

## CHAPTER III METHODOLOGY

### 3.1 Materials

1. Oleic acid (Technical grade)
2. Methanol (Analytical grade), Fisher Scientific
3. Sulfuric acid 98%
4. Corncob
5. Potassium hydroxide
6. Sodium sulphate, Riedel-de Haen
7. 2-propanol HPLC grade, Carlo Erba
8. n-hexane HPLC grade, Carlo Erba
9. n-heptane, Labscan
10. Methyl heptadecanoate, Sigma Aldrich

### 3.2 Equipment

1. Temperature-Programmed Desorption (TPD)
2. X-ray Diffraction (XRD)
3. Scanning Electron Microscopy with Energy Dispersive Spectrometer (SEM-EDS)
4. Fourier Transform Infrared Spectrophotometer (FTIR)
5. Gas Chromatograph (GC), Hewlett Packard GC model 5890
6. Condenser
7. Magnetic stirrer
8. Stirring plate
9. Hot plate
10. Thermometer
11. Temperature controller
12. Parr reactor

### 3.3 Methodology

#### 3.3.1 Catalyst Preparation

##### 3.3.1.1 *Preparation of Pretreated Corncob by Sulfuric Acid*

###### *Pretreatment*

Corncob waste was obtained from the Betagro Company. The collected corncob waste was stored at the ambient room temperature in a large bag. The average particle size of corncob waste was around 1.6 mm homogenized in a single lot and stored until used according to the method of Nantapipat (2012). Corncob waste was dried at 110 °C for 1 week period to pretreatment process. Dilute Sulfuric acid pretreatment of corncobs was performed in a laboratory scale stirred stainless steel reactor. The reactor is an acid resistant stainless steel and has a total volume of 1 L, with an electric heater and mechanic agitation. Corncob waste was suspended in 2% (w/w) H<sub>2</sub>SO<sub>4</sub> solution using a liquid-to-solid ratio of 10:1. The mixture was stirred until homogeneous before transferring to a reactor. The pretreatment of H<sub>2</sub>SO<sub>4</sub> was conducted under condition 120 °C for 5 min. After that, the liquid product was filtrate out and the solid was washed thoroughly with tap water until no color and neutral pH in the resulting water was obtained, and then dried at 110 °C for 24 h to obtain the pretreated lignin (Nantapipat, 2012).

##### 3.3.1.2 *Preparation of Sulfonated Lignin Catalyst by Sulfonation*

###### *Reaction*

The sulfonation of corncob was performed in a laboratory scale stirred stainless steel reactor. The reactor is an acid resistant stainless steel and has a total volume of 1 L, with an electric heater and mechanic agitation. The 5 g of pretreated corncob was suspended in 30 ml 98% (w/w) H<sub>2</sub>SO<sub>4</sub>. The mixture was stirred until homogeneous and put into the reactor at 150 °C for 5 h. After the treatment, the suspension was washed by warm deionized water to eliminate the residue ions, and then dried at 110 °C for 48 h to obtain the sulfonated lignin catalyst, the sulfonated catalyst was stored in a silica gel desiccators prior to use (Pua *et al.*, 2011).

### 3.3.1.2.1 *Effect of Sulfonation Temperature on Biodiesel*

#### *Yield*

The esterification reaction was fixed at 60 °C, a methanol to oil ratio of 12:1, catalyst of 5 wt%, and 300 rpm stirrer speed. These conditions were fixed to study the effect of sulfonation temperature during the catalyst preparation in the range of 110 to 150 °C on biodiesel yield.

### 3.3.1.2.2 *Effect of Sulfonation Time on Biodiesel Yield*

The initial reaction condition of esterification was fixed at 60 °C, a methanol to oil ratio of 12:1 during catalyst preparation, catalyst of 5 wt%, and 300 rpm stirrer speed. The optimum sulfonation temperature was obtained from procedure 3.3.2.1.1. These conditions were used to study the effect of sulfonation time in the range of 3 to 7 h on biodiesel yield.

## 3.3.2 Biodiesel Production

### 3.3.2.1 *Esterification of Oleic Acid using Sulfonated Lignin Catalyst*

The esterification reaction was carried out in a Parr reactor with a 200 ml volume. 50 g of oleic acid, catalyst, and methanol were used for each experiment. The catalyst amount was used base on weight percentage of oleic acid. The mixture was stirred at the same speed of 300 rpm for all test runs. The temperature range of 60-80 °C was maintained during this experiment. The reaction was carried out until it reaches the desired reaction time. After that the reaction was stopped by cool down the reactor to room temperature. The catalysts were separated out from the product by using a suction flask. The products were placed in a separatory funnel overnight to ensure that the phase of methyl oleate and phase of water are separated completely. The water phase (upper phase) was removed and left in a separated container. Methanol was removed by water bath. The 25 wt% of sodium sulfate based on weight of methyl oleate product was added into methyl esters to remove water.

