

## CHAPTER III EXPERIMENTAL

### 3.1 Materials

1. Refined Palm oil, the Naval Engineering Command
2. Methanol (Analytical grade), Fisher Scientific
3. Potassium hydroxide, Lab-scan
4. Zirconium(IV) Oxide, Sigma-Aldrich
5. Na-Mordenite, Zeolyst International
6. Sodium Sulfate Anhydrous, Sigma-Aldrich
7. Chloroform-D1 (for NMR Spectroscopy, Stabilized with silver), Merck
8. n-Heptane 99% (Analytical grade), Lab-scan
9. Methyl heptadecanoate (Standard for GC, 99.7%), Fluka
10. Hydrochloric acid, Lab-scan
11. Acetone, Burdick & Jackson

### 3.2 Equipment

1. Gas Chromatograph (GC)
2. Proton Nuclear Magnetic Resonance ( $^1\text{H-NMR}$ )
3. Fourier Transform Infrared Spectrophotometer (FTIR)
4. Scanning Electron Microscope (SEM) with Energy Dispersive Spectrometer (EDS)
5. X-ray Diffraction (XRD)
6. Temperature-Programmed Desorption of  $\text{CO}_2$  ( $\text{CO}_2\text{-TPD}$ )
7. Surface Area Analyzer
8. 500-ml three-necked flask
9. Magnetic stirrer
10. Hot plate
11. Thermometer
12. Peristaltic pump

13. Glass-tube reactor
14. Water bath
15. Separatory funnel

### 3.3 Methodology

#### 3.3.1 Catalyst Preparation

##### 3.3.1.1 *KOH/ZrO<sub>2</sub> Catalyst*

The 20% K loading of KOH/ZrO<sub>2</sub> catalysts was done by the impregnation of a ZrO<sub>2</sub> support (Sigma-Aldrich) with an aqueous solution of KOH (Lab-Scan). The prepared catalysts were dried in an oven at 110°C for 24 hours and calcined at 500°C for 3 hours.

##### 3.3.1.2 *KOH/Mordenite Catalyst*

The KOH/Mordenite was prepared by an impregnation method. The mordenite zeolite was calcined at 600°C for 3 hours to remove the adsorbed water on the surface and then it was stored in a silica gel desiccator. To prepare the modified mordenite zeolite with 20%K loading, the mordenite zeolite was impregnated with an aqueous solution of KOH for 24 hours to ensure that KOH solution diffused and dispersed thoroughly on the surface of the support. And then it was dried at 110°C for 24 hours before use as a catalyst in the reaction (Iangthanarat, 2008).

#### 3.3.2 Transesterification

Fifty grams of vegetable oil was weighed and placed into a three-neck 500 ml round-bottom flask. The refined palm oil was heated to 60°C. When the desired temperature was reached, 28 grams of methanol (Fisher Scientific) was introduced into the flask. The mixture was stirred at the desired temperature at ambient pressure and was driven by a peristaltic pump at a rate of 11 ml/min to the bottom of a fixed-bed reactor containing 6 grams of catalyst. The products were sent to the other side of the reactor and were circulated back to the system. The reaction was carried out until it reached the desired reaction time. After that, the mixture was

placed in a separatory funnel and allowed to stand overnight to ensure that the separation of the methyl esters and the glycerol phase occurred completely. The glycerol phase (bottom phase) was removed and left in a separate container. Finally, the methyl esters (biodiesel) were dried by adding 25 wt% Na<sub>2</sub>SO<sub>4</sub> (Sigma-Aldrich), based on the weight of the oil.

#### *3.3.2.1 Influence of Reaction Time on Methyl Ester Content*

The dependence of the methyl ester content on the reaction time was studied in the presence of a catalyst at 60°C. The catalyst amount was 12 wt% with 40–50 mesh. The methanol-to-oil molar ratio was 15:1 and the reaction time was varied from 2 to 4, 6, and 8 hours.

#### *3.3.2.2 Influence of Catalyst Particle Size on Methyl Ester Content*

The effect of the catalyst particle size on the methyl ester content was studied by using KOH/ZrO<sub>2</sub> and KOH/Mordenite. The starting condition was set at 60°C with the optimum reaction time. The catalyst particle size was varied at 40–50, 20–40, and less than 20 mesh. The catalyst amount was 12 wt% and the methanol-to-oil molar ratio was 15:1.

#### *3.3.2.3 Stability of Catalyst in Transesterification*

In order to study the stability of catalyst, the solid catalyst recovered after the first run was reused without any treatment. The reaction conditions were fixed at 60°C, 15:1 of the methanol-to-oil molar ratio and 12 wt% of catalyst amount with the optimum reaction time and catalyst particle size.

#### *3.3.2.4 Regeneration of Catalyst*

To determine the regeneration of catalyst, the spent catalyst was treated by flowing with acetone through the fixed-bed reactor. After that, it was dried in an oven for 24 hours at 110°C to remove acetone before use in the next experiment.

### 3.3.3 Biodiesel Analysis

The methyl esters content were analyzed by using Gas Chromatograph (GC) and Proton Nuclear Magnetic Resonance (<sup>1</sup>H-NMR).

