

CHAPTER III

EXPERIMENT

3.1 Material and Equipment

3.1.1 Material

1. Corncob, Animal food grade (Betagro)

3.1.2 Chemical

1. Oleic Acid
2. Methanol, AR
3. Sulfuric acid 98 wt%, AR
4. p-Toluenesulfonic acid (Sigma Aldrich)
5. Sodium hydroxide
6. Sodium chloride
7. n-Heptane 99 wt%, AR
8. Methyl heptadecanoate (Sigma Aldrich)
9. Phenolphthalein Indicator, AR
10. Boric Acid for XRF
11. Potassium Bromide for FT-IR

3.1.3 Equipment

1. Laboratory balance
2. Magnetic stirrer
3. Beaker, 25 ml, 50 ml, 100 ml, 250 ml, 500 ml, 1000 ml
4. Stirring rod
5. Dropper
6. Auto pipette, 5 ml
7. Filter paper, no.4
8. Weighing paper
9. Kimwipes
10. Syringe, 1 ml

11. Stirring plate
12. Hot plate
13. Water bath
14. Thermometer
15. Thermocouple
16. Temperature controller
17. pH meter
18. Conductivity meter
19. Closed-system reactor, 400 ml
20. Acid digestion bomb reactor, 125 ml
21. Parr reactor, 1L
22. Syringe for GC, 10 μ l
23. Stub for SEM-EDS
24. Glass Sample for XRD
25. Sample Cell for SAA
26. Pan for XRF
27. Pan for TGA
28. Scanning Electron Microscopy with Energy Dispersive Spectrometer (SEM-EDS)
29. Fourier Transform Infrared Spectrophotometer (FTIR/Nicolet)
30. Surface Area Analyzer (SAA/Sorptomatic)
31. X-ray Diffractometer (XRD)
32. X-ray Fluorescence Spectrometer(XRF)
33. Temperature Programmed Desorption Reduction Oxidation Analyzer (TPDRO/TF)
34. Thermo Gravimetric Analysis (TGA)
35. Gas Chromatograph (GC/FID)

3.2 Methodology

3.2.1 Solid Acid Catalyst Preparation

3.2.1.1 *Acid Pretreatment of Corncob for Pretreated Corncob*

The acid pretreatment of corncob was performed as follows: 10 g of corncob and 100 ml of 2 wt % H₂SO₄, the solution was mixed in a Teflon-line reactor and stirred for 15 min. Afterward, the mixture was then heated at 120 °C for 5 min. After that, the pretreated corncob was washed with deionized water, until its acid-base value was about 7, and dried at 110 °C for 12 h in an oven to obtain the starting material of sulfonation process. (Nantapipat, 2012)

3.2.2.2 *Sulfonation of Pretreated Corncob for Sulfonated Lignin*

The sulfonation of pretreated corncob was performed as follows: (1) 5 g of pretreated corncob with 50 ml of H₂SO₄ (98 wt %) at 110 °C for 5 h in a closed-system reactor, samples were synthesized and denoted as C-H₂SO₄-184 (C represents the fresh corncob and 184 represents 184 g (50 ml) of H₂SO₄); (2) 5 g of pretreated corncob with different amounts of TsOH (5, 10, 15, and 20 g) at 180 °C for 24 h in an acid digestion bomb reactor, samples with different amounts of TsOH were synthesized and denoted as C-TsOH-x (C represents the fresh corncob and x represents the mass of TsOH); (3) 5 g of corncob was pretreated with a mixture of different ratios (1:3 and 3:2 wt/wt) of H₂SO₄ (98 wt %) and TsOH at 180 °C for 24 h in the acid digestion bomb reactor, samples with different ratios of H₂SO₄ and TsOH were synthesized and denoted as C-M-x-y (C represents the fresh corncob, M represents the mixture of acids, and x and y represents the mass of H₂SO₄ and TsOH, respectively). Each sample was put into a flask, mixed by a magnetic stirrer for 15 min, and then taken into the reactor. After that, the sulfonated lignin was washed by warm deionized water, until their pH value was about 7, and residual ions were about 0-10 mS. Then, they were dried at 110 °C for 12 h in an oven. The catalyst was stored in a silica gel desiccator. The procedures were repeated with commercial lignin as raw solid material, all samples were denoted as L instead of C (L represents the commercial lignin). All abbreviations of the prepared catalysts are shown in Table 3.1. (Namwong, 2014 and Zhang *et al.*, 2012)

