CHAPTER IV
RESULTS AND DISCUSSION

4.1 Biodiesel Analysis

4.1.1 Catalytic Activity

The catalytic activity of the prepared catalysts was investigated on esterification of oleic acid with methanol at the reaction conditions of 15:1 methanol to oil at 60°C for 8 h. A gas chromatography technique was used to analyze biodiesel yield. Table 4.1 shows the biodiesel yield of the prepared catalysts. The sulfonated catalyst by TsOH was used as a catalyst to study the effect of TsOH loading and compare to the sulfonated catalyst by H_2SO_4 from the previous work of Namwong (2014). The catalyst prepared from fresh corncob that activated by 184 g of H_2SO_4 gave the highest biodiesel yield, 86.49 %. Whereas, the catalyst activated by TsOH gave biodiesel yield in the range of 73 to 80 %, and the highest biodiesel yield of 80.4 % was obtained by C-TsOH-10. And the catalyst activated by the mixture of H_2SO_4 and TsOH gave the biodiesel yield about 75 %. Then the commercial lignin was used as reference to support the methodology applied and compare to the catalyst prepared from the fresh corncob. It was sulfonated either by 184 g of H_2SO_4 and 10 g of TsOH; however, the biodiesel yields obtained from both catalysts were lower than those obtained from pretreated corncob. The results indicated that the highest biodiesel yield obtained from C-H_2SO_4-184 catalyst and followed by the best novel catalyst (C-TsOH-10). The mixture of H_2SO_4 and TsOH and ratio of the mixture didn't affect the biodiesel yield. The catalysts that activated by 184 g of the pretreated corncob and 10 g of p-toluenesulfonic acid that prepared from the pretreated corncob had better catalytic activity than the commercial lignin for the biodiesel production.

Table 4.1 Biodiesel yield of the solid acid catalysts

Catalyst	Biodiesel Yield (%)
C-H$_2$SO$_4$-184	86.49±0.58
L-H$_2$SO$_4$-184	78.22±0.74
C-TsOH-5	73.18±1.09
C-TsOH-10	80.40±0.87
C-TsOH-15	77.64±1.14
C-TsOH-20	76.36±2.11
L-TsOH-10	39.46±2.04
C-M-3-10	74.18±1.22
C-M-15-10	75.41±1.35

4.1.2 Condition Variables

4.1.2.1 Effect of Catalyst Loading

From previous section, the C-TsOH-10 catalyst exhibited high activity. In this section, the C-TsOH-10 catalyst was used to catalyze the biodiesel production by varying the catalyst weight loading from 5 to 10 and 15 wt% of the oleic acid in the same conditions. The results in Figure 4.1 showed that the biodiesel yield was decreased from 80.40 to 79.14 and 75.76 %, respectively. This result indicated that 5 wt% of the catalyst was the best catalyst loading for biodiesel production.
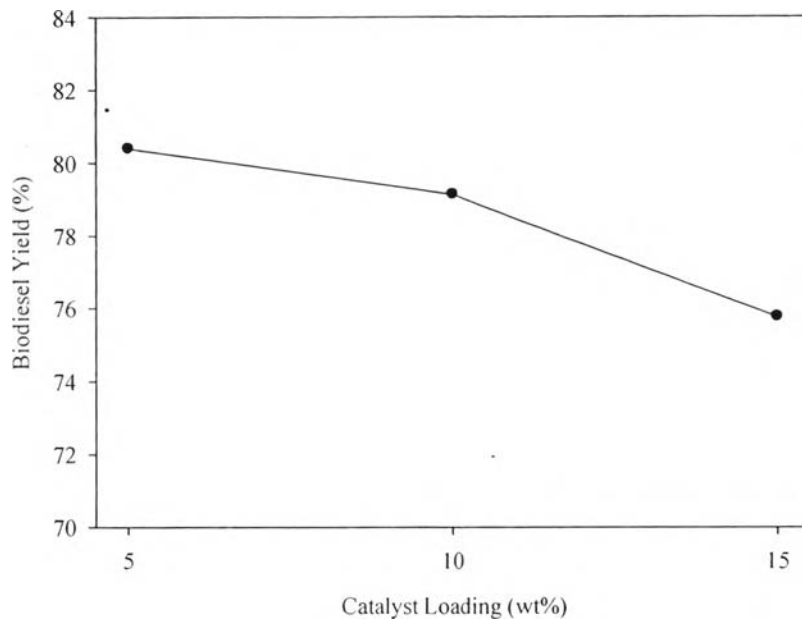
Figure 4.1 Effect of catalyst loading on biodiesel yield in the presence of C-TsOH-10 catalysts at 60°C.

4.1.2.2 Effect of Reaction Time

C-H$_2$SO$_4$-184 and C-TsOH-10 catalysts were studied in biodiesel production at varions reaction time of 2, 4, and 8 h at 60°C. The results in Figure 4.2 indicated that C-TsOH-10 catalyst could catalyze the reaction faster than C-H$_2$SO$_4$-184 catalyst at the reaction time of 2 h, and 53.09 % biodiesel yield was obtained. Then it was nearly steady at 72.72 and 75.47 % when the reaction time was increased to 4 and 8 h, respectively. While C-H$_2$SO$_4$-184 catalyst gave biodiesel yield just only 20.76 % at 2 h, and it increased to 69.16 and 86.90 % at 4 and 8 h of reaction time, respectively.
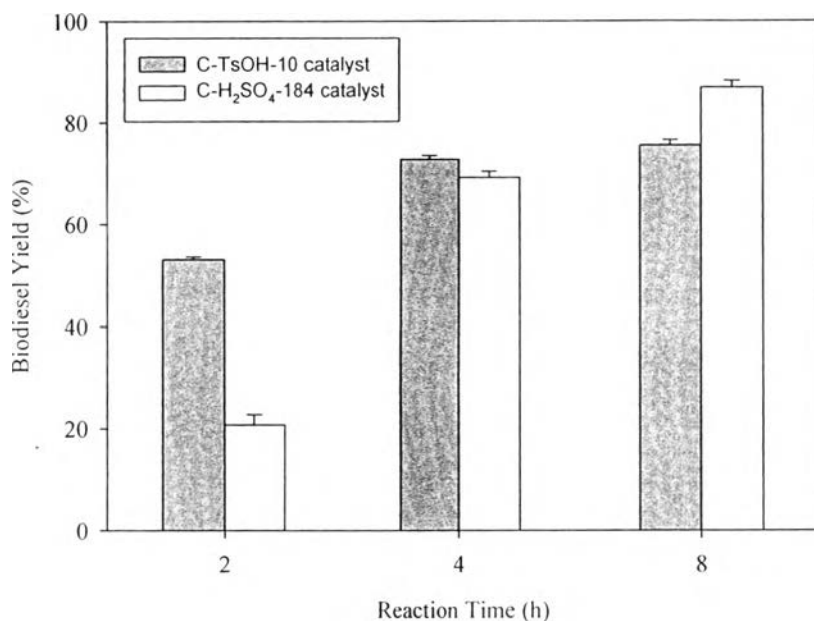
Figure 4.2 Effect of reaction time on biodiesel yield in the presence of C-TsOH-10 and C-H₂SO₄-184 catalysts at 60°C.