### 3.3.3.1 Gas Chromatograph (GC)

Gas Chromatograph (GC), Hewlett Packard GC model 5890, with a DB-WAX (30 m x 0.25 mm I.D.) fused-silica capillary column coated with a 0.1  $\mu\text{m}$  film was used. Samples of 1  $\mu\text{l}$  was injected under the following conditions: the carrier gas was helium at a flow rate of 70 ml/min, the injector temperature was 200°C with a split ratio of 25:1, and the temperature of detector was 220°C. Sample (0.1  $\mu\text{l}$ ) was injected at an oven temperature of 130°C. After an isothermal period of 2 minutes, the GC oven was heated 220°C at a rate of 2°C/min and held for 15 min. Run time was 62 minutes. The methyl ester content, yield, and conversion were determined using equations 3.1–3.3, respectively (Iangthanarat, 2008).

$$C = \frac{(\sum A) - A_{EI}}{A_{EI}} \times \frac{C_{EI} \times V_{EI}}{m} \times 100 \quad (3.1)$$

where C = methyl ester content  
 $\sum A$  = the total peak area of methyl ester from C<sub>14:0</sub> to C<sub>24:0</sub>  
 $A_{EI}$  = the peak area of methyl heptadecanoate solution  
 $C_{EI}$  = the concentration, in mg/ml, of methyl heptadecanoate solution  
 $V_{EI}$  = the volume, in ml, of methyl heptadecanoate solution  
m = the weight, in mg, of sample

$$\text{Yield \%} = \frac{\text{Mass of washed and dried methyl ester layer}}{\text{Theoretical mass of methyl ester from mass balance}} \times 100 \quad (3.2)$$

$$\text{Conversion \%} = \frac{\text{Methyl ester content (\%)} \times \text{Production yield (\%)}}{\text{Weight of vegetable oil used}} \quad (3.3)$$

### 3.3.3.2 Proton Nuclear Magnetic Resonance (<sup>1</sup>H-NMR)

<sup>1</sup>H-NMR Spectra was obtained on a Varian Mercury+ 400 NMR Spectrometer operating at 399.8620378 MHz using CDCl<sub>3</sub> (stabilized with silver) as a solvent. The characterization was obtained under the following

conditions: spectral width, 6389.8 Hz; repetition time, 8 s; data points, 32768, and pulse 45.0 degree. To determine the conversion of transesterified product, equation 3.4 was introduced (Longloilert, 2008).

$$C = 100 \times \left( \frac{2A_{ME}}{3A_{\alpha-CH_2}} \right) \quad (3.4)$$

where

C	=	the conversion of triacylglycerol feedstock (vegetable oil) to the corresponding methyl ester
$A_{ME}$	=	the integration value of the protons of the methyl esters (the strong singlet peak at 3.6 ppm)
$A_{\alpha-CH_2}$	=	the integration value of the methylene protons (the peak at 2.3 ppm)

### 3.3.4 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.

#### 3.3.4.1 *Fourier Transform Infrared Spectrophotometer (FTIR)*

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  $4 \text{ cm}^{-1}$  in the range of  $4,000$  to  $400 \text{ cm}^{-1}$ .

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

Scanning Electron Microscope (SEM), JOEL Model JSM 5200, was utilized to identify the microstructure and capture the micrograph of catalyst morphology. And 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 gold in sputtering device before place in the sample holder in SEM.

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

The X-ray diffraction method was thus 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 40 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  $10^\circ$  to  $70^\circ$  ( $2\theta$ ) range and a scan speed of  $0.02^\circ$  ( $2\theta$ )/ 0.5 second. The XRD patterns were compared to the standards to identify crystalline phases.

#### 3.3.4.4 Temperature-Programmed Desorption of CO<sub>2</sub> (CO<sub>2</sub>-TPD)

Temperature-programmed desorption (Micromeritics 2900) was used for observing desorbed molecules from the surface when the surface temperature is increased. The basic properties of the samples were determined using the temperature-programmed desorption of CO<sub>2</sub> (CO<sub>2</sub>-TPD), which was used as the probe molecule.

A 0.15 g sample was degassed by heating in a flow of helium at a rate of  $10^\circ\text{C}/\text{min}$  from room temperature to  $500^\circ\text{C}$ , and was kept at  $500^\circ\text{C}$  for 1 hour. And then, adsorption of CO<sub>2</sub> gas occurred at  $50^\circ\text{C}$  for 1 hour. After that, the physically adsorbed CO<sub>2</sub> gas was purged by a He flow at  $30^\circ\text{C}$  for 1 hour. CO<sub>2</sub>-TPD was performed at the rate of  $5^\circ\text{C}/\text{min}$  up to  $600^\circ\text{C}$ .

#### 3.3.4.5 Titration Method

Because some of the basic species of catalyst might be covered by the upper layer of overlap structure, it would react with an acidic agent. Hence, in order to find the total basicity of catalyst, the titration method was another choice for utilization. The catalyst sample was shaken in the 5 ml, 0.02 M aqueous

HCl, and the remaining acid was then titrated with standard base (0.02 M aqueous KOH) (Wang *et al.*, 2001).

#### 3.3.4.6 Surface Area Analyzer

The specific surface area was determined by the Brunauer-Emmet-Teller (BET) method using the Quantachrome (Autosorb-1). Before analyzing, the volatile species adsorbed on surface was eliminated by outgassing at 150°C for 24 hours. 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.