CHAPTER III

EXPERIMENTAL

3.1 Materials

1. Palm oil (Royal Thai Naval Dockyard)
2. Methanol (Fisher Scientific)
3. Sodium Hydroxide (Lab-Scan)
4. Sodium Sulphate Anhydrous (Ajax Finechem)
5. Zirconium(IV) Hydroxide (Aldrich)
6. Fatty acid methyl esters mixture (Supelco)
7. Hexane (Lab-Scan)
8. Deuterated chloroform (Merck)

3.2 Instruments

1. Surface Area Analyzer
2. X-ray Diffraction (XRD)
3. Scanning Electron Microscopy with Energy Dispersive Spectrometer (SEM-EDS)
4. ^{1}H-Nuclear Magnetic Resonance spectrometer (^{1}H-NMR)
5. Gas Chromatograph (GC)

3.3 Methodology

3.3.1 Preparation of NaOH/ZrO_2 Catalyst

ZrO_2 support obtained from Aldrich was loaded with various amounts of NaOH (0.1-1.5%wt in methanol) via impregnation. The prepared catalysts were dried in an oven at 110°C for 24 h, followed by calcination at 500°C for 5 h. To investigate the effect of the calcination temperature, the catalysts were calcined at various temperatures (100°, 300°, 500°, 700° and 900°C). The obtained catalyst were characterized by the X-ray Diffraction (XRD), Surface Area Analyzer, Scanning Electron Microscopy (SEM) and Energy Dispersive Spectrometer (EDS).

3.3.2 Catalyst Characterization

3.3.2.1 X-ray Diffraction (XRD)

A Rigaku X-ray diffractometer equipped with CuK_α as an X-ray source was used to obtain X-ray patterns of samples in the range of 20° to 80° (2θ), using a scan speed of 2°/min. XRD patterns were compared to standard files, ICDD file 17-293 and ICDD file 37-64 (Ksapabutr *et al.*, 2004), to identify crystalline phases.

3.3.2.2 Surface Area Analyzer

To investigate surface area and pore volume, BET method using a Quantachrome (Autosorb-1) was used. The prepared catalyst was degasssed at 250°C for 18 h prior to use.

3.3.2.3 Scanning Electron Microscopy with Energy Dispersive Spectrometer (SEM-EDS)

The morphology of samples was investigated using SEM (JEOL model JSM-5410LV), and EDS (Oxford model ISIS 300) was used for determining element in the sample. This technique was done at a faculty of Dentist, Chulalongkorn University.

3.3.3 Transesterification of Palm Oil using Heterogeneous catalyst

Twenty five grams of palm oil was weighed and placed in a 100-ml three-necked round bottom flask equipped with a reflux condenser, thermometer and a sampling port, as can be seen in figure 3.1. The palm oil was heated to 70°C before adding 18 mol equivalent of methanol to palm oil and 5wt% catalyst. The reaction was carried out for a desired reaction time, followed by cooling down the reactor to room temperature. The catalyst was separated from the product mixture immediately. The mixture was placed in a separatory funnel and allowed to stand overnight to ensure that the separation of the methyl esters and the glycerol phases occurred completely. The glycerol phase at the bottom was removed and the methyl esters on the top were washed with warm distilled water (50°C) until the water after washing was clear. Finally, the methyl esters (biodiesel) were dried over anhydrous sodium sulphate and left it overnight to obtain dried biodiesel.

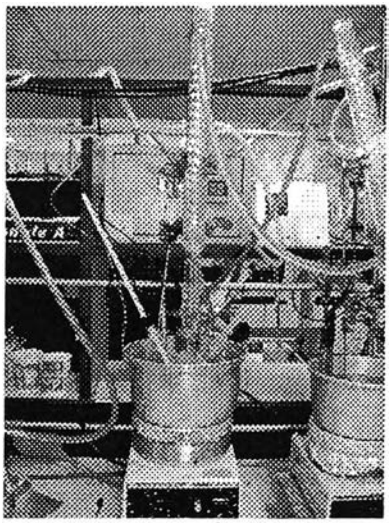

Figure 3.1 Experimental set up for the transesterification reaction

The reaction initially containing 18:1 molar ratio of methanol and oil mixture was carried out, using 5%wt catalyst to palm oil at 70°C reaction temperature for 2 h reaction time, and 500 rpm stirring speed. This condition was used throughout the study.

3.3.3.1 Effect of the amount of NaOH loading on zirconia support on biodiesel yield

After heating the 18:1 of methanol to oil mixture at 70°C reaction temperature, 1.25 g of catalyst was added. The various amounts of NaOH were studied within a range of 0.1-1.5%wt in methanol. The reaction was stopped after 2 h.