4.1.2.3 Effect of Reaction Temperature

From the previous section, .C-TsOH-10 catalyst could catalyze the reaction very fast, but it still gave low biodiesel yield. Then the effect of reaction temperature on biodiesel yield was also studied. It was found that the biodiesel yield increased about 30 % when the temperature was increased from 60 to 80°C. And, when the temperature was increased to 100°C, the biodiesel yields were slightly lower than that at 80°C. The results indicated that 80°C was the suitable temperature for the biodiesel production in the presence of C-TsOH-10 catalyst. This temperature was the same condition reported by Zhang *et al.* (2010) for biodiesel production in the presence of TsOH activated solid acid catalyst.
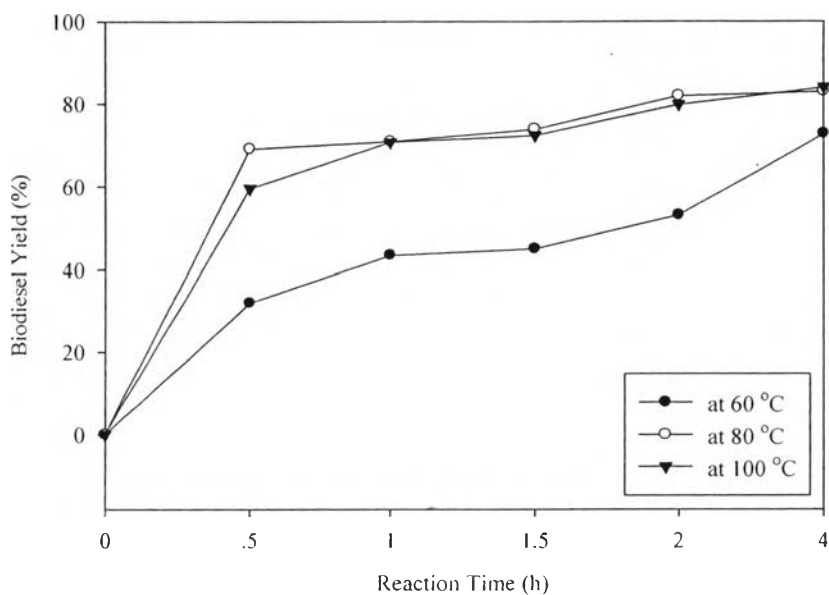
Figure 4.3 Effect of reaction temperature on biodiesel yield in the presence of C-TsOH-10 catalyst.

4.1.3 Reusability

Spent C-TsOH-10 catalyst was utilized to catalyze the biodiesel production reaction at 80°C for 1 h, for many cycles to test the reusability. After the first cycle, methyl ester was removed out from PARR reactor by filtration, while the catalyst was still in the reactor and used continuously without regeneration. The results in Figure 4.4 showed that the biodiesel yield was decreased from about 80 % of the first cycle to about 45 and 30 % of the second and third cycles, respectively. This result indicated that C-TsOH-10 catalyst didn't have an ability to use in many cycles of biodiesel production since acid sites were leached out from the catalyst. This assumption was supported by the acid quantity obtained by titration method.
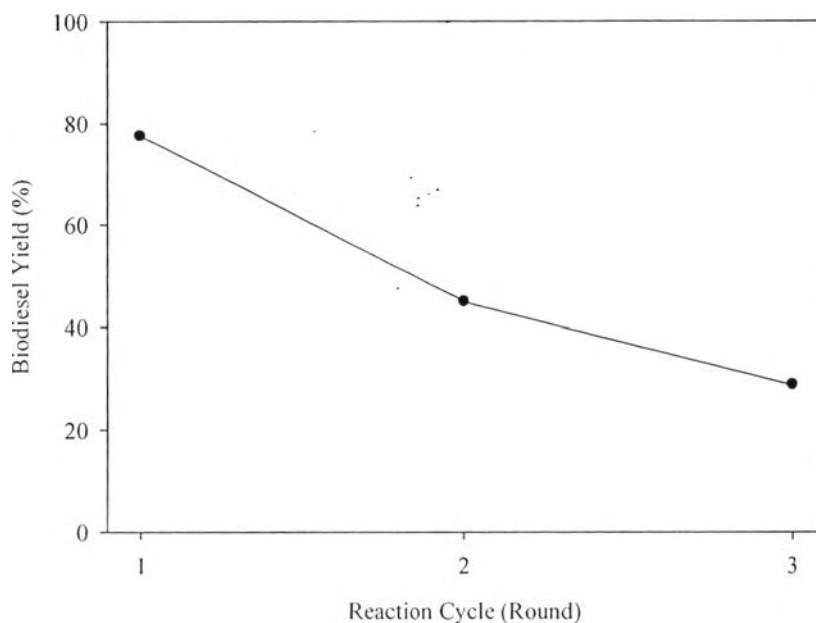
Figure 4.4 Reusability of C-TsOH-10 catalyst for biodiesel production at 80°C.

4.2 Catalyst Characterization

4.2.1 Scanning Electron Microscope (SEM)

Morphologies of the starting materials and solid acid catalysts were investigated, in micrometer scale, by scanning electron microscopy technique. The results of fresh corncob, pretreated corncob, and C-H_2SO_4-184 catalysts are shown in Figures 4.5(a), 4.5(b), and 4.5(c), respectively. It is clearly seen that the fresh corncob had the typical regular and compact structure. An amorphous structure of solid particles became more complex sequentially when the samples were pretreated with acid. This indicated that the acid pretreatment and sulfonation processes were effectively to expose the surface area and pore structure of the particles. Small pores appeared on the surface of pretreated corncobs (Figure 4.5(b)) and large pores were visible with the sample treated by H_2SO_4 (Figure 4.5(c)).
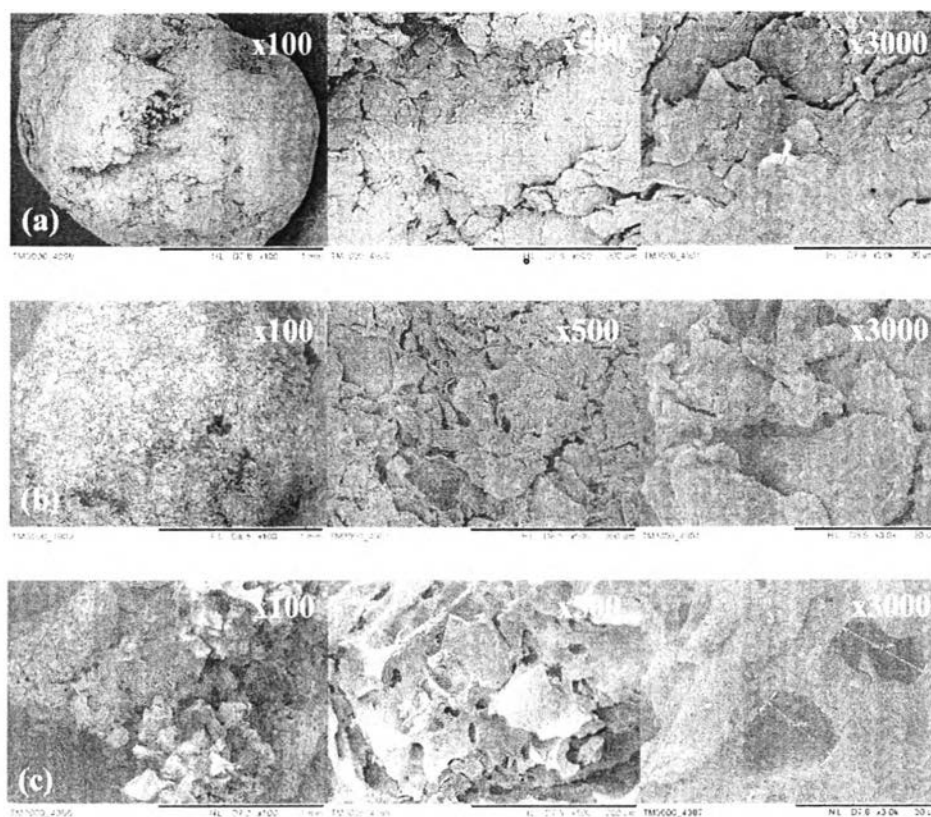
Figure 4.5 SEM images at different magnifications of (a) fresh corncobs, (b) pretreated corncobs, and (c) C-H$_2$SO$_4$-184 catalyst.

