

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Characterization of Catalyst

This research studied the catalytic activity of sulfonated lignin catalyst as a heterogeneous acid catalyst for biodiesel production via esterification reaction in a batch reactor. In order to investigate the optimum conditions for this reaction, the catalyst was varied with many important parameters, such as amount of catalyst, reaction temperature, molar ratio of methanol to oil, sulfonation temperature and sulfonation time. In order to explain the catalytic activity, the catalysts were characterized by several techniques, such as BET, TPD-NH₃, titration method, SEM, FT-IR, and XRD.

4.1.1 BET Method

The properties of the sulfonated lignin catalysts with various sulfonation temperatures and sulfonation times were characterized by Brunauer-Emmett-Teller (BET) method and the results are given in Table 4.1. For sulfonated catalysts with various sulfonation temperatures, the BET surface areas are in the ranges of 6.24-8.66 m²/g. BET analysis showed that all synthesized samples have very low surface area and mesopores texture. The catalyst sulfonation at 110 °C gave the highest surface area about 8.66 m²/g. On the other hand, the catalyst sulfonated at 150 °C gave the lowest surface area at 6.24 m²/g. For pore diameter of catalyst, it was found that sulfonation can cause a dramatic increased of pore diameter from 1.54 nm of the catalyst sulfonated at room temperature to 8.77, 9.55, and 10.08 nm at 110 °C, 130 °C, and 150 °C, respectively. From the result, it can be concluded that sulfonation temperature promoted pore diameter of sulfonated lignin catalyst. The results coincides with the results reported by Pua *et al.* (2011).

For sulfonated catalysts with various sulfonation times, the surface area gradually increased from 8.14 m²/g of catalyst sulfonated at 3 h to 8.66 m²/g of catalyst sulfonated for 5 h, whereas the surface area of catalyst sulfonated for 7 h dramatically decreased to 2.12 m²/g. For pore diameter of the catalyst sulfonated for

3 h and 5 h gave the value 8.58 nm and 8.77 nm, respectively. On the other hand, the catalyst sulfonated for 7 h gave the highest pore diameter at 177.9 nm and the lowest surface area due to an increase of period of time to attack on the structure by strong acid, resulting in shrinkage of structure and broken bonds (Pua *et al.*, 2011). From the result, it can be concluded that the suitable sulfonation temperature and sulfonation time for preparing the sulfonated lignin catalyst were 110 °C for 5 h.

Table 4.1 Textural properties of the sulfonated lignin catalysts

Sulfonation Temperature (°C)	Sulfonation Time (h)	Surface Area (m ² /g)	Pore Volume (cm ³ /g)	Pore Diameter (nm)
Room temperature	5	6.35	0.0215	1.54
150	5	6.24	0.0169	10.08
130	5	7.21	0.0172	9.55
110	5	8.66	0.0190	8.77
110	3	8.14	0.0175	8.58
110	7	1.14	0.0019	6.67

4.1.2 NH₃ Temperature-Programmed Desorption (TPD-NH₃)

NH₃-TPD test certified the extent of sulfated species adsorption by evaluated the acidity of the materials. The NH₃-TPD profiled of all catalysts are shown in Figure 4.1, the desorption peaks at higher than 550 °C are assigned to strong acid sites, whereas those at 400-550 °C are classified as medium acid sites and for peaks found between 100 and 400 °C are regarded as weak acid sites. From Table 4.2 shows the amount of acid sites present in the catalysts is estimated by calculating the desorption peak area of ammonia and the acidity is determined by the maximum peak temperature (T_{max}) of desorption peak (Zhang *et al.*, 2014).

The NH₃-TPD profiles of sulfonated lignin catalysts with various sulfonation temperatures are shown in Figure 4.1 and the acid quantity of sulfonated lignin catalyst by NH₃-TPD profiles are shown in Table 4.2, the catalyst sulfonated at

110 °C gives weak acidity, medium acidity, and strong acidity value of 1.252, 0.296, and 0.480 mmol/g, respectively which are higher than sulfonation temperature at 130 and 150 °C. At the catalyst sulfonation temperature of 130 °C, weak acidity has higher value than that of catalyst sulfonated at 150 °C but the medium acidity and strong acidity have lower value than that of catalyst sulfonated at 150 °C. Moreover, the total acidity decreased when the sulfonation temperature was increased by 110 °C give highest total acidity of 2.028 mmol/g.

For sulfonated lignin catalysts with various sulfonation time from 3 to 7 h, it was found that weak acidity, medium acidity, and strong acidity increased when the sulfonation time was increased from 3 to 5 h. In addition, when increasing sulfonation time to 7 h, the acidity decreased significantly. And the catalyst sulfonated at 5 h give the highest total acidity of 2.028 mmol/g.

From the results, the catalyst sulfonated at 110 °C 5 h give the highest acidity because it had high amount of sulphate ion on the catalyst, which resulted in the high amount of desorbed NH₃ and consequently the high catalytic acidity. It was probably due to its large number of acid sites (Shu *et al.*, 2010).

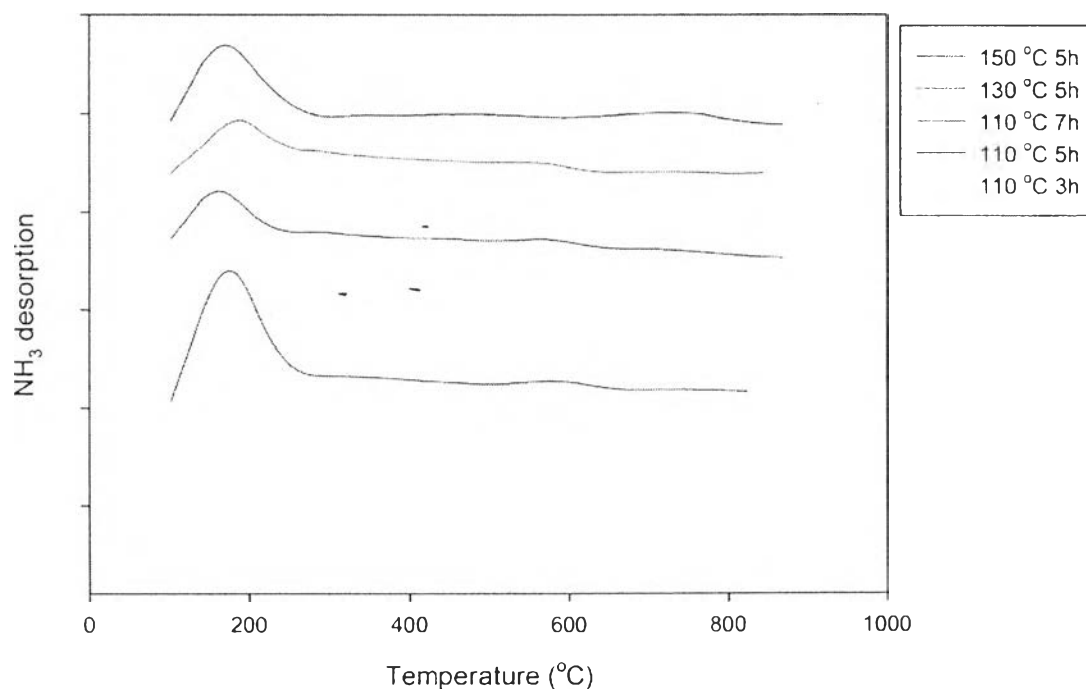


Figure 4.1 NH₃-TPD profiles of sulfonated lignin catalyst.

