CHAPTER III
EXPERIMENTAL

3.1 Materials

1. Refined Palm oil, the Naval Engineering Command
2. Montmorillonite k-10 powder (Analytical Grade), Aldrich
3. Hydrochloric acid, 37% purity (Analytical Grade), Carlo
4. Potassium hydroxide, KOH, Lab-scan
5. Methanol (Analytical grade), Fisher Scientific
6. Sulfuric acid, H_2SO_4 (Analytical Grade), Carlo
7. Sodium Sulfate Na_2SO_4 ,Lab-scan

3.2 Equipment

1. Atomic Absorption Spectrophotometer (AAS), Varian/SpectrAA 300
2. Buchner funnel 110 mm diameter
3. Fourier Transform Infrared spectrometer (FTIR), Nicolet/Nexus 670
4. Furnace, CARBOLITE/CWF11/13/201
5. Gas Chromatography (GC), Hewlett Packard GC model 5890
6. Heating magnetic stirrer, VELP® SCIENTFICA /ARE
7. Peristatic pump
8. X-ray Diffraction (XRD)
9. Scanning Electron Microscopy (SEM), JOEL Model JSM 5200 with Energy Dispersive Spectrometry (EDS), Oxford Model 6111
10. Three-necked flask 500ml
11. Thermometer mercury 0–100 °C
12. TPD/TPR Instrument, Micromeritics 2900

3.3 Methodology

3.3.1 Characterization of Vegetable Oil

Vegetable oil (Refined palm oil) was redeived from the Naval Engineering Command and then 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) (langthanarat, 2008)

3.3.2 Catalyst Preparation

3.3.2.1 KOH/Montmorillonite

Montmorilloniote was first pretreated at 110 °C for 2 h and it was impregnated with an aqueous solution of KOH with 5 – 30 %wt K. After an aqueous solution of KOH was diffused and dispersed thoroughly on the surface, KOH/montmorillonite was dried at 110 °C for 24 h to remove the adsorbed water and humidity on the surface before testing catalytic activity.

3.3.3 Transesterification

Vegetable oil (Refined palm oil) was placed in a 500 ml three-necked flask. The refined palm oil and methanol were mixed into a three-necked flask with a 1:15 oil to methanol molar ratio and stirrer speed of 300 rpm for a well mixing. Reaction were studied at 60 °C, a reaction time of 10 h, and catalyst loading of 6wt%. After that the products were placed in a separatory funnel overnight to ensure that the separation of methyl ester and glycerol phase occurred completely. The methyl ester, the desired product, which was on the top, was washed with deionized water at 50 °C until the washed water was clear. The glycerol phase, which was in the bottom phase, was removed out. Finally, the methyl esters were dried by adding 25% wt Na_2SO_4 based on weight of refined palm oil.

3.3.4 Biodiesel Analysis

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

3.3.4.1 Gas Chromatography

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).

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

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

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

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

3.3.5 Catalyst Characterization

The fresh and spent catalysts were characterized for their properties, and characteristics, structure, morphology, and metal composition by various techniques.

3.3.5.1 X-Ray Diffraction (XRD)

The 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 an individual fingerprint of each 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 2.2 kW Cu anode long fine focus ceramic X-Ray tube for generating a CuK_α radiation (1.5405 A), was used as an X-Ray source to obtain the XRD patterns at running conditions for 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 from $10°$ to $90°$ (2θ) range and a scan speed of $0.02°$ (2θ)/0.5 second. The XRD patterns of samples were compared to the standards to identify crystalline phases.

3.3.5.2 Scanning Electron Microscopy Instrument with Energy Dispersive Spectroscopy (SEM-EDS)

Scanning Electron Microscopy (SEM), JOEL Model JSM 5200, was utilized to identify the microstructure and capture the micrograph of catalyst morphology. Energy Dispersive Spectroscopy (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 a stub and coated by gold in sputtering device before it was placed in the sample holder in SEM.

3.3.5.3 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 this temperature 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.

3.3.5.4 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).

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

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