

CHAPTER III

EXPERIMENTAL

3.1 Materials

1. Vegetable oil (Palm oil), Naval Engineering Command
2. Methanol (99.9%), Carlo Erba
3. Potassium hydroxide, Lab Scan
4. Alumina, ALCOA World Chemicals
5. NaY zeolite, TOSOH Corporation
6. Sodium sulfate, Fisher Scientific
7. Methyl esters mixture, Supelco

3.2 Equipment

1. Gas Chromatograph (GC)
2. Surface Area Analyzer (SAA)
3. Temperature Programmed Desorption / Temperature Programmed Reduction analyzer (TPD/TPR)
4. X-ray Diffraction (XRD)
5. Scanning Electron Microscope with Energy Dispersive Spectrometer (SEM-EDS)
6. Condenser
7. Magnetic stirrer
8. Stirring plate
9. Hot plate
10. Thermometer
11. Temperature controller
12. 500-ml three-necked flask

3.3 Methodology

3.3.1 Characterization of Vegetable Oil

The palm oil was obtained from the Naval Engineering Command and was analyzed based on density at 27°C, kinematics viscosity (ASTM D-445), free fatty acid content (AOCS Cd 3a-63), moisture content (AOCS Aa 3-38), and fatty acid composition (AOCS Ce 1-62).

3.3.2 Preparation of Catalyst

3.2.2.1 *KOH/Al₂O₃ Catalyst*

An Al₂O₃ support was obtained from ALCOA World Chemicals, USA. A series of KOH/Al₂O₃ catalysts with varying KOH loadings (10, 15, 20, 25, 30 and 35 wt%) was prepared by impregnation of Al₂O₃ support with an aqueous solution of KOH. The prepared catalysts were dried in an oven at 110°C for 24 hours and were calcined at 500°C for 3 hours.

3.2.2.2 *KOH/NaY Catalyst*

KOH/NaY was prepared by the method reported by Xie *et al.*, (2007). NaY zeolite obtained from TOSOH Corporation was dried in an oven at 110°C for 2 hours to remove the absorbed water on the surface. The NaY zeolite was impregnated with an aqueous solution of KOH with various loadings (8, 9, 10, 13 and 15 wt%) for 24 hours. Finally, it was dried in air at 110°C for 24 hours.

3.3.3 Transesterification of Vegetable Oils using Heterogeneous Catalyst

One hundred grams of vegetable oil was weighed and placed in a 500 ml three-necked flask. The vegetable oil was heated to 60°C by heater. The desired amount of methanol and catalyst were weighed and added into the oil reactor. A magnetic stirrer was used for mixing the oil, methanol and catalyst at the desired speed. The reaction was carried out until it reached the desired reaction time. After that the reaction had to be stopped by cooling down the reactor to room temperature and the catalyst was immediately separated from the product mixture by using a suction flask. The mixture was placed in the 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. And then the methyl esters (top phase) were washed with warm distilled water (50°C) until the wash-water was clear. Finally, the methyl esters (biodiesel) were dried by adding 25wt% base on weight of the methyl esters product.

The reaction initially contained methanol and oil in a 15:1 molar ratio and was carried out at a reaction temperature of 60°C, a catalyst amount of 3 wt% by weight of vegetable oil, and a stirrer speed of 300 rpm.

3.3.3.1 Effect of reaction time on yield of biodiesel

The initial conditions were a reaction temperature of 60°C, stirrer speed of 300 rpm, a molar ratio of methanol to oil of 15:1, and 3 g of catalyst when the reaction was carried out until reached the desired reaction time. The reaction must be stopped by cooling to room temperature and the solid catalyst was separated from the reaction mixture. The reaction time varied in the range 1 to 6 hours.

3.3.3.2 Effect of wt% loading of KOH on Al₂O₃ or KOH on NaY support on yield of biodiesel

The fixed conditions are: T = 60°C; stirrer speed = 300 rpm; reaction time = that obtained from procedure 3.3.3.1; 3 wt% catalyst base on vegetable oil; and molar ratio of methanol to oil = 15:1. These conditions were used to investigate the effect of wt% loading (in the range 0 to 35 wt%) of KOH on Al₂O₃ or KOH on NaY support on the yield of biodiesel.

3.3.3.3 Effect of molar ratio of methanol to oil on yield of biodiesel

The fixed conditions are: T = 60°C; stirrer speed = 300 rpm; reaction time = that obtained from procedure 3.3.3.1; 3 wt% catalyst base on vegetable oil; and wt% loading of KOH = that obtained from procedure 3.3.3.2. These conditions were used to investigate the effect of molar ratio of methanol to oil (in the range 3:1 to 21:1) on the yield of biodiesel.