Table 4.2 Total acidity of the prepared catalyst by NH₃-TPD

Sulfonation Temperature (°C)	Sulfonation Time (h)	Weak acidity (mmol/g)	Medium acidity (mmol/g)	Strong acidity (mmol/g)	Total Acid Quantity (mmol/g)
150	5	0.984	0.209	0.222	1.415
130	5	1.194	0.166	0.199	1.559
110	5	1.252	0.296	0.480	2.028
110	7	1.047	0.046	0.045	1.455
110	3	0.684	0.211	0.098	0.993

4.1.3 Titration Method

The acidity of catalyst surface is an important issue for this study. In this study in order to measure the surface acidity changes during catalyst preparation, a titration method was used. Table 4.2 shows the total acid quantity of sulfonated lignin catalysts with various sulfonation temperatures and sulfonation times. The total acid quantity of all sulfonated lignin catalysts determined by NaOH titration were around 1.12-1.36 mmol/g. This value suggested that a large fraction of the acidity was associated with weak acid groups (mainly phenolic and carboxylic functionalities), thereby endowing the carbon microspheres with polarity. It should be noted that only the -SO₃H acid groups (strong acidity) present in the catalyst are active as catalytic sites in many reactions (Liu *et al.*, 2013).

In the part of discussion, the sulfonated lignin catalyst prepared at sulfonation temperature of 110 °C for 5 h gave the highest acid density of 1.36 mmol/g and the highest catalytic activity. As mentioned before, it can be concluded that the catalytic activity depended on the total acid density for esterification of oleic acid.

Table 4.3 Total acid density of the sulfonated lignin catalysts

Sulfonation Temperature (°C)	Sulfonation Time (h)	Acid Quantity (mmol/g)
150	5	1.17
130	5	1.12
110	7	1.13
110	5	1.36
110	3	1.19

4.1.4 Scanning Electron Microscope (SEM) with Energy Dispersive Spectrometer (EDS)

The morphology of the catalyst from SEM characterization and elements present in the samples (O, C, Si and S) from EDS characterization of corncob, pretreated corncob, sulfonated lignin catalysts with various sulfonation temperatures and sulfonated lignin catalysts with various sulfonation times are shown in Figure 4.2.

The SEM images show that corncob is non-porous, bulging, smooth and uniform surfaces. In contrast, SEM images of pretreated corncob shows significant collapse and destruction structures. After the sample was treated by sulfonation of concentrated H₂SO₄, the structure of sulfonated lignin catalyst would be more compact. This indicated that the structure of catalyst was more difficult to be sulfonated. However, the structure of sulfonated lignin catalyst prepared at sulfonation temperature of 110 °C for 5 h and sulfonated lignin catalyst prepared at sulfonation temperature of 110 °C for 7 h showed significant collapse and destruction structures. Hence, the intercalation of concentrated H₂SO₄ with destruction structure will be easier than the case with a compact structure (Shu *et al.*, 2010).

The EDS results of pretreated corncob, sulfonated lignin catalysts with various sulfonation temperatures, sulfonated lignin catalysts with various sulfonation times and spent catalyst showed the content of carbon, oxygen, silica and sulfur. The content of sulfur of pretreated corncob was 0.01 wt%. After the

sulfonation treatment, the contents of sulfur were increased to around 1-4 wt%. The sulfonated lignin catalyst prepared at sulfonation temperature of 110 °C for 5 h had the highest sulfur content of 4.04 wt%. The sulfur content decreased from 4.04 wt% of fresh catalyst to 3.47 wt% of spent catalyst due to the lowering of active site and losing acidity after do the first experiment.

