CHAPTER III
EXPERIMENTAL

3.1 Materials

1. Vegetable oil (Palm oil) from the Naval Engineering Command
2. Methanol
3. Potassium hydroxide
4. Sodium sulfate
5. Methyl esters mixture

3.2 Equipment

1. Gas Chromatograph (GC)
2. X-ray Diffraction (XRD)
3. Scanning Electron Microscopy with Energy Dispersive Spectrometer (SEM-EDS)
4. X-ray fluorescence (XRF)
5. Condenser
6. Magnetic stirrer
7. Stirring plate
8. Hot plate
9. Thermometer
10. Temperature controller
11. 500-ml three-necked flask

3.3 Methodology

3.3.1 Characterization of Vegetable Oil

Palm oil was obtained from the Naval Engineering Command and was analyzed based on density at 27°C, kinematic 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 Catalyst Preparation

3.3.2.1 KOH/ZrO₂ Catalyst

A series of KOH/ZrO$_2$ catalyst varying K loadings (5, 10, 15, 20, 25, 30, 35, and 40 wt.%) were prepared by impregnation of a ZrO$_2$ support with an aqueous solution of KOH. The prepared catalyst was dried in an oven at 110 °C for 24 hours and was calcined at 500 °C for 3 hours.

3.3.2.2 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. The mordenite zeolite was stored in silica gel desicator. To prepare modified mordenite zeolite with different amount of K loadings (5, 10, 15, 20, 25, and 30 wt.%), 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.

3.3.3 Transesterification of Vegetable oil Using Heterogenous Catalyst

One hundred grams of vegetable oil was placed in a 500 ml three-necked flask. The vegetable oil was heated to 65°C. And then the catalyst and methanol were added to a three-necked flask. 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 was stopped by cooling down the reactor to room temperature. The catalysts were separated from the product mixture by using a suction flask. The products were placed in the reparatory funnel overnight to ensure that the separation of methyl esters and glycerol phase occurred completely. The methyl ester (top phase) was washed with distilled water (50°C) until the washed water was clear. And the glycerol phase (bottom phase) was

removed and left in a separated container. Finally, the methyl esters were dried by adding 25 wt.% Na_2SO_4 base on weight of the vegetable oil.

The starting conditions were set at reaction temperature of 65 °C, a methanol to oil molar ratio of 15:1, 3 wt.% of the catalyst (base on weight of the vegetable oil) and a stirrer speed of 300 rpm.

3.3.3.1 Effect of Catalyst Size

The effect of size of catalyst on the methyl ester content was investigated by using KOH/ZrO_2 catalysts. The reaction was fixed at a reaction temperature of 65°C at 2 hours of reaction time, a molar ratio of methanol to oil of 15:1, 3 wt.% of the catalyst (base on weight of the vegetable oil), and a stirrer speed of 300 rpm. The size of catalyst was varied in the range 10-60 mesh.

3.3.3.2 Effect of Reaction Time

The effect of reaction time on the methyl ester content was studied by varying the reaction time from 30 minutes to 7 hours. The initial conditions were set at reaction temperature of 65°C, 20 wt.% loading amount of K on ZrO_2 and Mordenite support at a molar ratio of methanol to oil of 15:1, 3 wt.% of the catalyst (base on weight of the vegetable oil), a stirrer speed of 300 rpm, and the size of KOH/ZrO_2 catalysts was obtained from 3.3.3.1.

3.3.3.3 Effect of Loading Amount of K

The effect of wt.% K on the methyl ester content was investigated by using KOH/ZrO_2 and KOH/mordenite catalysts. The reaction was fixed at a reaction temperature of 65°C at a molar ratio of methanol to oil of 15:1, 3 wt.% of the catalyst (base on weight of the vegetable oil), a stirrer speed of 300 rpm, the size of KOH/ZrO_2 catalysts was obtained from 3.3.3.1, and the reaction time was obtained from 3.3.3.2. The wt.% of K was varied in the range 5 to 40 wt.%.

3.3.3.4 Effect of Molar Ratio of Methanol to Oil

The effect of molar ratio of methanol to oil on the methyl ester content was studied by using KOH/ZrO_2 and KOH/mordenite catalysts. The reaction was fixed at the reaction temperature of 65°C, 3 wt.% of the catalyst (base on weight of the vegetable oil), a stirrer speed of 300 rpm, the size of KOH/ZrO_2 catalysts was obtained from 3.3.3.1, the reaction time was obtained from 3.3.3.2, and wt.% loading

of K was obtained from 3.3.3.3. The molar ratio of methanol to oil was varied in the range 6:1 to 21:1.

3.3.3.5 Effect of Amount of Catalyst

The effect of amount of catalyst on the methyl ester content was observed by using KOH/ZrO_2 and KOH/mordenite catalysts. The reaction was fixed at the reaction temperature of 65°C, a stirrer speed of 300 rpm, the size of KOH/ZrO_2 catalysts was obtained from 3.3.3.1, the reaction time was obtained from 3.3.3.2, wt.% loading amount of K was obtained from 3.3.3.3, and the molar ratio of methanol to oil was obtained from 3.3.3.4. The amount of catalyst was varied in the range 1 to 5 wt.% of the catalyst (base on weight of the vegetable oil).

3.3.3.6 Effect of Calcination Temperature

The effect of calcination temperature on the methyl ester content was studied by using KOH/mordenite catalysts. The starting conditions were set at reaction temperature of 65°C, the reaction time of 3 hours, 20 wt.% loading amount of K, a methanol to oil molar ratio of 15:1, 3 wt.% of the catalyst (base on weight of the vegetable oil) and a stirrer speed of 300 rpm. The calcination temperature was varied in the range of 400-600 °C.

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 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 3:1 and the temperature of detector was 220°C. Sample (0.1 μl) were 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.

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

C	Methyl ester content
$\sum A$	The overall area of methyl eater from C_{14} to C_{241}
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 hepyta decanoate solution
m	Weight in mg of sample

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

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

3.5 Catalyst Characterization

3.5.1 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.

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 2θ by starting at the $10°$ to $90°$ (2θ) range and a scan speed of $0.02°$ $(2\theta)/$ 0.5 second. The XRD patterns were compared to the standards to identify crystalline phases.

3.5.2 Scanning Electron Microscopy with Energy Dispersive Spectrometer

Scanning Electron Microscopy (SEM), JSM-5800LV, was used to capture the morphology of the catalyst. And Energy Dispersive Spectrometer (EDS) was analyzed the element in examined region of the catalyst by using the X-ray beam. The catalyst sample was placed on stub with carbon tape before placing the sample holder in SEM machine.

3.5.3 Energy Dispersive X-ray Fluorescence Spectrometry (XRF)

XRF is a well-established technique for non-destructive analysis of metals in different materials. X-ray fluorescence spectrometry (XRF), Oxford model ED2000, was used to examine the composition in the catalyst. The preparation of the catalyst was milled for 15 minutes by ball mill before putting the sample on the aluminium support and compressed at 500 kg/cm^2 of hydraulic pressure; finally put the sample in the XRF machine.