

CHAPTER III EXPERIMENTAL

3.1 Materials

1. Vegetable Oil (Refined palm oil), Morakot Industries PCL.
2. Methanol (Analytical grade), Fisher Scientific
3. Calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), Sigma Aldrich
4. Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), Sigma Aldrich
5. Zinc Oxide (ZnO), Sigma Aldrich
6. Sodium hydroxide
7. Sodium carbonate
8. Hydrochloric acid, 37% purity (Analytical Grade), CarloErba
9. Sodium sulphate, Riedel-de Haen
10. 2-propanol HPLC grade, Carlo Erba
11. n-hexane HPLC grade, Carlo Erba
12. n-heptane, Labscan
13. Methyl heptadecanoate, Sigma Aldrich

3.2 Equipment

1. Gas Chromatograph (GC), Hewlett Packard GC model 5890
2. Surface Area Analyzer (SAA), Brunauer-Emmet-Teller (BET)
3. Temperature-Programmed Desorption of CO_2 (CO_2 -TPD), Micromeritics 2900
4. Temperature-Programmed Reduction (TPR)
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 Catalyst Preparation

3.3.1.1 Preparation of CaO–ZnO Catalyst by Incipient-Wetness Impregnation (IWI) Method

3.3.1.1.1 Preparation of ZnO Support by Precipitation Method

Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was weighed for a desired amount, and then dissolved in deionized water under continuous stirring and heating at 80 °C. The pH of solution (~8) was adjusted by adding Na_2CO_3 or NaOH at various concentrations, then the mixture was aged for 1 h. The suspension was washed by warm deionized water to eliminate the residue ions. Deionized precipitate was dried at 110 °C overnight and calcined in air at various temperatures for 6 h. After calcination, the sample was stored in a silica gel dessicator prior to use.

3.3.1.1.2 Preparation of Ca Support on ZnO Catalyst by Impregnation Method

A Zinc oxide was dried in an oven at 110 °C for 2 h to remove the absorbed water on the surface. To prepare modified ZnO with different Ca loadings, the ZnO was impregnated with an aqueous solution of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$. Samples with various Ca loadings, given in weight percentage, were impregnated for 24 h to ensure that the Ca diffused and dispersed thoroughly on the surface of ZnO. The loading amounts of Ca were calculated on the basis of the amounts of the starting materials. The pretreated samples were dried in an oven at 110 °C for overnight and then calcined at different temperatures.

3.3.1.2 Preparation of CaO–ZnO Catalyst by Co-Precipitation (CP)

Method

Calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) and Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) were weighed for a desired amount, and then dissolved in deionized water under continuous stirring and heating at 80 °C. The pH of solution (~8) was adjusted by adding Na_2CO_3 or NaOH at various concentrations then the mixture was aged for 1 h. The suspension was washed by warm deionized water to eliminate the residue ions. Deionized precipitate was dried at 110 °C overnight, and calcined in air at various temperatures for 6 h. After calcination, the sample was stored in a silica gel dessicator prior to use.

3.3.2 Transesterification of Vegetable Oil using CaO–ZnO Catalyst

The vegetable oil was weighed and heated to 60 °C in a 500 ml three-necked flask. Then, 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 cool down the reactor to room temperature. The catalysts were separated out from the product by using a suction flask. The products were placed in a separatory funnel overnight to ensure that the phase of methyl esters and phase of glycerol are separated completely. 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 left in a separated container. The 25 wt% of sodium sulfate based on weight of methyl ester product was added into methyl esters to remove water.

The initial condition was carried out at reaction temperature of 60 °C, a methanol to oil molar ratio of 15:1, the amount of catalyst of 6 wt%, and 300 rpm of stirrer speed.

3.3.2.1 *Effect of Ca:Zn Atomic Ratio on Biodiesel Yield*

The reaction was fixed at the reaction temperature of 60 °C, a methanol to oil molar ratio of 15:1, the amount of catalyst of 6 wt%, 300 rpm of stirrer speed, and the reaction time 8 h. These conditions were used to study the effect of Ca:Zn atomic ratio (in the range of 1:5 to 3:1) on biodiesel yield.