The morphologies of C-TsOH-5, C-TsOH-10, C-TsOH-15, and C-TsOH-20 catalyst are shown in Figures 4.6(a), 4.6(b), 4.6(c), and 4.6(d), respectively. From the results, it was clearly seen that clearly porous structure occurred. The morphology from SEM images indicated that varied weight loading of TsOH in sulfonation process slightly affected to their structure. However, for different types of acid, the morphology of catalyst activated by TsOH looked like more complex than the morphology of H$_2$SO$_4$ activated catalyst. It means that the catalyst activated by TsOH probably has more porous structure than H$_2$SO$_4$ activated catalyst. That was a good property for the solid catalyst to be provided the area for active sites.
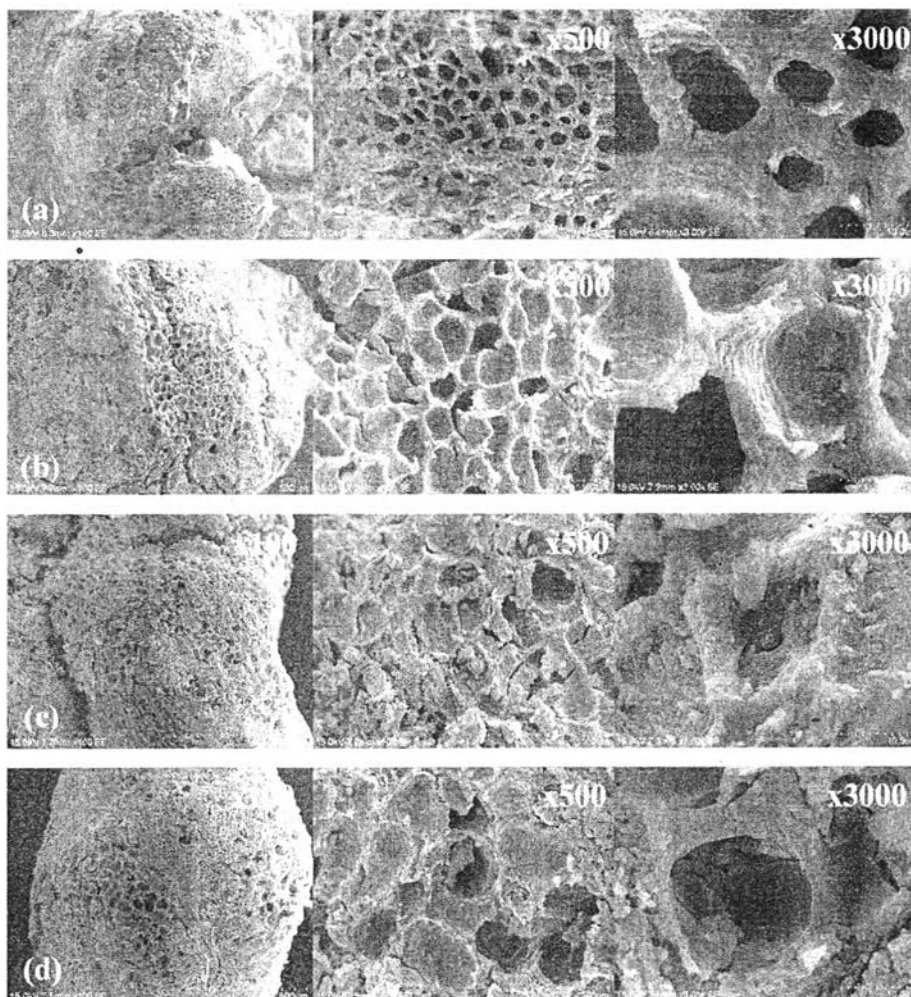
Figure 4.6 SEM images at different magnifications of (a) C-TsOH-5 catalyst, (b) C-TsOH-10 catalyst, (C) C-TsOH-15 catalyst, and (D) C-TsOH-20 catalyst.

The morphologies of C-M-3-10 and C-M-15-10 catalysts are shown in Figures 4.7(a), and 4.7(b), respectively. The mixture of H_2SO_4 and TsOH slightly affected to the structure of the catalysts when compared to the catalyst activated by pure TsOH. Clearly porous structures of the catalysts are also shown in the images.
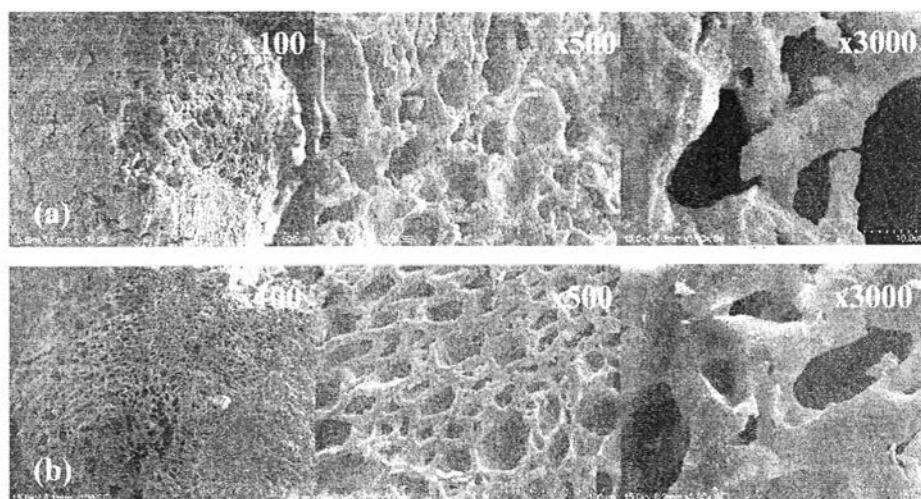
Figure 4.7 SEM images at different magnifications of (a) C-M-3-10 catalyst and (b) C-M-15-10 catalyst.