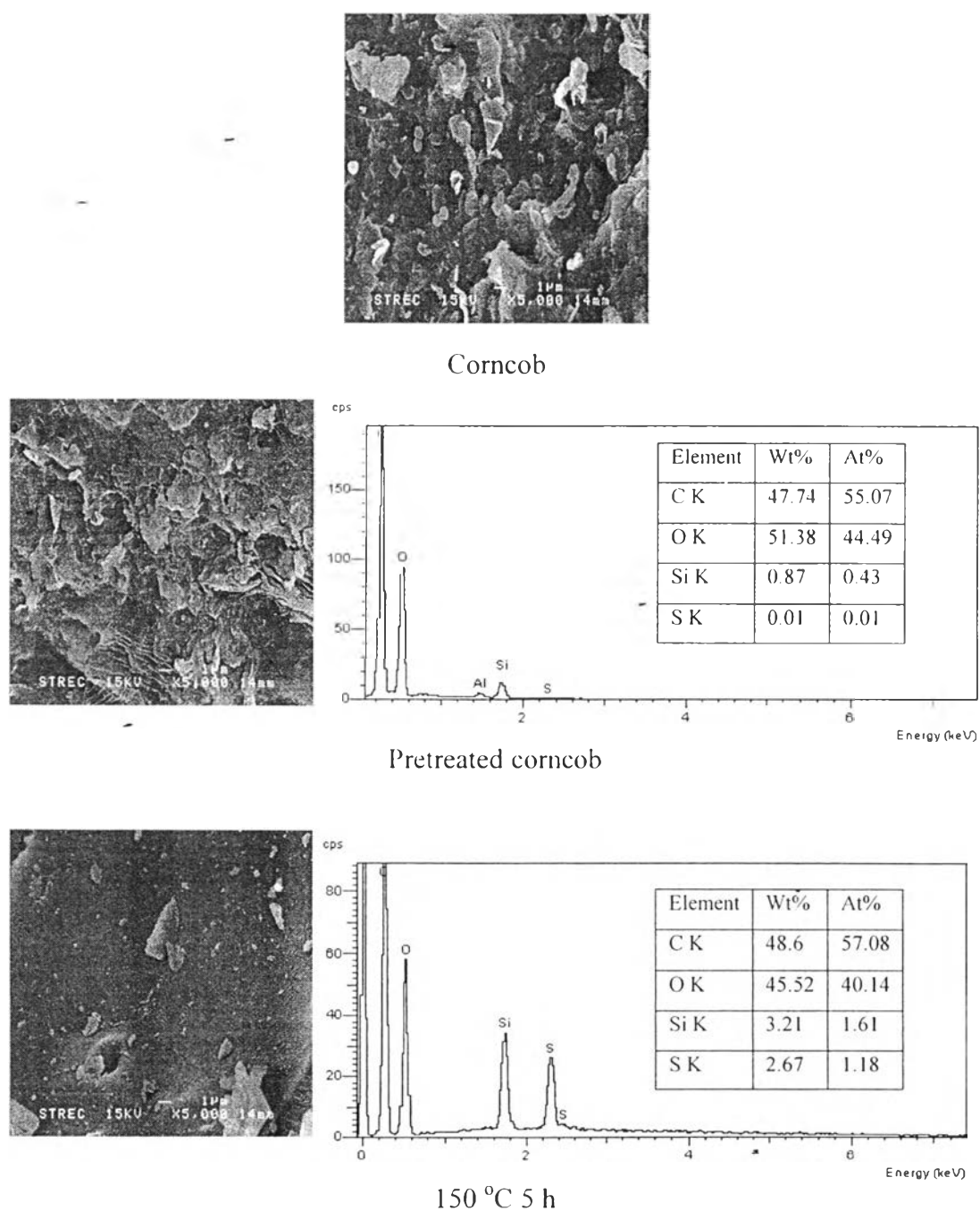
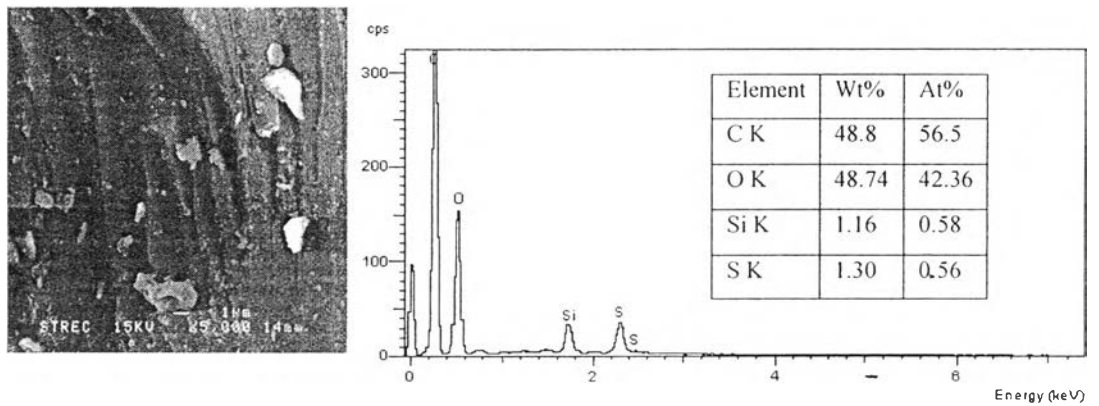
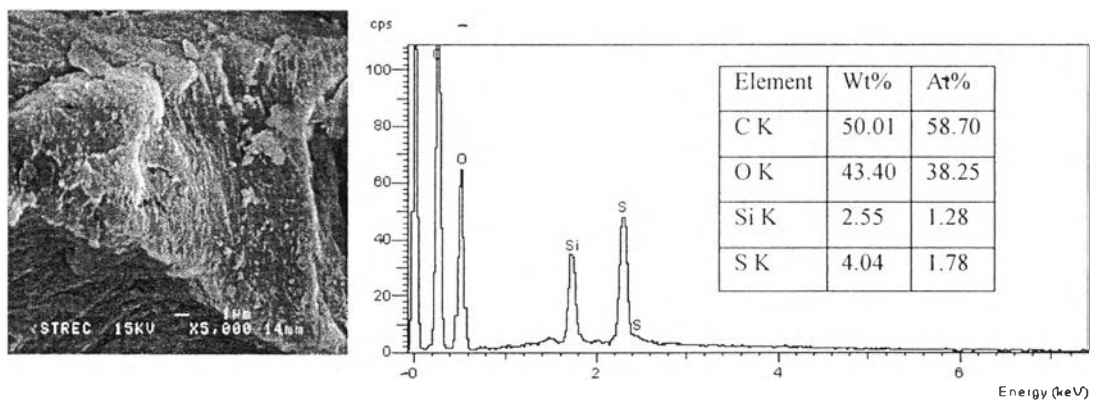


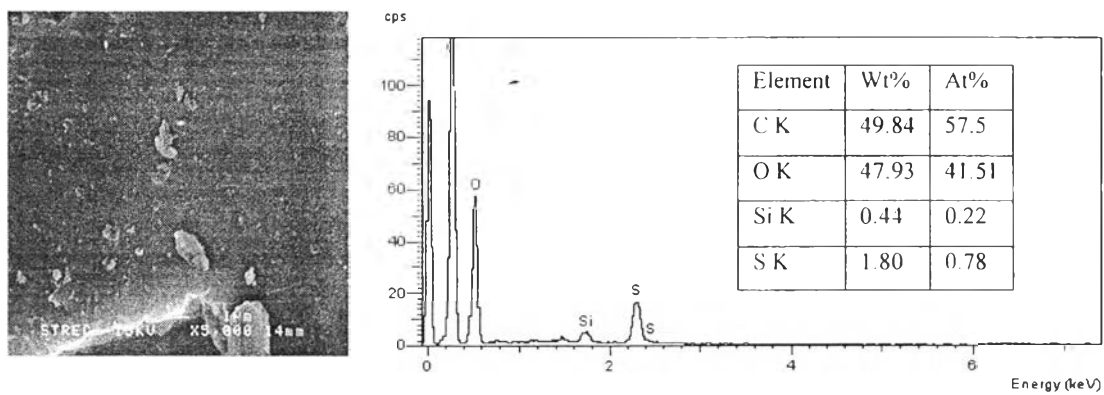
Figure 4.2 SEM images and EDX spectra of samples.



130 °C 5 h



110 °C 5 h



110 °C 3 h

Figure 4.2 (Cont) SEM images and EDX spectra of samples.