Table 3.1 Abbreviation of the prepared solid acid catalysts

Abbreviation of Catalyst	Raw Solid Material	Sulfonating Agent	
		Type	Amount (g)
C-H ₂ SO ₄ -184	Fresh Corncob	98 wt% Sulfuric Acid	184 g / 5 g pretreated corncob
L-H ₂ SO ₄ -184	Commercial Lignin	98 wt% Sulfuric Acid	184 g / 5 g commercial lignin
C-TsOH-5	Fresh Corncob	p-Toluene Sulfonic Acid	5 g / 5 g pretreated corncob
C-TsOH-10	Fresh Corncob	p-Toluene Sulfonic Acid	10 g / 5 g pretreated corncob
C-TsOH-15	Fresh Corncob	p-Toluene Sulfonic Acid	15 g / 5 g pretreated corncob
C-TsOH-20	Fresh Corncob	p-Toluene Sulfonic Acid	20 g / 5 g pretreated corncob
L-TsOH-x	Commercial Lignin	p-Toluene Sulfonic Acid	x g / 5 g commercial lignin
C-M-x-y*	Fresh Corncob	p-Toluene Sulfonic Acid	1:3 H ₂ SO ₄ :TsOH (wt/wt) / 5 g pretreated corncob
C-M-x-y	Fresh Corncob	98 wt% Sulfuric Acid and p-Toluene Sulfonic Acid	3:2 H ₂ SO ₄ :TsOH (wt/wt) / 5 g pretreated corncob

* x and y - waiting for the best amount of p-toluenesulfonic acid

3.2.2 Biodiesel Production

3.2.2.1 Catalytic Activity

Esterification of oleic acid using the solid acid catalysts derived from residual lignin and commercial lignin were performed by using of 1 L Parr reactor as a laboratory scale reactor for these experimental purposes. Condition

of the reaction was carried out at 60 °C, a methanol to oil molar ratio of 15:1, catalyst loading 5 wt% by weight of vegetable oil, 300 rpm of stirrer speed for 8 h reaction time with 3 bar nitrogen gas. The solid acid catalyst and methanol were weighed and mixed together, and then mixed with oleic acid in the Parr reactor. After that, the sample was taken into a beaker. The residual methanol was vaporized out at 90 °C in a water bath. Methyl ester was separated from the solid acid catalyst by filter paper no. 4, and kept in the sample bottle. The products were analyzed by gas chromatography.

3.2.2.2 Condition Variables

The best catalyst of p-toluenesulfonic acid or a mixture of p-toluenesulfonic and sulfuric acid was used to catalyze the reaction by varying the catalyst loading, reaction time, and reaction temperature to find the optimal condition. Its activity was compared with the biodiesel yield obtained from the catalyst activated by sulfuric acid.

3.2.2.3 Reusability

To demonstrate the reusability of the prepared catalysts, the esterification was performed, and after the completion of the reaction, the catalyst was separated by filtration. The catalyst was reused in 2nd and 3th successive run under the same condition, respectively.

3.2.3 Biodiesel Analysis

Methyl esters were analyzed by using a Hewlett Packard GC model 5890. A DB-WAX (30 m x 0.25 mm I.D.) fused-silica capillary column coated with 0.1 μ m film was used. Sample of 0.5 μ l was injected under the following conditions, the carrier gas was helium with a flow rate at 60 ml/min, the injector temperature was 200 °C with a split ratio of 25:1, and the temperature of detector was set at 220 °C. A 0.5 μ l of samples was injected at an oven temperature of 130 °C. After an isothermal period of 2 min, the GC oven was heated to 220 °C with a heating rate of 2 °C/min and held for 15 min. One cycle run-time was 62 min. The methyl ester yield was determined using Equation (A.1) in Appendix A.

3.2.4 Catalyst Characterization

The starting materials and solid acid catalysts were characterized by using several techniques including SEM-EDS, Acid-Base titration method, TPD-NH₃, SAA, TGA, XRD, XRF, and FT-IR.

3.2.4.1 *Scanning Electron Microscopy (SEM)*

Scanning Electron Microscope (SEM), Hitachi: TM 3000, was utilized to identify the microstructure and captured the micrograph of solid acid catalyst morphology. The catalyst sample was placed on stub and coated by platinum in sputtering device before place in the sample holder in SEM.