The reaction condition was carried out at 60 °C, a methanol to oil ratio of 12:1, catalyst of 5 wt%, and 300 rpm stirrer speed.

#### *3.3.2.1.1 Effect of Reaction Time on Biodiesel Yield*

The reaction was fixed at 60 °C, a methanol to oil ratio of 12:1, catalyst of 5 wt%, and 300 rpm stirrer speed. The optimum conditions of catalyst preparation were obtained from procedure 3.3.1.2.1 and 3.3.1.2.2. These conditions were fixed to study the effect of reaction time (in the range of 0 to 8 h) on biodiesel yield.

#### *3.3.2.1.2 Effect of Amount of Catalyst on Biodiesel Yield*

The reaction was fixed at 60 °C, a methanol to oil ratio of 12:1 and 300 rpm stirrer speed. The optimum conditions of catalyst preparation were obtained from procedure 3.3.1.2.1 and 3.3.1.2.2. These conditions were used to study the effect of amount of catalyst (in the range of 5 to 7 wt% by weight of vegetable oil) on biodiesel yield.

#### *3.3.2.1.3 Effect of Molar Ratio of Methanol to Oleic Acid on Biodiesel Yield*

The reaction was fixed at 60 °C, 300 rpm stirrer speed and the amount of catalyst was obtained from procedure 3.3.2.1.2. The optimum conditions of catalyst preparation were obtained from procedure 3.3.1.2.1 and 3.3.1.2.2. The molar ratio of methanol to oleic acid ranged from 9:1 to 18:1 in this section.

#### *3.3.2.1.4 Catalyst Stability on Biodiesel Yield*

The reaction was fixed at 60 °C, 300 rpm stirrer speed, the amount of catalyst was obtained from procedure 3.3.2.1.2 and a methanol to oil ratio was obtained from procedure 3.3.2.1.3. The optimum conditions of catalyst preparation were obtained from procedure 3.3.1.2.1 and 3.3.1.2.2. These conditions were fixed to study the catalyst stability.

#### *3.3.2.1.5 Catalyst Reusability on Biodiesel Yield*

The reaction was fixed at 60 °C, 300 rpm stirrer speed, the amount of catalyst was obtained from procedure 3.3.2.1.2 and a methanol to oil ratio was obtained from procedure 3.3.2.1.3. The optimum conditions of catalyst preparation were obtained from procedure 3.3.1.2.1 and 3.3.1.2.2. These conditions were fixed to study the catalyst reusability of prepared catalyst. During recycling the catalyst were recovered by filtration using vacuum pump. The

recovered catalyst was weighted and used for the next batch of esterification reaction.

### 3.4 Biodiesel Analysis

After the reaction, the catalyst was separated by centrifugation and lower layer product was methyl esters. Methyl heptadecanoate was added to the samples as internal standard. The internal standards were analyzed by using a Hewlett Packard GC model 5890 equipped with a FID detector.

#### 3.4.1 Gas Chromatography (GC)

Gas chromatograph (GC) Agilent 5890 equipped with a DB-WAX (30 m x 0.25 mm I.D.) fused-silica capillary column coated with 0.1  $\mu\text{m}$  film was used. Sample of 0.1  $\mu\text{l}$  was injected under the following conditions, the carrier gas was helium with a flow rate at 60 ml/min, the injector temperature was 200  $^{\circ}\text{C}$  with a split ratio of 25:1, and the temperature of detector was set at 220  $^{\circ}\text{C}$ . A 0.1  $\mu\text{l}$  of samples was injected at an oven temperature of 130  $^{\circ}\text{C}$ . After an isothermal period of 2 min, the GC oven was heated to 220  $^{\circ}\text{C}$  with a heating rate of 2  $^{\circ}\text{C}/\text{min}$  and held for 15 min. One cycle run-time was 62 min. The methyl ester content, yield, and conversion were determined using Equations 1-3, respectively.

$$\text{Methyl ester content (wt\%)} = \frac{\text{Area of methyl ester}}{\text{Total area} - \text{Area of solvent}} \times 100 \quad (1)$$

$$\text{Yield \%} = \frac{\text{Mass of washed and dried methyl ester layer}}{\text{Theoretical mass of methyl ester from mass balance}} \times 100 \quad (2)$$

$$\text{Conversion \%} = \frac{\text{Methyl ester content (\%)} \times \text{Production yield (\%)}}{\text{Weight of vegetable oil used}} \quad (3)$$

### 3.5 Catalyst Characterization

The fresh and spent catalysts were characterized for their characteristic, structure, morphology, and metal composition for describing the results from experiment. The catalysts were characterized by using several techniques, including FTIR, SEM-EDS, XRD, BET, TPD-NH<sub>3</sub> and Titration Method.