3.3.3.2 Effect of the $NaOH/ZrO_2$ catalyst amount on biodiesel yield

The conditions were fixed at 70°C reaction temperature for 2 h reaction time, using 18:1 ratio of methanol to oil. Selecting the best result from procedure 3.3.3.1, various amounts of $NaOH/ZrO_2$ catalyst were studied within a range of 1-10 wt% to determine the effect of the catalyst amount on biodiesel yield.

3.3.3.3 Effect of the reaction time on biodiesel yield

The conditions were fixed at 70°C reaction temperature for various reaction times using 18:1 ratio of methanol to oil. The best amounts of the NaOH loading on zirconia support and the catalyst amount obtained from procedures 3.3.3.1.and 3.3.3.2, respectively, were used to determine the optimal reaction time by collecting sample at 15, 30, 45, 60, 90, 120 min.

3.3.3.4 Effect of the molar ratio of methanol to oil on biodiesel yield

The optimal conditions obtained from procedures 3.3.3.1-3.3.3.3 were studied in this step at 70°C reaction temperature. The molar ratio of methanol to oil was varied within 3 to 18.

3.3.3.5 Effect of the temperature on biodiesel yield

The obtained conditions from procedures 3.3.3.1-3.3.3.4 were used for investigating the temperature affecting to the biodiesel yield. The reaction temperature was varied within a range of 30° to 80°C.

3.3.3.6 Effect of the calcination temperature on biodiesel yield

Using the optimal conditions obtained from procedures 3.3.3.1-3.3.3.5, the effect of the calcination temperature of the NaOH/ZrO_2 catalyst was studied by varying the calcination temperature at 100, 300, 500, 700, and 900°C.

3.3.3.7 Reused Catalyst

To study the reusability of the catalyst, the solid catalyst recovered after the first run reaction was filtered and washed with hexane. The used catalyst was dried in an oven for 24 h to remove hexane. Then, it was calcined at 500°C in furnace for 15 h before reusing in the second run reaction.

3.3.4 Biodiesel Analysis

3.3.4.1 ^{1}H-Nuclear Magnetic Resonance

The ^{1}H-NMR spectra were obtained on Varian Mercury Plus-400 from the faculty of Science, Chulalongkorn University, using deuterated chloroform and tetramethyl silane (TMS) as solvent and reference, respectively. To determine % conversion of transesterified products, equation 3.1 was introduced.

$$C = 100 \times \left(\frac{2A_{ME}}{3A_{\alpha-CH_2}} \right) \tag{3.1}$$

where C = conversion of triacylglycerol feedstock (vegetable oil) to the corresponding methyl ester.

A_{ME} = integration value of the protons of the methyl esters (the strong singlet peak at 3.6 ppm)

$A_{\alpha-CH_2}$ = integration value of the methylene protons at 2.3 ppm

3.3.4.2 Gas Chromatography (GC) Analysis

The methyl ester products were analyzed on an Agilent GC-6890. A ZEBRON-WAX (30 m x 0.25 mm I.D.) fused-silica capillary column coated with a 0.1 μm film. Samples of 1 μL were injected under the following conditions: the carrier gas was helium and set at 103.4 kPa. Hydrogen and compressed air used for FID were maintained at 275.6 kPa. The oven temperature was set at 50°C, held for 2 min, raised to 220°C at a rate of 4°C/min, and held at 220°C for 35 min, while the injector and detector temperatures were set at 250°C and 260°C, respectively. The fatty acid methyl ester content (FAME) and linolenic acid methyl ester content was confirmed based on EN 14103 and using equations 3.2 and 3.3, respectively.

$$C = \frac{(\sum A) - A_{EI}}{A_{EI}} \times \frac{C_{EI} \times V_{EI}}{m} \times 100\% \tag{3.2}$$

where C = ester content

$\sum A$ = the total peak area from the FAME $C_{14:0}$ to $C_{24:0}$

A_{EI} = the peak area of methylheptadecanoate

C_{EI} = the concentration, in mg/mL of the methylheptadecanoate solution

V_{EI} = the volume, in mL, of the methylheptadecanoate solution

m = the mass, in mg, of the sample

$$L = \frac{A_L}{\sum A - A_{EI}} \times 100\% \qquad (3.3)$$

where A_L = the peak area of linolenic acid methyl ester

3.3.4.3 Properties of Biodiesel

Fatty acid methyl ester content, kinematic viscosity, flash point, and heating value were analyzed, followed EN 14103, ASTM D445, ASTM D92 (open cup), and ASTM D611, respectively. Viscosity values was measured on TAMSON model TV4000. The chromatograms was obtained on SHIMADZU-GC-14B, flash point on HER200-HFP386, and heating value on PARR-6200 at Chemical Technology, Chulalongkorn University.