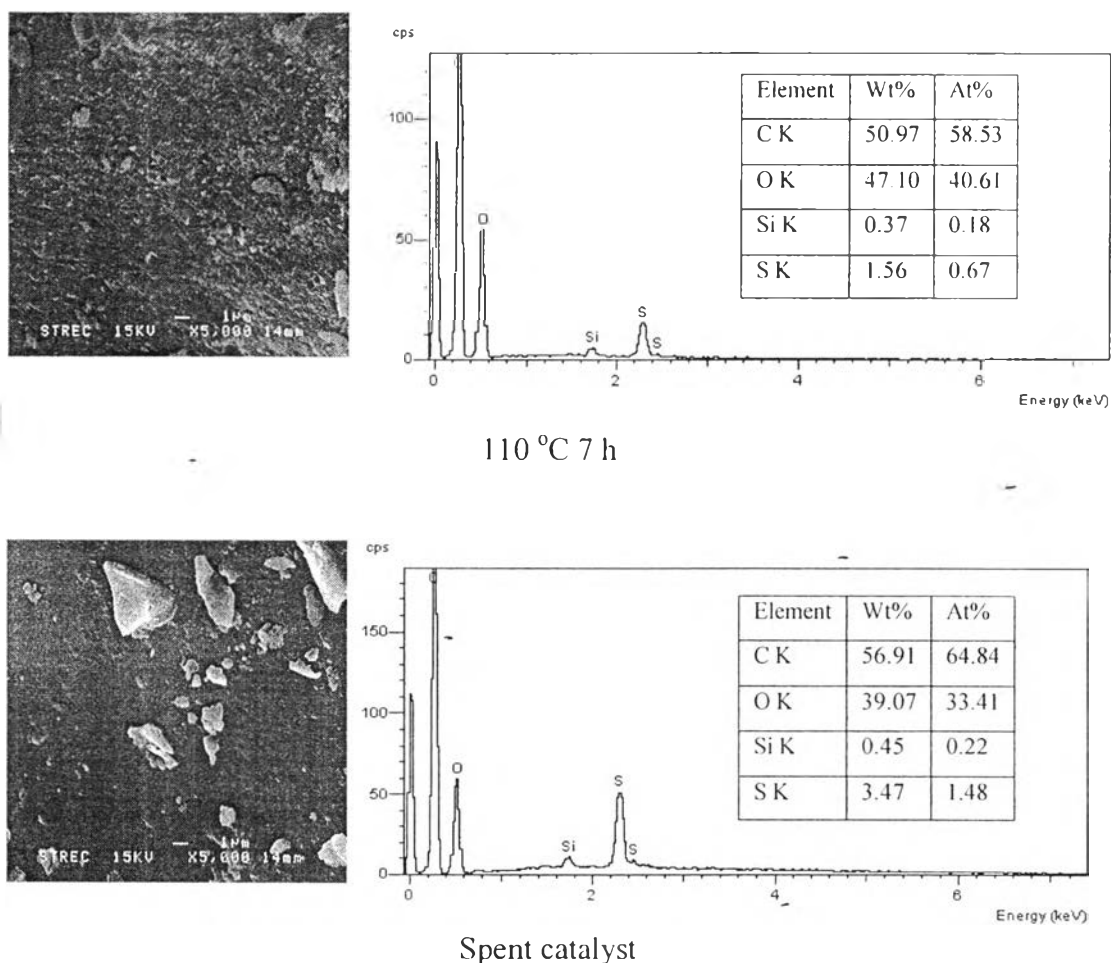


Figure 4.2 (Cont) SEM images and EDX spectra of samples.

4.1.5 Fourier Transform Infrared Spectroscopy (FT-IR)

FTIR spectroscopy was used to investigate the functional groups on the sulfonated lignin catalyst. This is an effective tool for a semi-quantitative estimation of structural information on functional groups in complex solids (Shu *et al.*, 2009). The FTIR transmittance spectra of the sulfonated lignin catalysts are shown in Figures 4.3. FT-IR spectra showed that the catalyst contain resident functionalities including C=C (1570 cm^{-1}), C-C (1140 cm^{-1}), C=O (1650 cm^{-1}), and OH (3400 cm^{-1}) which was assigned to the presence of lignin content. In addition, it shows the vibration bands at 1040 cm^{-1} is SO_3 stretching and 1377 cm^{-1} O=S=O stretching in the FTIR spectrum as a result of inducing the SO_3H groups in catalyst (Xing *et al.*,

2007). Therefore, it can be confirmed the existence of the sulfonic acid group of the catalysts sulfonated at different sulfonation temperatures.

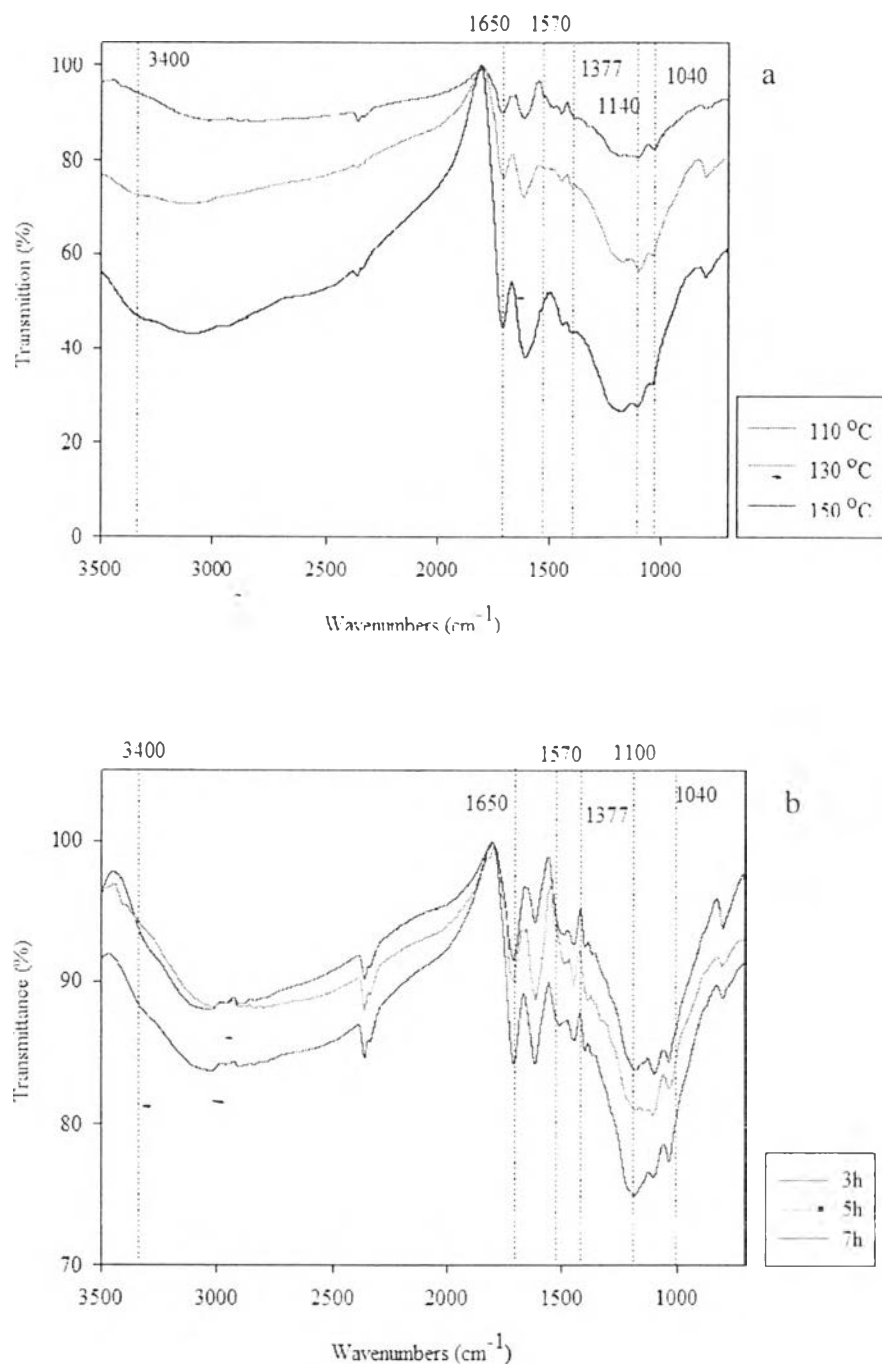


Figure 4.3 FTIR spectra of sulfonated lignin catalyst (a) at various sulfonation temperatures and (b) at various sulfonation times.