3.3.3.4 Effect of amount of catalyst on yield of biodiesel

The fixed conditions are: T = 60°C; stirrer speed = 300 rpm; reaction time = that obtained from procedure 3.3.3.1; wt% loading of KOH = that

obtained from procedure 3.3.3.2; and molar ratio of methanol to oil = that obtained from procedure 3.3.3.3. These conditions were used to investigate the effect of amount of catalyst (in the range 1 to 9 wt% based on weight of oil) on the yield of biodiesel.

3.3.3.5 Effect of stirrer speed on yield of biodiesel

The fixed conditions are: T = 60°C; reaction time = that obtained from procedure 3.3.3.1; wt% loading of KOH = that obtained from procedure 3.3.3.2; molar ratio of methanol to oil = that obtained from procedure 3.3.3.3; and an amount of catalyst = that obtained from procedure 3.3.3.4. These conditions were used to investigate the effect of stirrer speed (in the range 150 to 600 rpm) on the yield of biodiesel.

3.3.3.6 Effect of reaction temperature on yield of biodiesel

The fixed conditions are: reaction time = that obtained from procedure 3.3.3.1; wt% loading of KOH = that obtained from procedure 3.3.3.2; molar ratio of methanol to oil = that obtained from procedure 3.3.3.3; and an amount of catalyst = that obtained from procedure 3.3.3.4. These conditions were used to investigate the effect of reaction temperature (in a range from 30 to 70°C) on the biodiesel yield.

3.4 Biodiesel Analysis

The methyl esters 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 a 0.1 µm film was used. Samples of 1 µl were injected under the following conditions: the carrier gas was helium at a flowrate of 70 ml/min; the injector temperature was 170°C with a split ratio 1:50; and, the temperature of the detector was 230°C. Oven temperature started at 170°C for 20 min, increased to 230°C at a rate of 1°C/min, and was held for 5 min. The run time was 115 min. The

methyl ester content, yield and conversion were determined using Equations 3.1-3.3, respectively.

$$\text{Methylester content (wt\%)} = \frac{\text{Area of methylester}}{\text{Total area} - \text{Area of solvent}} \times 100 \quad (3.1)$$

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

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

Moreover, mono-, di- and tri-glycerides contents were determined by using a gas chromatograph, equipped with a DB-5HT (15 m x 0.32 mm I.D.) fused-silica capillary column coated with a 0.1 μm film. Samples of 1 μl were injected on-column at an oven temperature of 50°C. After an isothermal, the GC oven was heated at 15°C/min to 180°C, 7°C/min to 230°C, and 10°C/min to 370°C. The final temperature was held for 10 min. The molar concentrations of mono-, di- and tri-glycerides were evaluated from the area of relevant peaks, using standard grade reagents as the calibration curve.

3.5 Catalyst Characterization

Several techniques were used to characterize the prepared catalysts, including X-ray Diffraction (XRD), Brunauer-Emmet-Teller (BET), Scanning Electron Microscopy with Energy Dispersive Spectrometer (SEM-EDS), and Temperature-Programed Desorption (TPD).

3.5.1 X-ray Diffraction (XRD)

The X-ray diffraction method is 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 is like a fingerprint of the substance.

A Bruker X-ray diffractometer system (D8 Advance) equipped with a 2.2kW Cu anode long fine focus ceramic X-ray tube for generating a CuK_α 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 2θ by starting at the 10° to 90° (2θ) range with a scan speed of 0.02° (2θ)/ 0.5 second. XRD patterns were compared to the standards to identify the crystalline phases.

3.5.2 BET Surface Area Measurement

The specific surface area and pore size distribution were determined by Brunauer-Emmet-Teller (BET) method Sorptomatic model 1990 instrument (Thermo Finnigan). Before analyzing, the volatile species that adsorbed on the catalyst surface must be eliminated by heating the catalyst under vacuum atmosphere at 250°C (Al_2O_3 support) and 300°C (NaY zeolite support) for 24 hours. Helium gas was used as an adsorbate for blank analysis and nitrogen gas was used as an adsorbate for analysis. And then, the software calculated the specific surface area and pore size distribution of the catalyst.

3.5.3 Scanning Electron Microscopy with Energy Dispersive Spectrometer

A scanning electron microscopy (SEM), JOEL Model JSM 5200, was utilized to identify the microstructure and capture the image of the catalyst morphology. An energy dispersive spectrometer (EDS), Oxford Model 6111, was used to identify the presence of elements (from characteristic x-ray) in the catalyst region being examined. The catalyst sample was placed on the stub and coated by gold in the sputtering device before being placed in the sample holder in the SEM.

3.5.4 Temperature-Programed Desorption (TPD)

Temperature-Programed 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-programed desorption of CO₂ (CO₂-TPD), which was used as the probe molecule. A 50-mg sample was degassed by heating in a flow of helium gas at a rate of 8°C/min from room temperature to 600°C, and was kept at 600°C for 2 hours. And then, adsorption of CO₂ gas occurred at 100°C. After that, the physically adsorbed CO₂ gas was purged by a He flow at 25°C for 2 hours. CO₂-TPD was performed at the rate of 10°C/ min up to 600°C.