The morphologies of commercial lignin, L-H_2SO_4-184 catalyst, and L-TsOH-10 catalysts are presented in Figures 4.8(a), 4.8(b) and 4.8(c), respectively. The structure of commercial lignin looked like a spherical powder. It combined together and formed bigger amorphous solid particles that had more porous structure after the sulfonation process for both H_2SO_4 and TsOH. The spherical powder structure of commercial lignin was supported by referable SEM image result of the commercial lignin (Soygun *et al.*, 2013) as shown in Figure C.1, Appendix C.

However, these all morphology results showed just the micrometer scale structure that was macroporous structure of the catalysts that could indicate just the roughly different structure between each catalyst. To relate this result with the activity of the catalysts, the smaller scale of mesoporous or microporous structure was also investigated by another technique of surface area analysis.
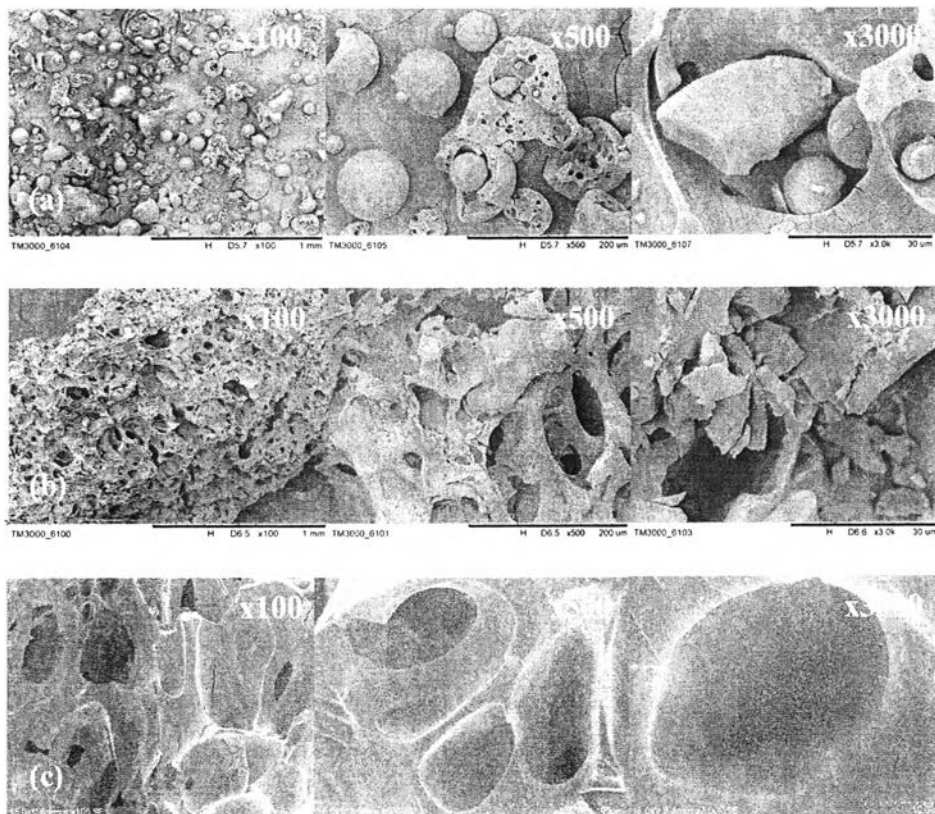
Figure 4.8 SEM images at different magnifications of (a) commercial lignin, (b) L-H$_2$SO$_4$-184 catalyst, and (c) L-TsOH-10 catalyst.

4.2.2 Carbon, Hydrogen, Nitrogen, and Sulfur Analysis (CHNS)

Elements of the starting materials and solid acid catalysts were investigated by carbon, hydrogen, nitrogen, and sulfur analysis. The results in Table 4.2 show that the samples had the element of carbon, hydrogen, and nitrogen were in range of 50-70, 3-6, and 0.1-0.7 wt%, respectively. The sulfur element of fresh and pretreated corncob was initially very low, about 0.3 wt%. After sulfonation process, it was obviously increased, and the highest percentage of 5.98 wt% sulfur was obtained from C-TsOH-10 catalyst. For commercial lignin, the sulfur element was initially high, about 5 wt%, and also increased after the sulfonation process. The sulfur contents were 6.4 and 7.9 wt% for L-H$_2$SO$_4$-184 and L-TsOH-10, respectively. This result indicated a good evidence of an increasing of sulfur content after the sulfonation process that was related to the amount of –SO$_3$H active site.

Table 4.2 Element of the starting materials and solid acid catalysts

Catalyst	Element (wt %)			
	Carbon	Hydrogen	Nitrogen	Sulfur
Fresh Corncob	50.50	6.03	0.68	0.26
Pretreated Corncob	52.40	6.26	0.30	0.39
C-H$_2$SO$_4$-184	56.30	3.44	0.24	3.72
C-TsOH-5	67.90	4.34	0.27	5.69
C-TsOH-10	68.20	3.88	0.18	5.98
C-TsOH-15	72.50	4.50	0.13	4.62
C-TsOH-20	71.80	4.59	0.14	4.41
L-M-3-10	71.00	4.37	0.24	3.22
L-M-15-10	69.90	4.13	0.15	3.93
Commercial Lignin	49.90	5.41	0.11	4.81
L-H$_2$SO$_4$-184	53.40	3.32	0.13	6.44
L-TsOH-10	67.30	3.88	0.10	7.90

4.2.3 Acid-Base Titration Method

Total acid quantities of the solid acid catalysts were investigated by titration method. The results in Table 4.3 showed that the acid quantities of C-H$_2$SO$_4$-184, L-H$_2$SO$_4$-184, C-TsOH-5, C-TsOH-10, C-TsOH-15, C-TsOH-20, L-TsOH-10, C-M-3-10, and C-M-15-10 catalysts were 1.93, 0.35, 0.58, 0.60, 0.62, 0.63, and 0.60 mmol/g, respectively. The acid quantity of C-H$_2$SO$_4$-184, 1.93 mmol/g, was close to the previous work of Namwong (2014). The corncob that activated by 10, 15, and 20 g of TsOH and the mixture of the acid reagents, had the acid quantities closely and gave the biodiesel yield nearly the same in the range of 73-80 %, except C-TsOH-5 catalyst gave the lower acid quantity and biodiesel yield of 73.18 %. Among the fresh corncob treated by TsOH samples, C-TsOH-10 catalyst seemed to be the best catalyst. When considering the acid quantity result, C-H$_2$SO$_4$-184 catalyst had the acid quantities much higher than C-TsOH-10; however, it does not gave much difference in biodiesel yield. A comparison of acid quantities of the catalysts that activated by H$_2$SO$_4$ and TsOH was supported by Zhang *et al.* (2010). They reported that the acid quantity of their staring material was 1.02 mmol/g and increased to 3.2 and 1.99 mmol/g after the sulfonation of

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H_2SO_4 and TsOH, respectively. These values supported the result that acid quantity of C-H_2SO_4-184 was higher than that of C-TsOH-10. Furthermore, the catalysts prepared from commercial lignin were also investigated. L-H_2SO_4-184 and L-TsOH-10 had the acid quantities of 1.20 and 0.32, respectively. The results indicated that the fresh corncob was the suitable starting material to prepare the solid acid catalyst than the commercial lignin, referred to the higher acid quantity and consequently high biodiesel yield. From the catalyst characterization results, it seemed that another parameter could affect the activity of the catalysts besides the acid quantity. However, this titration method just roughly investigated the acid quantity of the prepared catalyst and the general trend of the acid quantity was related with the biodiesel yield. More accuracy technique was explained in next section.