4.1.6 X-ray Diffraction (XRD)

Corncob consists of a crystalline structure and amorphous structure, which cellulose is crystalline portion whereas lignin and hemicelluloses are amorphous portion. Figure 4.4 shows the XRD patterns of pretreated corncob and sulfonated lignin catalysts with various sulfonation temperatures and various sulfonation times. The XRD patterns of pretreated corncob exhibited two diffraction peaks at 2θ angles of $10-20^\circ$ and $20-30^\circ$, which represented to typical cellulose crystal form (Lu *et al.*, 2013). In the case of all sulfonated lignin catalyst, the diffraction peak ($2\theta=20-30^\circ$) was attributed to amorphous composed of aromatic carbon sheets, due to cellulose was hydrolyzed by concentrated H_2SO_4 during sulfonation reaction. Therefore, the crystalline structure of the catalyst prepared by sulfonation at different temperatures and times can be destroyed and turned into amorphous form (Nakajima and Hara, 2007).

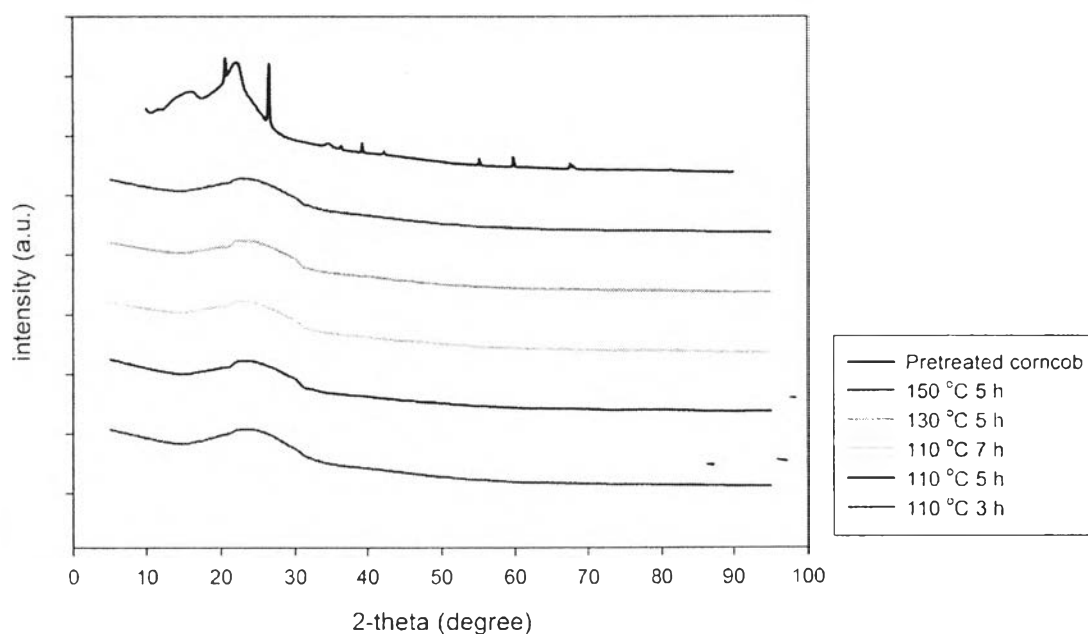


Figure 4.4 XRD patterns of samples: (a) Pretreated corncob, (b) 110°C 7 h, (c) 110°C 3 h, (d) 110°C 5 h, (e) 130°C 5 h, and (f) 150°C 5 h.

4.2 Effect of Catalyst Preparation

4.2.1 Effect of Sulfonation Temperature on Biodiesel Yield

The sulfonated lignin catalysts have been prepared by sulfonation reaction to give an active and stable solid catalyst that can catalyze the esterification of methanol and oleic acid to form methyl oleate (Zhang *et al.*, 2014). Figure 4.5 shows the effect of sulfonation temperature under the conditions of reaction temperature of 60 °C, 300 rpm of stirrer speed, 12:1 molar ratio of methanol to oil, amount of catalyst 5 wt%, and reaction time 8 h. From Figure 4.5, it can be observed that the biodiesel yield of catalyst sulfonated at room temperature gradually increased with the reaction time. The %FAME of the catalyst sulfonated at room temperature was about 28% at reaction time of 1 h and continues to increase (~65 %FAME) up on the reaction time is further increased to 8 h. In addition, the catalyst sulfonated at room temperatures gave lower biodiesel yield than the catalyst sulfonated at high temperatures, suggesting that sulfonation temperature affected the catalytic activity of sulfonated catalyst. From Brunauer-Emmett-Teller (BET) results in Table 4.1 can be seen that the catalyst sulfonated at room temperature shows small pore size diameter as compared with the catalyst sulfonated at high temperature that resulted in the lowest biodiesel yield. It seemed that when the pore size of catalyst is small, the entry of bulky organic molecule reactant will be obstructed. On the other hand, the catalysts sulfonated at high temperature that have the large pore size diameter can give higher biodiesel yield, therefore, it can easily diffuse into the interior of the catalyst. This allows reactants to contact with more acid sites, and the catalyst had better activity (Shu *et al.*, 2009).

For the catalyst sulfonated high temperature, the catalyst sulfonated at 150 °C had lower biodiesel yield than the catalyst sulfonated at 110 °C, which gave the highest biodiesel. This result can be explained by BET results and NH₃-TPD, from BET result show that the catalyst sulfonated at 110 °C gave higher surface area than the catalysts sulfonated at 130 °C and 150 °C, indicating that the catalyst with high surface area had a chance to contact with more acid site and subsequently resulted in high activity. Moreover, from the acid quantity measured by NH₃-TPD in Table 4.2, the catalyst sulfonated at 110 °C had the total acidity higher than those at

130 °C and 150 °C sulfonation temperature. In the esterification reaction, oleic acid (FFA) initially requires the activation of protonation of carbonyl group to initiate the reaction. Acid sites on the catalyst could activate the protonation of the carbonyl groups. The catalyst with higher acidity supplies more acid sites and stronger acid strength would lead to a more effective protonation of the carbonyl group of FFA that can give more products. Therefore, the catalyst sulfonated at 110 °C gave the highest biodiesel since it had the highest total acidity. This agrees well with the titration result, the catalyst sulfonated at 110 °C had the highest acid density of 1.36 mmol/g. From these results, it can be concluded that the catalyst had more $-SO_3H$ groups as acid sites in catalyst, subsequently resulted in high activity (Shu *et al.*, 2010).

