CHAPTER III
EXPERIMENTAL

3.1 Materials

1. Vegetable Oil (Refined palm oil), the Naval Engineering Command
2. Methanol (Analytical grade), Fisher Scientific
3. Potassium hydroxide, Lab-scan
4. Hydrochloric acid, 37% purity (Analytical Grade), Carlo Erba
5. Sodium sulphate, Riedel-de Haen
6. Bentonite clay, SAC grade
7. 2-propanol HPLC grade, Carlo Erba
8. n-hexane HPLC grade, Carlo Erba
9. Methyl heptadecanoate, Sigma Aldrich
10. Potassium phatalate, Fluka

3.2 Equipment

1. Gas Chromatograph (GC), Hewlett Packard GC model 5890
2. High Performance Liquid Chromatography (HPLC), PERKIN ELMER series 200
3. Surface Area Analyzer (SAA), Brunauer-Emmet-Teller (BET)
4. Temperature-Programmed Desorption of CO_2 (CO_2-TPD), Micromeristics 2900
5. X-ray Diffraction (XRD), A Bruker X-ray diffractometer system (D8 Advance)
6. Scanning Electron Microscopy with Energy Dispersive Spectrometer (SEM-EDS), Hitachi S4800
7. Fourier Transform Infrared Spectrophotometer (FTIR), Nicolet/Nexus 670
8. Energy dispersive X-ray fluorescence (XRF) spectrometry (Oxford model ED2000)
9. Condenser
10. Magnetic stirrer
11. Stirring plate

12. Hot plate
13. Thermometer
14. Temperature controller
15. 500-ml three-necked flask

3.3 Methodology

3.3.1 Preparation of Catalyst

A series of KOH/bentonite catalysts for biodiesel production was prepared by impregnation. The effect of K loading (15, 20, 25, and 30 wt%.) were studied. The catalyst preparation was conducted in a 500 ml three-neck round bottom flask equipped with a reflux condenser, temperature controller, and mechanical stirrer. KOH/bentonite was prepared by impregnation method. Bentonite was dried at 110°C for 24 h to remove the adsorbed water on the surface. The bentonite was impregnated for 24 h to ensure that KOH solution diffuses and dispersed on the surface of the support. The samples was dried at 110°C for 24 h and sieved to 20-40 mesh before use as a catalyst in the reaction.

3.3.2 Transesterification of Vegetable Oil Using Heterogenous Catalyst

The vegetable oil was placed in a 500 ml three-necked flask and was heated to 60°C. And the catalyst and methanol were added to a three-necked flask. A magnetic stirrer was used for mixing oil, methanol, and catalyst. The reaction was carried out until it reaches the desired reaction time. After that the reaction was stopped by cooled down the reactor to room temperature. The catalysts were separated out from the product by using a suction flask. The product was placed in a separatory funnel in overnight. The methyl ester (top phase) was washed with distilled water (50°C) until the washed water is clear. The glycerol phase (bottom phase) was removed and 25 wt% of sodium sulfate base on weight of methyl ester product was added into methyl esters to remove water.

The initial condition was carried out at 60°C, methanol: oil molar ratio of 15:1, the amount of catalyst of 3 wt% by weight of vegetable oil, and 300 rpm of stirrer speed.

3.3.2.1 Effect of wt% Loading of K on Bentonite Support on Biodiesel Yield

The catalysts were prepared with different potassium loadings in the range of 0 to 30 wt% of K on bentonite support. The reaction was operated at temperatures of 60°C at a 1:15 molar ratio of palm oil to methanol, a catalyst amount of 3 wt%, 20–40 mesh of catalyst size, and 300 rpm of stirrer speed for 3 h. The effect of wt% loading of KOH on bentonite support on yield of biodiesel was varied in the range of 0 to 30 wt%.

3.3.2.2 Effect of Calcined Temperature on Biodiesel Yield

The reaction was fixed at the reaction temperature at 60°C, 300 rpm of stirrer speed. The reaction time and wt% loading of KOH was obtained from 3.3.2.1. The effect of calcination temperature was varied from 400 to 600°C

3.4 Biodiesel Analysis

The methyl ester contents were analyzed by using a Hewlett Packard GC model 5890.

3.4.1 Gas Chromatograph (GC)

A DB-WAX (30 m x 0.25 mm I.D.) fused-silica capillary column coated with 0.1 μm film was used. Sample of 1 µl 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 0.1 μl 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 content, yield, and conversion were determined using Equations (1)-(3) (Iangthanarat, 2008).

$$C = \frac{\left(\sum A\right) - A_{EI}}{A_{EI}} \times \frac{C_{EI} \times V_{EI}}{m} \times 100 \qquad (1)$$

C	Methyl ester content or Fatty acid methyl ester (FAME)
$\sum A$	The overall area of methyl ester from C_{14} to C_{24}
A_{EI}	The peak area of that which is aligned with methyl hepta decanoate solution
C_{EI}	Concentration in mg/ml of methyl hepta decanoate solution
V_{EI}	Volume of methyl hepta decanoate solution
m	Weight in mg of sample

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

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

3.4.2 High Performance Liquid Chromatography (HPLC)

The composition of the reaction mixture samples was determined by the somewhat modified HPLC method of Holćapek *et al.,* (1999) using a Perkin Elmer High Performance Liquid Chromatography, equipped with a degasser, a binary pump, a Zorbax Eclipse XDB-C18 capillary column (4.6 m x 150 mm x 5 μm) and an UV/VIS detector. The flow rate of a binary solvent mixture methanol, (solvent A), and 2-propanol/n-hexane, 5:4 by volume, (solvent B) was 1 ml/min with a linear gradient (from 100% A to 40% A + 60% B in 15 min) and held for 15 min. The components were detected at 205 nm. The fatty acids were identified by comparison of retention times of the oil components with those of standards. The samples of the reaction mixture were dissolved into a mixture of 2-propanol/n-hexane, 5:4 v/v. All samples and solvents were filtered through 0.45 μm Millipore filters.

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.

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^{-1} in the range of 4,000 to 600 cm^{-1}.

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)

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 CuKα 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 2θ by starting at the 4° to 90°

(2θ) range and a scan speed of 0.02° (2θ)/0.5 second. The XRD patterns were compared to the standards to identify crystalline phases.

3.5.4 Temperature-Programmed Desorption of CO_2 (CO_2-TPD)

Temperature-programmed desorption (Micromeristics 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_2 (CO_2-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°C/min from room temperature to 500°C, and was kept at 500°C for 1 h. And then, adsorption of CO_2 gas occurred at 50°C for 1 h. After that, the physically adsorbed CO_2 gas was purged by a He flow at 30°C for 1 h. CO_2-TPD was performed at the rate of 5°C/min up to 600°C.

3.5.5 Surface Area Analyzer

The specific surface area was determined by the Brunauer-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°C (Bentonite support) 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.

3.5.6 X-ray Fluorescence (XRF)

Energy dispersive X-ray fluorescence (XRF) spectrometry (Oxford model ED2000) was used to determine the bulk composition of a catalyst. The potassium content was measured by XRF in the fresh and spent catalysts. Leached potassium referred to the total amount of potassium in the fresh catalyst withdrawn from the amount of potassium in the spent catalyst.

3.5.7 Titration Method

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).