Table 4.3 Acid quantity of the solid acid catalysts

Catalyst	Biodiesel Yield (%)	Acid Quantity (mmol/g)
C-H_2SO_4-184	86.49	1.93±0.01
L-H_2SO_4-184	78.22	1.20±0.03
C-TsOH-5	73.18	0.35±0.03
C-TsOH-10	80.40	0.58±0.03
C-TsOH-15	77.64	0.60±0.02
C-TsOH-20	76.36	0.62±0.03
L-TsOH-10	39.46	0.32±0.01
C-M-3-10	74.18	0.63±0.03
C-M-15-10	75.41	0.60±0.02

After each cycle of biodiesel production via esterification, when methyl ester was separated out from PARR reactor, spent C-TsOH-10 catalyst sample was taken out about 0.05 g to determine the acid quantity by filtration method. The results in Table 4.4 show that C-TsOH-10 catalyst gave 77.51 % yield of biodiesel for the first cycle and had the acid quantity of 0.58 mmol/g. Then, the acid quantity was decreased from 0.58 to 0.5 and 0.44 for of the second and third

cycles, respectively. The lower yield of biodiesel of 44.91 and 28.76 % were obtained from the second and third cycles of spent C-TsOH-10 catalyst, respectively. These results indicated a deactivation of the spent catalyst due to the leaching of active acid site from the catalyst after the biodiesel production process (Kiss *et al.*, 2005).

Table 4.4 Acid quantity of spent C-TsOH-10 catalyst

Biodiesel Production Cycle	Acid Quantity (mmol/g)	Biodiesel Yield (%)
1st	0.58	77.51
2nd	0.50	44.91
3th	0.44	28.76

4.2.4 Temperature-Programmed Desorption – Ammonia (TPD-NH_3)

Acidity of the solid acid catalysts were also investigated by temperature-programmed desorption technique with ammonia. The temperature profiles are presented in Figures 4.9 and 4.10 and the values are summarized in Table 4.5. Total acid quantity was determined from the total desorption peak area of ammonia in the temperature profile. And the desorption peaks at between 100 to 400, between 400 to 550°C, and higher than 550°C are assigned to weak, medium and strong acid strength, respectively. This acid quantity and its strength ascribed the amount of acid sites that present in the catalysts. (Zhang *et al.*, 2014)
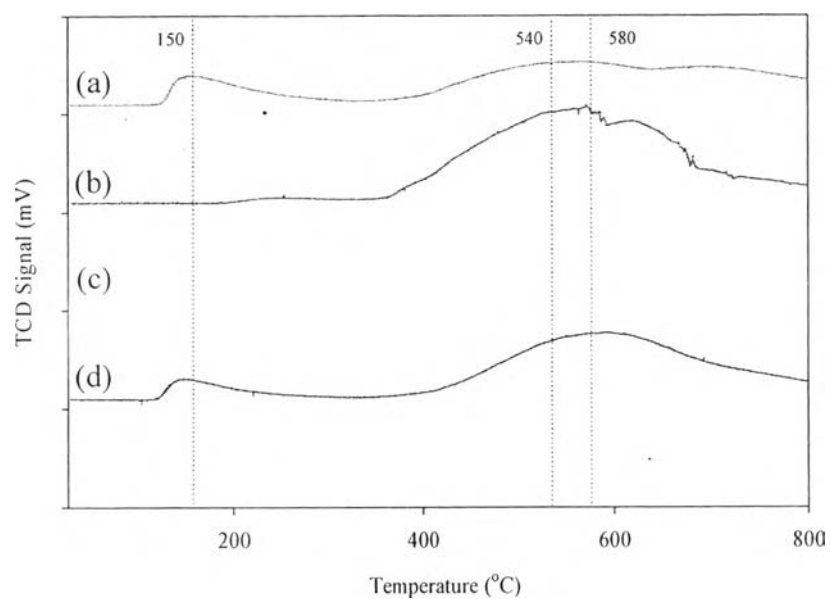
Figure 4.9 TPD-NH$_3$ temperature profiles of (a) C-H$_2$SO$_4$-184 catalyst, (b) L-H$_2$SO$_4$-184 catalyst, (c) C-TsOH-5 catalyst, and (d) C-TsOH-10 catalyst.
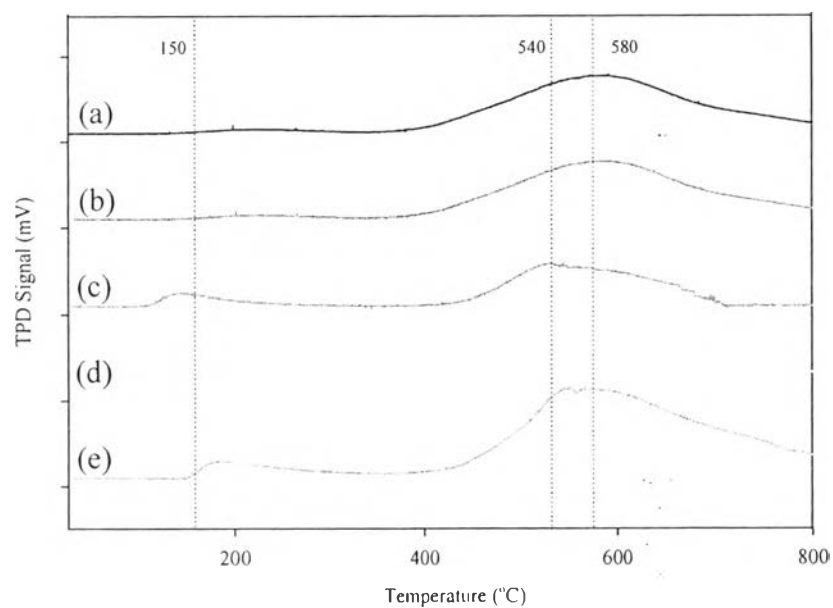

Figure 4.10 TPD-NH$_3$ temperature profiles of (a) C-TsOH-15 catalyst, (b) C-TsOH-20 catalyst, (c) L-TsOH-10 catalyst, (d) C-M-3-10 catalyst, and (e) C-M-15-10 catalyst.