As mentioned above, the catalyst has high surface area, pore diameter, and acidity, leading to high activity for esterification. It should be noted that the catalytic activities of the sulfonated lignin catalysts could be related with variables during sulfonation reaction. The sulfonation temperature and the suitable sulfonation temperature for preparing the sulfonated lignin catalyst belonged to 110 °C.

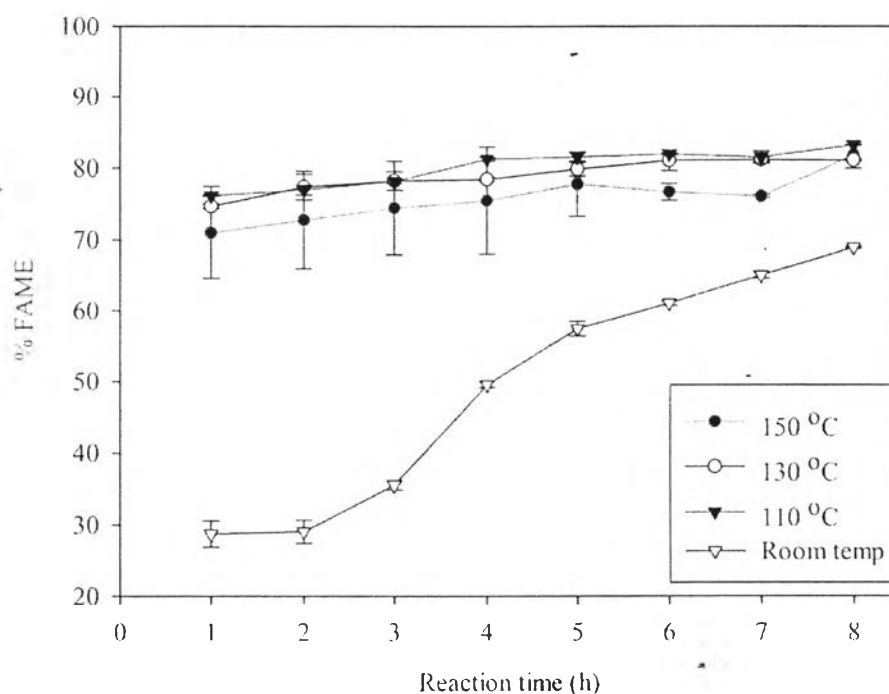


Figure 4.5 Effect of sulfonation temperature on biodiesel yield. Reaction condition: 50 g oleic acid, 68 g methanol, 2.5 g catalyst, reaction temperature 60 °C.

4.2.2 Effect of Sulfonation Time on Biodiesel Yield

The sulfonated lignin acid catalysts prepared by sulfonation reaction were expected to give an active and stable solid catalyst that can catalyze the esterification of methanol and oleic acid to form methyl oleate. Figure 4.6 shows the effect of sulfonation time under the reaction conditions at 60 °C, a methanol to oil ratio of 12:1, and 300 rpm stirrer speed and sulfonation temperature at 110 °C. From the Figure 4.6 indicates that the sulfonated lignin catalyst at sulfonation time of 7 h gave the lowest biodiesel yield because it had the lowest surface area (Table 4.1). The catalyst sulfonated at 5 h exhibited the highest biodiesel yield. From BET results (Table 4.1) can be seen that the catalyst sulfonated at 3 h and 5 h had high surface areas that could result in high active sites surface area.

Moreover, from the acid quantity measured by NH₃-TPD, as shown in Table 4.2, the catalyst sulfonated at 5 h had the highest acid density of 2.687 mmol/g. According to titration result, the catalyst sulfonated at 5 h also had the highest acid density of 1.36 mmol/g. Obviously, the catalyst with higher acidity supplies more acid sites and stronger acid strength would lead to high activity for the esterification (Shu *et al.*, 2010). On the other hand, all catalysts prepared at different sulfonation times displayed a similar %FAME (~80%) and esterification rate despite a big difference in total acid quantified by NH₃-TPD.

As mentioned above, the catalyst with high surface area and acidity would lead to high activity for esterification. This should be noted that the catalytic activities of the sulfonated lignin catalysts could be related with the sulfonation temperature and the suitable sulfonation temperature for preparing the sulfonated lignin catalyst belonged to 5 h.

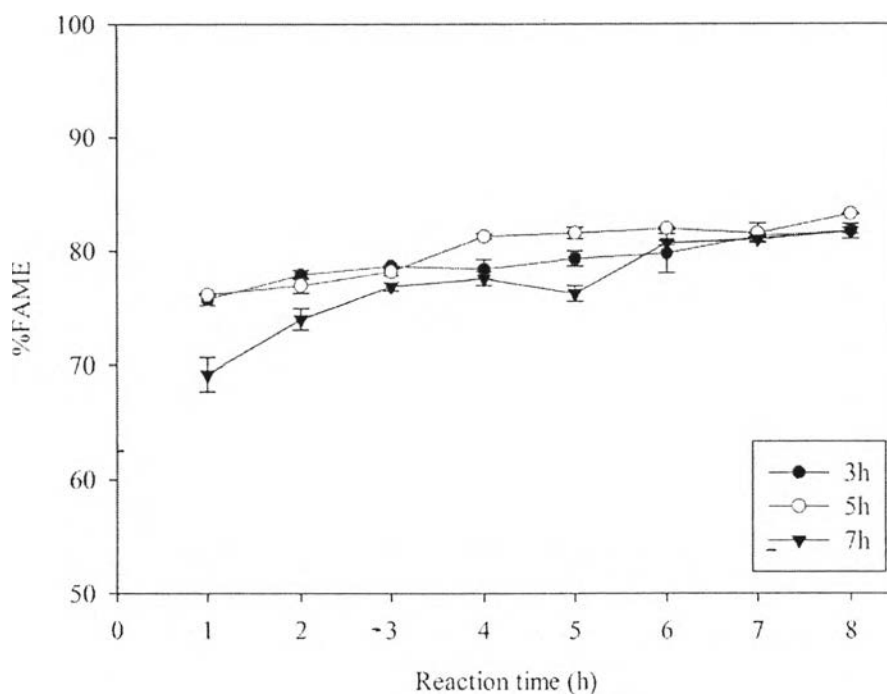


Figure 4.6 Effect of sulfonation time on biodiesel yield. Reaction conditions: 50 g oleic acid, 68 g methanol, 2.5 g catalyst, reaction temperature 60 °C.

4.3 Esterification Reaction

The esterification reaction was performed in a laboratory scale Parr reactor. The sulfonated lignin catalyst was used as a heterogeneous acid catalyst in the esterification reaction. To investigate the optimum conditions of these catalysts in esterification of oleic acid, the starting conditions of esterification reaction over the sulfonated lignin catalyst were 60 °C, 300 rpm of stirrer speed, 12:1 molar ratio of methanol to oil, amount of catalyst 5 wt% (based on weight of oleic acid), and reaction time of 8 h.