3.3.2.2 *Effect of Calcination Temperature on Biodiesel Yield*

The reaction was fixed at the reaction temperature of 60 °C, a methanol to oil molar ratio of 15:1, the amount of catalyst of 6 wt%, 300 rpm of stirrer speed, and the reaction time 8 h. The Ca:Zn atomic ratio was obtained from procedure 3.3.2.1. These conditions were used to study the effect of calcination temperature (in the range of 600 to 900 °C) on biodiesel yield.

3.3.2.3 *Effect of Catalyst Preparation on Biodiesel Yield*

The reaction was fixed at the reaction temperature of 60 °C, a methanol to oil molar ratio of 15:1, the amount of catalyst of 6 wt%, 300 rpm of stirrer speed, and the reaction time 8 h. The Ca:Zn atomic ratio, and calcination temperature were obtained from procedure 3.3.2.1, and 3.3.2.2, respectively. These conditions were used to study the effect of catalyst preparation (Incipient-Wetness Impregnation (IWI) and Co-Precipitation (CP) techniques) on biodiesel yield.

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 μ m film was used. Sample of 0.1 μ l 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 μ l 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).

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

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 methylheptadecanoate solution
C_{EI}	Concentration in mg/ml of methyl heptadecanoate solution
V_{EI}	Volume of methyl heptadecanoate solution
m	Weight in mg of sample

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

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

3.4.2 High Performance Liquid Chromatography (HPLC)

The composition of the reaction mixture samples was determined by the somewhat modified HPLC method of Holčapek *et al.*, (1999) using a Perkin Elmer High Performance Liquid Chromatograph, equipped with a degasser, a binary pump, a Zorbax Eclipse XDB-C18 capillary column (4.6 m x 150 mm x 5 μ m) and an UV/VIS detector. The flow rate of a binary solvent mixture methanol, (solventA), and 2-propanol/n-hexane, 5:4 by volume, (solventB) 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 μ m 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, including XRD, FTIR, SEM-EDS, BET, TPD, TPR, XRF, and titration method.

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 Temperature-Programmed Reduction Technique (TPR)

Temperature-Programmed Reduction (TPR) was conducted using an in-house TPR system. A measurement was carried out by placing a sample in a quartz reactor. The sample was subjected to TPR analysis using 10% H_2 in Ar for 30 ml/min. The reduction temperature is raised from 30 to 850 °C at a ramp rate of 10 °C/min. A thermal conductivity detector is used to monitor the difference of hydrogen content before and after the reduction. The temperature, at which the reduction is completed, could be determined from TPR pattern.

3.5.4 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 $\text{CuK}\alpha$ 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 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 10° to $80^\circ(2\theta)$ 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.

3.5.5 Temperature-Programmed Desorption of CO_2 (CO_2 -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_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 $10^\circ\text{C}/\text{min}$ 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 $5^\circ\text{C}/\text{min}$ up to 600°C .

3.5.6 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.

3.5.7 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 calcium content was measured by XRF in the fresh and spent catalysts. Leached calcium referred to the total amount of calcium in the fresh catalyst withdrawn from the amount of calcium in the spent catalyst.

3.5.8 Hammett Indicator

Basic strengths of the catalysts (H_-) were determined by using Hammett indicator. About 0.3 g of the catalyst sample was shaken with 1.0 ml of a solution of Hammett indicator diluted with methanol, and left to equilibrate for 2 h. After the equilibration, the color on the catalyst was noted. The following Hammett indicators were used: bromothymol Blue ($H_- = 7.2$), phenolphthalein ($H_- = 9.8$), Tropaeolin ($H_- = 11$), 2,4-dinitroaniline ($H_- = 15$), and 4-nitroaniline ($H_- = 18.4$).