The results showed that the highest acidity was obtained by the catalyst activated by the mixture of H_2SO_4 and TsOH, referred to the highest total acid quantity. The result supported literature of Aldana-Pérez *et al.* (2012) that reported high acid quantity of mixture acid treated solid catalyst. They reported that the $ClSO_3H$ and H_2SO_4 mixture was a suitable activating reagent for the sulfonation process. The highest acidity of the catalyst activated from TsOH was C-TsOH-10 catalyst. The value of the acid quantity of the C-TsOH-10 catalyst was close to the acid quantity of C-H_2SO_4-184 catalyst that was 1.150 and 1.167 mmol/g, respectively. For the acidity of catalyst prepared from the commercial lignin, L-H_2SO_4-184 catalyst had the acid quantity of 1.95 mmol/g that was higher than the acid quantity of C-H_2SO_4-184 catalyst. And L-TsOH-10 catalyst had the acid quantity of 0.634 mmol/g that was lower than the acid quantity of C-TsOH-10 catalyst.

However, the biodiesel yield seemed to not follow in the same direction as the total acid quantity of the catalysts obtained by TPD-NH_3 results. It seemed to the acid strength had an important role to the catalytic activity. The biodiesel yield seemed to follow in the same direction as the strong acidity of the catalysts (Takagaki *et al.*, 2006). The temperature profiles of C-TsOH-10, C-TsOH-15, and C-TsOH-20 catalyst show a large peak at the temperature higher than 550°C. The results indicated that these catalysts had high strong acidity. The highest strong acidity was 0.985 mmol/g of C-TsOH-10 catalyst, supported the highest yield of biodiesel production among the presence of TsOH activated catalysts. C-TsOH-15 and C-TsOH-20 catalysts had strong acidity of 0.921 and 0.702 mmol/g, respectively. The results agree with the lower biodiesel yields. Though C-TsOH-5 had the highest acid quantity of 2.19 mmol/g, a large peak of this catalyst shows at the temperature between 400-550 °C. This indicated the medium acidity and supported to the lower biodiesel yield of this catalyst. The catalyst prepared from commercial lignin also had the strong acidity corresponded to the biodiesel yield. It was lower than the catalyst prepared from the fresh corncob. Even though C-H_2SO_4-184 catalyst had the acid quantity nearly the same with C-TsOH-10 catalyst, the temperature profile shows three peaks in the range of 100-400 °C, 400-550 °C, and higher than 550 °C. The result indicated to 0.306,

0.346, and 0.515 mmol/g of weak, medium and strong acidity, respectively. That was the C-H$_2$SO$_4$-184 catalyst had the strong acidity lower than C-TsOH-10 catalyst, it probably affected to the lower reaction time of C-TsOH-10 catalyst in biodiesel production. However, C-M-3-10 and C-M-15-10 catalyst had very high strong acidity, as same as the result of Aldana *et al.* (2012) that the mixture of ClSO$_3$H and H$_2$SO$_4$ developed the acid strength of the solid acid catalyst. But the strong acididty of C-M-3-10 and C-M-15-10 catalyst didn't correspond to the biodiesel yield. This indicated that the active acid site could be described by the strong acidity of the catalysts. However, to catalyze the biodiesel production reaction effectively, other parameters of catalyst had to consider besides the amount of active acid site, an explanation was showed in next section. (Takagaki *et al.*, 2006 and Aldana *et al.*, 2012)

Table 4.5 Acidity of the solid acid catalysts

Catalyst	Biodiesel Yield (%)	Acid Quantity (mmol/g)			
		Weak Acidity	Medium Acidity	Strong Acidity	Total
C-H$_2$SO$_4$-184	86.49	0.306	0.346	0.515	1.167
L-H$_2$SO$_4$-184	78.22	0.464	1.046	0.442	1.95
C-TsOH-5	73.18	0.015	2.179	0	2.19
C-TsOH-10	80.40	0.165	0	0.985	1.150
C-TsOH-15	77.64	0.041	0	0.921	0.962
C-TsOH-20	76.36	0.394	0	0.702	1.095
L-TsOH-10	39.46	0.091	0.543	0	0.634
C-M-3-10	74.18	0.174	0.936	2.146	3.255
C-M-15-10	75.41	0.198	0	4.453	4.651

4.2.5 Surface Area Analysis (SAA)

Specific surface area and specific pore volume of the solid acid catalysts were analyzed by surface area analysis technique and calculated by Brunauer, Emmet, and Teller (BET) 3-Parameters Fit. Pore diameter was analyzed by surface area analysis technique and calculated by Barrett, Joyner, and Halenda (BJH) method. The results in Table 4.6 showed that the specific surface area, specific pore volume, and pore diameter of C-H_2SO_4-184 were 14.09 m^2/g, 0.027 cm^3/g, and 154.48 nm, respectively. The result corresponded to the previous work of Namwong (2014). The results of C-TsOH-10 catalyst were 241.03 m^2/g, 0.140 cm^3/g, and 3.49 nm, respectively, corresponded to the results of Zhang *et al.* (2010). These indicated that C-TsOH-10 catalyst had very high surface area, since it had high pore volume with small pore diameter. While C-TsOH-5 had bigger pore diameter of 58.8 nm, it probably affected to lower surface area and biodiesel yield sequentially. Furthermore, the specific surface areas, specific pore volume, and pore diameter of C-TsOH-15 and C-TsOH-20 catalysts were close to C-TsOH-10 catalyst. These were important parameters besides the acid quantity. They affected to catalytic activity of the catalysts. Shokrolahi *et al.* (2012) reported that too small of pore diameter affected to low biodiesel yield since oleic acid reactant was long chain molecule and it could not get inside the pore that too small to react at the positions of active sites. They reported that the best diameter of solid acid catalyst for biodiesel production from oleic acid was in range of 3-8 nm, and the smaller pore size decreased the biodiesel yield sequentially. This information supported the lower biodiesel yield results of C-M-3-10 and C-M-15-10 catalysts that had the pore diameter very small about 2 nm. And, for L-H_2SO_4-184 and L-TsOH-10 catalyst, though the pore diameters were small, 3.28 and 6.28 nm, respectively, the specific pore volume was very low, 0.055 and 0.013, respectively. That was the reason why it gave the very low biodiesel yield.