4.3.1 Effect of Amount of Catalyst on Biodiesel Yield

The amount of catalyst used in this reaction also affects the biodiesel yield. The catalyst sulfonated at 110 °C 5 h was used as a catalyst to study the effect of amount of catalyst on biodiesel yield. The fixed parameters were 60 °C, a methanol to oil ratio of 12:1, and 300 rpm stirrer speed.

The effect of amount of catalyst was studied at 5 wt%, 6 wt% and 7 wt% on the biodiesel yield, as illustrated in Figure 4.7. The biodiesel yield was about 75% at a low amount of catalyst (5%) at a reaction time of 1 h and increased slightly with increased reaction time. The highest biodiesel yield of oleic acid was 83.3% when the amount of catalyst was 5 wt% after 8 h. However, a significant decrease in the biodiesel yield was clearly observed when the amount of catalyst was 6 wt%. This was probably due to the growth of side effect resulted from the increasing acidity of the reaction system with larger amount of catalyst, and the adsorption of the product molecules by the excessive of catalyst that could lead to higher mass transfer resistance (Liu *et al.*, 2013). When further increasing amount of catalyst from 5 wt% to 7 wt%, no improvement in the biodiesel yield was observed. Therefore, 5 wt% seem to be optimal in this section.

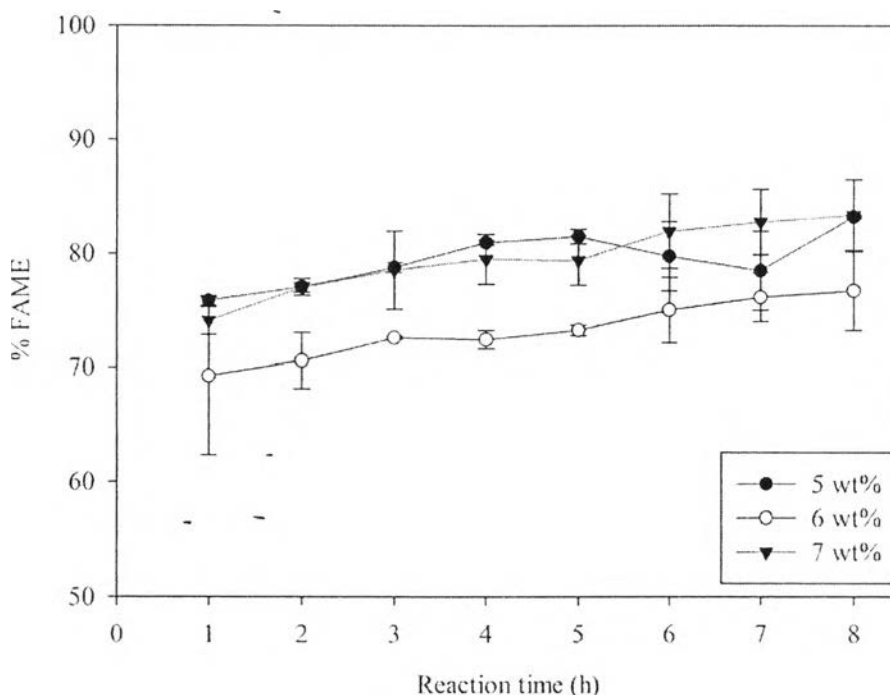


Figure 4.7 Effect of amount of catalysts on biodiesel yield. Reaction conditions: 50 g oleic acid, 68 g methanol, reaction temperature 60 °C.

4.3.2 Effect of Molar Ratio of Methanol to Oleic Acid on Biodiesel Yield

The esterification reaction requires one moles of alcohol and one mole of oleic acid to give one mole of esters and one mole of water (Borges and Diaz, 2012). Therefore, excess alcohol is required to drive the reaction toward the product side to increase biodiesel yield. To evaluate the influence of molar ratio of methanol to oleic acid on biodiesel yield. The reaction was evaluated at three different molar ratios of methanol to oleic acid: 9:1, 12:1, 15:1. The fixed parameters were 60 °C, catalyst amount of 5 wt%, and 300 rpm stirrer speed.

The effect of molar ratio of methanol to oleic acid on biodiesel yield is shown in Figure 4.8. The biodiesel yield was influenced by the molar ratio of methanol to oleic acid. As can be seen in Figure 4.8, the biodiesel yield increased with an increase in the molar ratio of methanol to oleic acid. The molar ratio of methanol to oleic acid at 15:1 and 18:1 gave biodiesel yield higher than 9:1 and 12:1. However, at a 15:1 and 18:1 molar ratio of methanol to oleic-acid the biodiesel yield during 1 h to 7 h reaction time are similar, but after that the molar ratio of methanol to oleic acid at 15:1 biodiesel yield is higher than 18:1. It seemed that at a 15:1 molar ratio of methanol to oleic acid seems to be optimal in this section. Therefore, the molar ratio of methanol to oleic acid at 15:1 was necessary to accelerate the rate of reaction and drive the equilibrium to obtain the high biodiesel yield for this reaction. It should be noted that the biodiesel yield could be related with the molar ratio of methanol to oleic acid (Rattanaphra *et al.*, 2012).

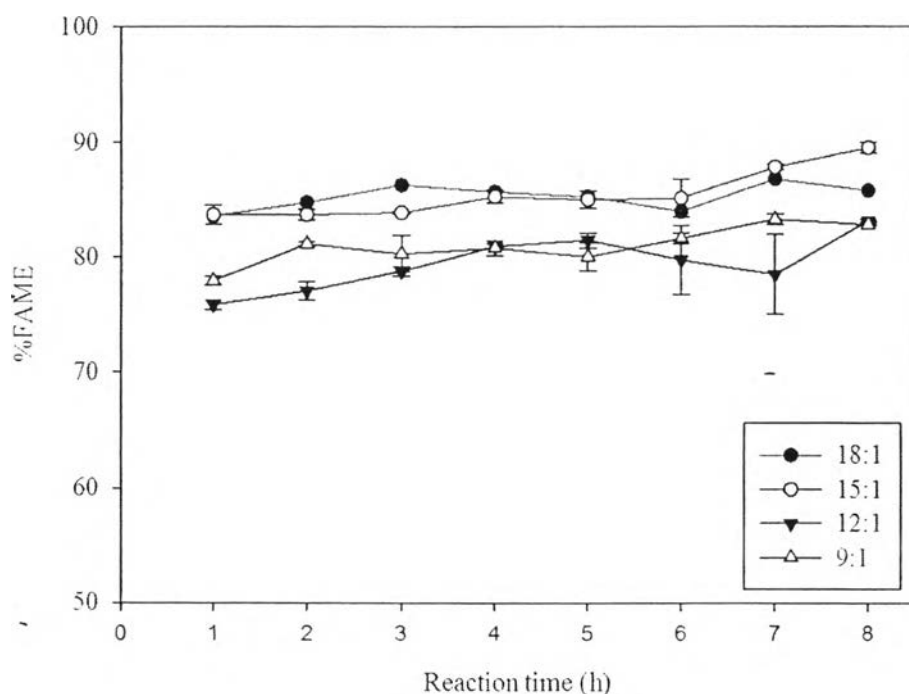


Figure 4.8 Effect of molar ratio of methanol to oleic acid on biodiesel yield. Reaction conditions: 50 g oleic acid, 2.5 g catalyst, reaction temperature 60 °C.