3.2.4.2 *Carbon, Hydrogen, Nitrogen, and Sulfur Analysis (CHNS)*

Carbon, Hydrogen, Nitrogen, and Sulfur Analyzer (CHNS) was utilized to identify the presence of element of the catalyst structure. The sample was weighed and placed into a tin foil/boat and then taken into the instrument.

3.2.4.3 *Acid-Base Titration Method*

Titration method was used to determine the acid site concentration of the solid acid catalysts. The sample, 0.05 g, was mixed with 15 ml of 2 M NaCl solution. As H⁺ ion existed in -SO₃H of sulfonated catalyst, it exchanged with Na⁺ ion by ultrasonic oscillation for 30 min. The sample was titrated with 0.02 M of NaOH, phenolphthalein was utilized as an indicator. When the color of the sample turned from colorless into slightly red, the end point of titration was reached. The accurate acid quantity was calculated from Equation (A.2) in Appendix B. (Liu *et al.*, 2013)

3.2.4.4 *Temperature Programmed Desorption – Ammonia (TPD-NH₃)*

Temperature Programmed Desorption Reduction Oxidation Analyzer (TPDRO), Thermo Finnigan: TPDRO 1100, offered the ability of the temperature desorption processes with ammonia to evaluate the acidity of the solid acid catalysts. The sample of 0.1 g was weighed and put into quartz reactor with quartz wool and a reducer. It was pretreated at 300 °C and held for 25 min, and, then analyzed at temperature range from room temperature to 800 °C, 10 °C/min, and held for 30 min. Temperature profile was derived and the acidity was calculated from peak area by compare with standard sample.

3.2.4.5 Surface Area Analysis (SAA)

Surface Area Analysis (SAA), ThermoFinnigan; Sorptomatic 1990 Series was utilized to determine specific surface area and specific pore volume by calculation from Brunauer, Emmet, and Teller (BET) 3-Parameters Fit method, and pore diameter by calculation from Barrett, Joyner, and Halenda (BJH) method. Before analyzing, the volatile species adsorbed on the catalyst surface must be eliminated by heating 1 g of the catalyst under vacuum atmosphere at 300 °C for 18 h. Helium gas was used as an adsorbate for blank analysis and nitrogen gas was used as the adsorbate for analysis.

3.2.4.6 Thermo Gravimetric Analysis (TGA)

Thermo Gravimetric Analysis (TGA), Perkin: Pyris Diamond, measured the weight change of a material as a function of temperature and time in a controlled atmosphere. It is ideally used to assess volatile content, thermal stability, degradation characteristics, aging/lifetime breakdown, sintering behavior and reaction kinetics of sample. The sample of 10 mg was weighed and analyzed in platinum pan. Thermogram was interpreted to be the composition of the sample.

3.2.4.7 X-Ray Diffraction (XRD)

X-Ray Diffraction (XRD), Rigaku: Smartlab (40 kV, 30 A), was thus ideally suited for characterization of the internal structure of the solid acid catalyst. The X-ray diffraction pattern of the sample was a fingerprint of the substance. The sample was prepared on a glass sample holder and held in the X-ray beam. The detector scans the intensity of diffracted radiation from the sample with the speed of 2°/min and step 0.01° for the range of 10-90° scanning.

3.2.4.8 X-Ray Fluorescence (XRF)

X-Ray Fluorescence (XRF), Panalytical: Axios, Model: PW 4400, was utilized to determine the bulk composition of a catalyst in form of oxide compound. Boric acid of 6 g was mixed with 1 g of fine sample, then was taken in to a pan and pressed of 10 ton for 2 min by hydraulic press machine. The pressed sample was taken in to the sample holder in XRF and analyzed. The amounts of compounds in the sample were obtained.

3.2.4.9 *Fourier Transform Infrared Spectrophotometer (FT-IR)*

Fourier Transform Infrared Spectrophotometer (FT-IR), Nicolet: Nexus 670, was used to identify the chemical functional groups in the solid acid catalyst. The sample was prepared by mixing the fine powder with KBr and pressing by hydraulic press machine, 7 ton for 2 min. The spectra were obtained in the range of $4,000$ to 600 cm^{-1} and interpreted to be the functional group.