Table 4.6 Specific surface area, specific pore volume, and pore diameter of the solid acid catalysts

Catalyst	Specific Surface Area (m^2/g)	Specific Pore Volume (cm^3/g)	Pore Diameter (nm)
C-H$_2$SO$_4$-184	14.09	0.027	154.48
L- H$_2$SO$_4$-184	62.35	0.055	3.28
C-TsOH-5	71.73	0.140	58.80
C-TsOH-10	241.03	0.140	3.49
C-TsOH-15	290.37	0.263	3.69
C-TsOH-20	297.54	0.277	3.71
L-TsOH-10	10.04	0.013	6.28
C-M-3-10	371.05	0.294	2.14
C-M-15-10	360.46	0.289	2.37

4.2.6 Thermo Gravimetric Analysis (TGA)

The compositions of the prepared catalysts were investigated by thermogravimetric analysis technique. Figure D.1-D.7 in Appendix D shows the thermal degradable characteristics of the solid starting materials and the catalysts. The thermogram results could indicated the composition of the sample (Burhenne et al., 2013), as shown in Table 4.7. Fresh corncob had cellulose, hemicelluloses, lignin, and residue composition of 32.15, 27.31, 39.41. and 1.21 wt%, respectively. After that the pretreatment process removed the hemicelluloses and some amorphous of lignin. The results in the table show that the cellulose, hemicelluloses, lignin, and residue of pretreated corncob were 74.66, 0, 23.99, and 1.31 wt% of, respectively (Nantapipat, 2012). The cellulose, hemicelluloses, lignin, and residue of C-H$_2$SO$_4$-184 catalyst were 12.21, 0, 68.87, and 13.37 wt%, respectively. Obviously, that the sulfonation process eliminated and removed the crystalline molecule of cellulose and hemicelluloses, and, the remaining main composition of the amorphous lignin in the solid acid catalysts was clearly observed (Namwong, 2014 and Zhang et al., 2010). The sulfonation by p-toluenesulfonic acid decreased the composition of C-TsOH-10 catalyst until it composed of just only lignin and

residue of 31.51 and 68.47, respectively. This result indicated that the sulfonation process could derive the lignin from the fresh corncob as expect.

Table 4.7 Composition of the starting materials and solid acid catalysts

Material and Catalyst	Composition (wt%)			
	Cellulose	Hemicelluloses	Lignin	Residue
Fresh Corncob	32.15	27.31	39.41	1.21
Pretreated Corncob	74.66	-	23.99	1.31
C-H$_2$SO$_4$-184	12.21	-	68.87	13.37
C-TsOH-10	-	-	31.51	68.47
Commercial Lignin	-	-	69.90	30.10
L-H$_2$SO$_4$-184	-	-	60.97	39.03
L-TsOH-10	-	-	38.91	61.09

For the results of commercial lignin, L-H$_2$SO$_4$-184 catalyst and L-TsOH-10 catalyst, they composed of 69.90 and 30.10; 60.97 and 39.03; 38.91 and 61.09 wt% of lignin and residue, respectively. The values were nearly to the catalysts prepared from the fresh corncob, indicating that the sulfonation process could derive lignin from the waste of lignocellulosic biomass effectively. Furthermore, it was fortuitous that our procedure of sulfonation process was nearly the same with isolation procedure of the lignin (Sameni *et al.*, 2014).

4.2.7 X-Ray Diffraction (XRD)

Internal structures of the C-H$_2$SO$_4$-184 and C-TsOH-10 catalysts were investigated by x-ray diffraction technique to compare with the internal structure of the fresh corncob and pretreated corncob. The result in Figure 4.11 shows that the XRD pattern of pretreated corncob had more crystalline structure than that of fresh corncob because the pretreatment process removed some amorphous lignin and hemicellulose out from the fresh corncob and remain the crystalline structure of cellulose in the pretreated corncob (Nantapipat, 2012). This XRD results agree well with TGA results. And the sulfonation process eliminated the crystalline structure of cellulose and removed it out. This resulted in the

amorphous structure, as evidenced by the XRD patterns of C-H₂SO₄-184 and C-TsOH-10 catalyst that composed of remaining amorphous lignin.
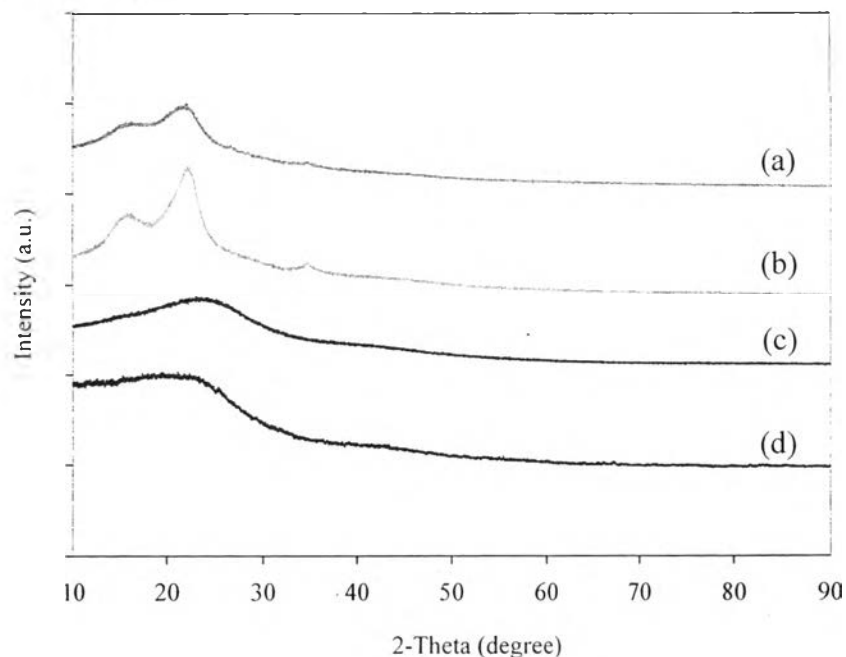

Figure 4.11 XRD patterns of (a) fresh corncobs, (b) pretreated corncobs, (c) C-H₂SO₄-184 catalyst, and (d) C-TsOH-10 catalyst.

4.2.8 X-Ray Fluorescence (XRF)

Chemical compounds, in form of oxide, in fresh corncob, pretreated corncob, C-H₂SO₄-184 catalyst and C-TsOH-10 catalyst were investigated by x-ray fluorescence technique. The results in Table 4.8 indicated that fresh corncob composed of Al, Si, P, Cl, K, Ca, and S oxide; 6.97, 18.16, 1.69, 5.85, 19.01, 44.09, and 4.22, respectively. Obviously, the sulfur compounds of the samples were increased from 5.85 wt % of fresh corncob to 18.83 wt% of pretreated corncob, and, 78.56 and 95.81 wt% of C-H₂SO₄-184 and C-TsOH-10 catalyst, respectively, as shown in Table 4.8. This result confirmed that the pretreatment followed by the sulfonation process was an effective procedure to increase the sulfur content in the catalysts. The higher of sulfur content probably implied the higher active acid site of the solid acid catalyst (Namwong, 2014 and Zhang *et al.*, 2012).