#### 3.5.1 Fourier Transform Infrared Spectrophotometer (FT-IR)

The IR spectra were obtained with a Thermo Nicolet Nexus 670. FTIR was used to identify the chemical functional groups of the samples. The solid samples were prepared by mixing the fine powder with KBr and pressing. The spectra were obtained at a resolution of 4 cm<sup>-1</sup> in the range of 4,000 to 600 cm<sup>-1</sup>.

#### 3.5.2 Scanning Electron Microscope (SEM) with Energy Dispersive Spectrometer (EDS)

Scanning Electron Microscope (SEM), Hitachi S4800, was utilized to identify the microstructure and capture the micrograph of catalyst morphology. Energy Dispersive Spectrometer (EDS), Oxford Model 6111, was utilized to identify the presence of element (from characteristic x-ray) in the catalyst region being examined. The catalyst sample was placed on stub and coated by platinum in sputtering device before place in the sample holder in SEM.

#### 3.5.3 X-ray Diffraction (XRD)

X-ray diffraction method was ideally suited for characterization and identification of the internal structure, bulk phase and composition in crystalline phases. The X-ray diffraction pattern of a substance was like a fingerprint of the substance. The sample was prepared and held in the X-ray beam. The detector scans the intensity of diffracted radiation and the peak position from the sample.

A Bruker X-ray diffractometer system (D8 Advance) equipped with a 2.2 kW Cu anode long fine focus ceramic X-ray tube for generating a CuK $\alpha$  radiation (1.5405 Å), was used as an X-ray source to obtain the XRD patterns at running conditions for the X-Ray tube (40 kV and 30 mA). The sample was prepared

and held in the X-ray beam. The detector scans the intensity of diffracted radiation and the peak position from the sample as a function of  $2\theta$  by starting at the  $5^\circ$  to  $90^\circ(2\theta)$  range and a scan speed of  $0.02^\circ(2\theta)/0.5$  s. The XRD patterns were compared to the standards to identify crystalline phases.

#### 3.5.4 Surface Area Analysis (BET)

The specific surface area was determined by the Brønauer-Emmet-Teller (BET) method using the Sorptomatic. Before analyzing, the volatile species adsorbed on the catalyst surface must be eliminated by heating the catalyst under vacuum atmosphere at  $300^\circ\text{C}$  for 24 h. Helium gas was used as an adsorbate for blank analysis and nitrogen gas was used as the adsorbate for analysis. The specific surface area was calculated using the BET equation.

#### 3.5.5 NH<sub>3</sub> Temperature-Programmed Desorption (TPD-NH<sub>3</sub>)

The acid strength of the catalyst was determined by thermodesorption of chemisorbed ammonia. The NH<sub>3</sub> desorption of acid catalyst was quantified by temperature-programmed desorption (TPD) of ammonia (NH<sub>3</sub>) in a quarter inch quartz tube reactor with 80 mg of catalyst connected to an online MS detector (MKS Cirrus). First, catalyst was initially pretreated at  $600^\circ\text{C}$  in a flow of He for 0.5 h. After the pretreatment, the sample was cooled in He to  $150^\circ\text{C}$  and then saturated with NH<sub>3</sub> gas. The sample was flushed in He flow for 0.5 h to remove the gas phase NH<sub>3</sub>. The temperature was then raised from  $150$  to  $600^\circ\text{C}$  at a heating rate of  $20^\circ\text{C}/\text{min}$  and maintained at  $600^\circ\text{C}$  for 1 min. The concentration of ammonia in the exit gas was determined continuously by mass spectrometry (MKS Cirrus), using the fragments with  $m/e$  of 17 as the representative of ammonia.

#### 3.5.6 Titration Method

Titration method was used to determine the acid value of the esterified products from oleic acid. The 0.05 g of sample were placed in a flask, and mixed with 15 ml 2 mol/L NaCl solution. As H<sup>+</sup> ion existed in -SO<sub>3</sub>H of sulfonated catalyst, it exchanged with Na<sup>+</sup> ion by ultrasonic oscillation for 30 min. Afterwards, the solid was filtered and titrated with 0.02 M NaOH using

phenolphthalein as a indicator. When the color of filtrate turned from colorless into slightly red, the end of point of titration was reached (Liu *et al.*, 2013). The accurate acid quantity was calculated as follows (Equation 4):

$$c(\text{H}^+) = \frac{c(\text{OH}) \times \Delta V}{m} \quad (4)$$

Where

$c(\text{H}^+)$  is the acid quantity of sulfonated samples

$c(\text{OH}^-)$  is the concentration of the NaOH solution

$\Delta V$  is the volume of the NaOH solution consumed in titration

$M$  is the quality of the catalyst samples in ultrasonic oscillation reaction