4.3.3 Catalyst Stability

The catalytic stability testing of the sulfonated lignin catalyst was tested for 32 h of time on stream under optimum conditions of 8 h of reaction time, 15:1 molar ratio of methanol to oil, amount of catalyst 5wt%, 300 rpm of stirrer speed, 110 °C sulfonation temperature and 5 h sulfonation time. The catalytic stability is shown in Figure 4.9. The experimental results demonstrated that the biodiesel yield of the catalyst still remain stable around 90 % until 20 h of reaction. After that, the biodiesel yield decreased to 75 % at 32 h of reaction. One possible cause for the depleting of activity during stability test is due to the reduction of active site and a loss of the catalyst acidity.

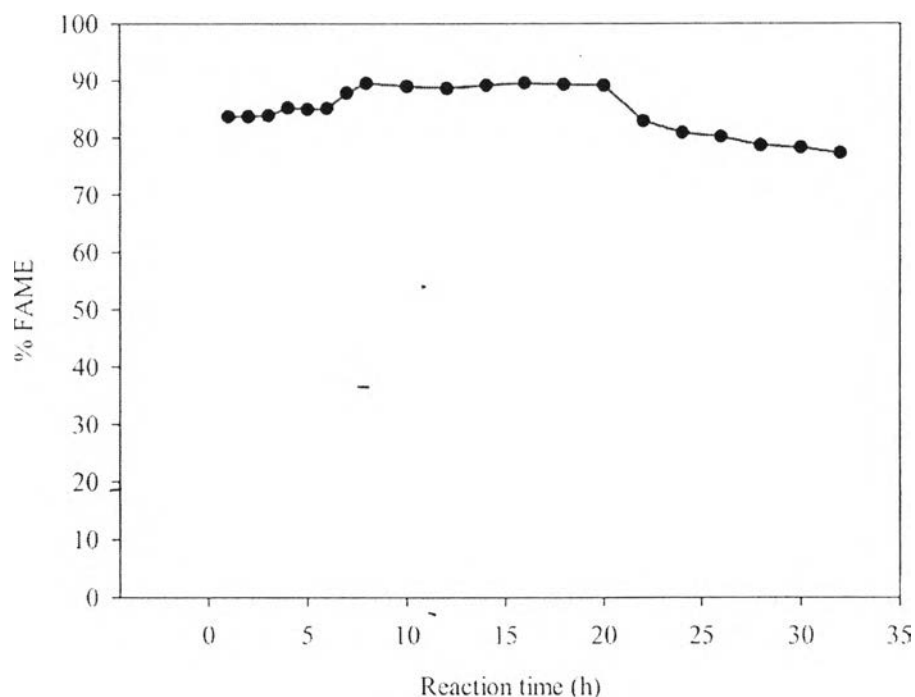


Figure 4.9 Catalyst stability of the pretreated sample. Reaction conditions: 50 g oleic acid, 85 g methanol, 2.5 g catalysts, reaction temperature 60 °C.

4.3.4 Catalyst Reusability

In the field of catalyst, the life time of the prepared catalyst is defined as one of the most important criteria for the present commercialization. The catalyst sulfonated of 110 °C 5 h was used to test the catalyst reusability under the optimum condition at 60 °C, a methanol to oil ratio of 15:1, catalyst of 5 wt%, and 300 rpm stirrer speed. It was repeatedly used for biodiesel production. The catalyst was filtered out from the reaction medium after 8 h of reaction and reused in the 2nd run without any treatment, which is typically done to reactivate the active sites of the catalyst. Figure 4.10 shows the catalyst reusability. It can be observed that biodiesel yield decreased as recycling time increased. The sulfonated lignin catalyst exhibited high catalytic activity about 90%FAME in the first run; however, the biodiesel yield decreased dramatically to 70% after the 2nd run. At the end of reaction, the spent catalyst was separated and the sulfur content was analysed by SEM-EDX technique. From EDX spectra, the sulfur content of fresh catalyst decreased about 14% after testing in esterification for 8 h due to leaching of -SO₃H group (Shu *et al.*, 2010).

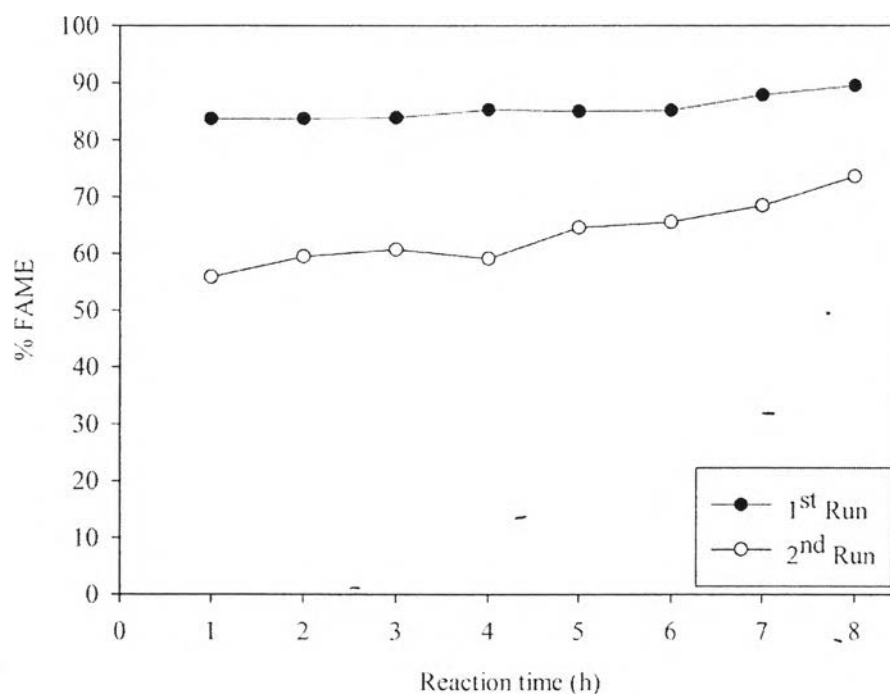


Figure 4.10 Catalyst reusability on biodiesel yield. Reaction conditions: 50 g oleic acid, 85 g methanol, 2.5 g catalyst. reaction temperature 60 °C.