Table 4.8 Compound concentration of the starting materials and solid acid catalysts

Material and Catalyst	Oxide Compound (wt%)						
	Al	Si	P	S	Cl	K	Ca
Fresh Corncob	6.97	18.16	1.69	5.85	19.01	44.09	4.22
Pretreated Corncob	7.73	33.00	-	18.83	32.40	-	8.04
C-H$_2$SO$_4$-184	-	4.38	-	78.56	8.58	-	8.49
C-TsOH-10	-	2.40	-	95.81	1.14	-	0.65

4.2.9 Fourier Transform Infrared Spectrophotometer (FT-IR)

Functional groups of the corncob, pretreated corncob, C-H$_2$SO$_4$-184 catalyst, and C-TsOH-10 catalyst were analyzed by fourier transform infrared spectrophotometry technique to confirm that the catalysts contained the active acid site of sulfonic acid group, -SO$_3$H. The spectra of the sulfonic group were dominated by three absorption bands with moderate to strong intensity of asymmetric O=S=O stretching at 1420 cm^{-1}, symmetric O=S=O stretching at 1155 cm^{-1}, and S-O (H) stretching at 1040 cm^{-1} (Varghese *et al.*, 2009). From the results in Figures 4.12 and 4.13, these bands appeared in the spectra of C-H$_2$SO$_4$-184 and C-TsOH-10 catalyst, while that of fresh corncob and pretreated corncob could not be observed. The peak at 1040 cm^{-1} in the spectra of corncob and pretreated corncob represented the presence of C-O stretching. The results indicated that the sulfonation process could give the active acid site of sulfonic functional group into the pretreated corncob as same as the sulfonation result reported by Varghese *et al.* (2009). And, the intensity of that of C-H$_2$SO$_4$-184 catalyst was higher than C-TsOH-10 catalyst, implying to the higher acid site of C-H$_2$SO$_4$-184. However, C-H$_2$SO$_4$-184 catalyst gave the lower biodiesel yield due to the other parameter of lower surface area.
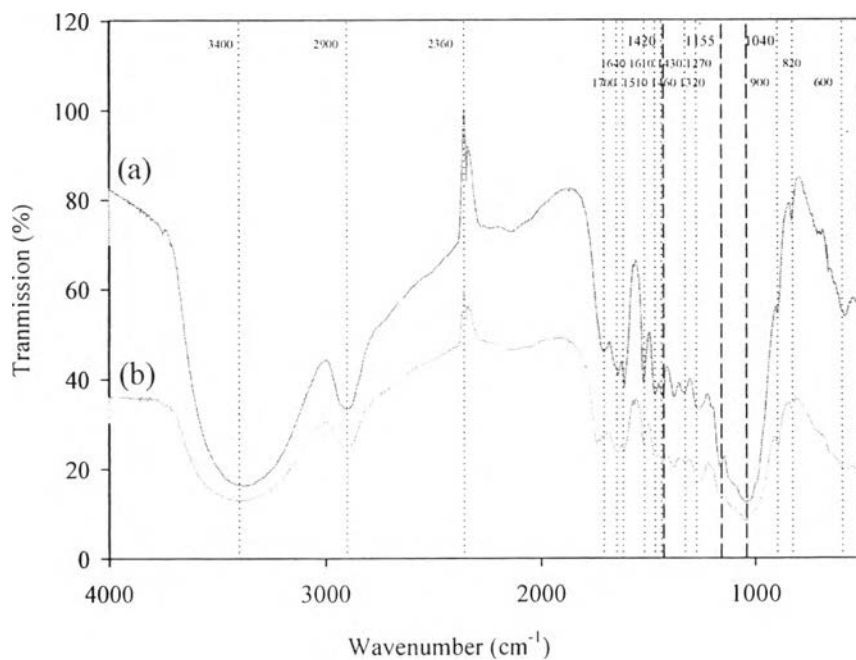
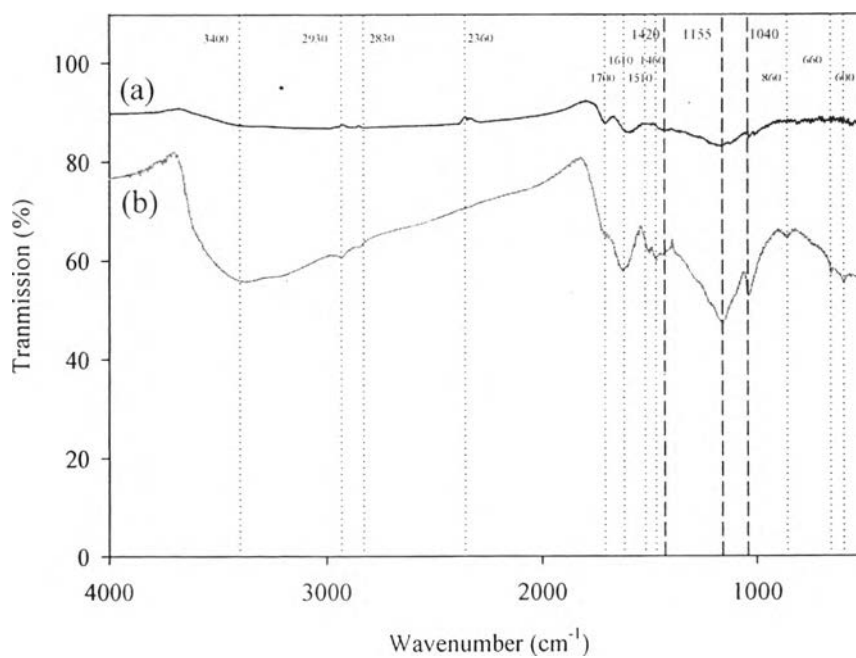**Figure 4.12** FT-IR spectra of (a) fresh corncobs and (b) pretreated corncobs.

Figure 4.13 FT-IR spectra of (a) C-H$_2$SO$_4$-184 catalyst and (b) C-TsOH-10 catalyst.

Moreover, other functional groups, as shown in Table 4.9, were decreased each step, especially after the sulfonation of 10 g of TsOH.

Table 4.9 Infrared interpretation for functional group

Wavenumber (cm^{-1})	3400	2930, 2900	2830	2360	1700
Functional Group	Alcohol	Alkyl (sp3)		Carbondioxide (Asymmetric Stretch)	Aldehyde/ Ketone/ Ester/Acid
	O-H	C-H	O=C-H	O=C=O	C=O
Wavenumber (cm^{-1})	1640, 1610, 1510, 1460, 1430, 1410			**1420** (Mod-Str)*	1320 (Mod)
Functional Group	Stretching (in aromatic ring)			Sulfonic (Asymmetric Stretching)	Acid
	C-C			O=S=O	C-O
Wavenumber (cm^{-1})	1270, 1217	**1155** (Strong)	**1040** (Strong)		
Functional Group	Stretching	Sulfonic (Symmetric Stretching)	Stretching	Sulfonic (Stretching)	
	C-O	O=S=O	C-O	S-O(H)	
Wavenumber (cm^{-1})	900, 860, 820	762	660	**600**	
Functional Group	Bending	Stretching	Bending	Scissoring	
	C-H	C-S	O=C=O	S=O$_2$	

*Mod - Moderate intensity, Str - Strong intensity

(Varghese *et al.*, 2009)

(https://www2.chemistry.msu.edu/faculty/reusch/virttxtjml/Spectrpy/InfraRed/infra red.htm),

(http://chemwiki.ucdavis.edu/Physical_Chemistry/Spectroscopy/Vibrational_Spectr oscopy/Infrared_Spectroscopy/Infrared%3A_Interpretation),

(http://www2.ups.edu/faculty/hanson/Spectroscopy/IR/IRInterpretation.htm)