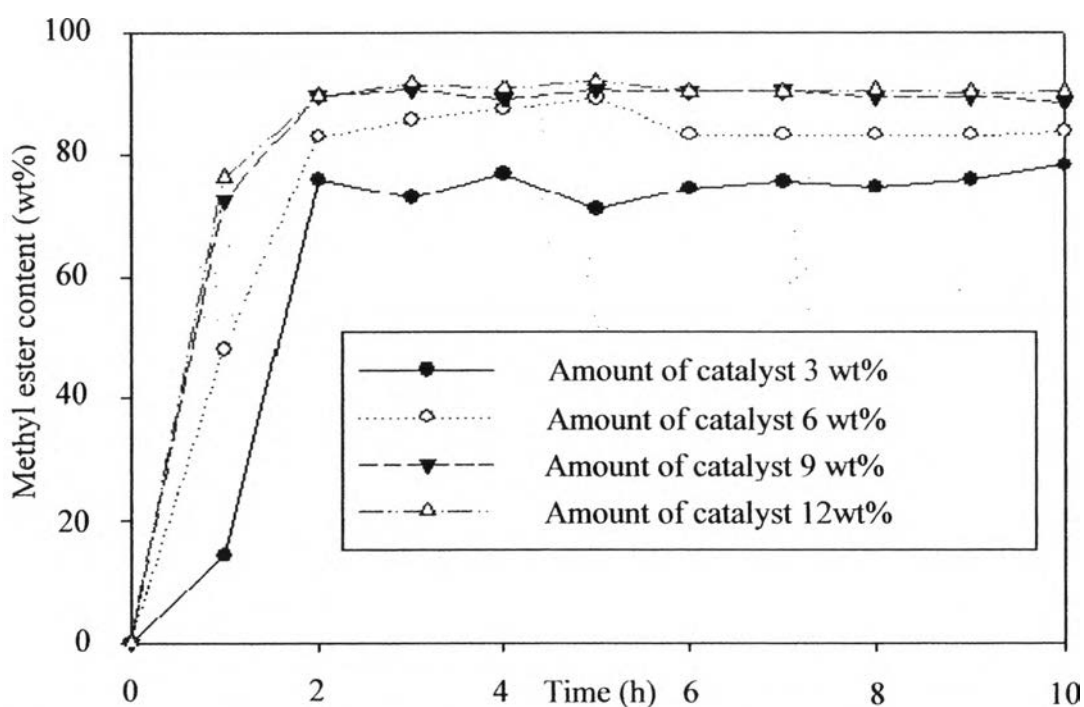### 4.2.3 Influence of Amount of Catalyst on Biodiesel Yield

Figure 4.10 Influence of amount of catalyst on the biodiesel yield.

Effect of catalyst amount on methyl ester content was studied, as shown in Figure 4.10, by varying the amount of catalyst from 3 wt% to 6 wt%, 9 wt%, and 12

wt% respectively. An optimum amount of catalyst loading was determined. When a small amount of catalyst (3 wt%) was used, the maximum methyl ester yield could not be reached. It can be seen that the methyl ester content increased, as the catalyst amount increase and 3 to 9wt%. However, when the increase of catalyst amount from 9 to 12wt%, the methyl ester yield are almost the same. Since the methyl ester did not change significant, the optimum catalyst amount was 9wt% and it was selected for further study on its reusability.

4.2.4 Reusability of Catalyst on Biodiesel Yield

A series of 10 h simultaneous transesterification were carried out to evaluate the reusability of 25%K/montmorillonite. The catalyst was filtered and reused in a new cycle without pretreatment. The reusability was tested for 3 cycles.
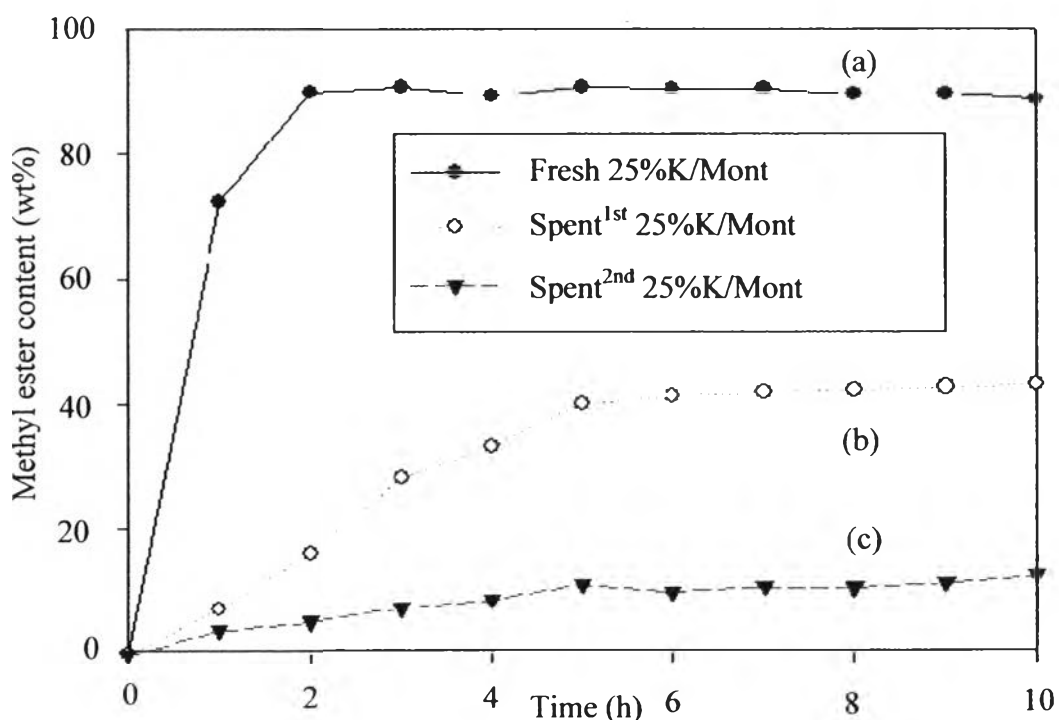

Figure 4.11 Reusability of 25%K/montmorillonite with reaction condition 9 wt%.

Figure 4.11 shows the reusability of 25%K/montmorillonite. It is clearly seen that the leaching occurs due to the methyl ester yield drastically decreased from about 90% FAME in the first cycle to 40 and 10% FAME in the second and third cycle, respectively It could be suggest that the leaching of the KOH species could responsible for a decrease in the catalytic active, as evidence in table.