

## **CHAPTER III**

### **EXPERIMENTAL**

#### **3.1 Materials**

##### 3.1.1 Vegetable Oils

Vegetable oils used in this research were crude palm kernel oil and crude coconut oil. Crude palm kernel oil was obtained from Chumporn Palm Oil Industry Public Company Limited (Chumporn Province). Crude coconut oil was obtained from Thai Taksin Company (Prachuap Kirikun Province). Both oils were used as received.

##### 3.1.2 Chemicals

Potassium Nitrate ( $\text{KNO}_3$ ) and Zinc Oxide ( $\text{ZnO}$  with purity higher than 99.0 % and Stannous Chloride ( $\text{SnCl}_2$ ) 98 % were purchased from Fluka. KL-zeolite were obtained from UOP LLC. Zirconium Oxide ( $\text{ZrO}_2$ ) and Anhydrous Sodium Sulfate 99.0% were received from Riedel-deHaën. Sulfuric Acid ( $\text{H}_2\text{SO}_4$ ) 96 %, Methanol 99.8 %, HPLC grade Acetonitrile and Acetone were purchased from Labscan. Ammonium Hydroxide was 28-30% (A.C.S.Reagent) and obtained from J.T.Baker.

Methyl ester used as standard for HPLC were Methyl Arachidate, Methyl Caprate, Methyl Caprylate, Methyl Laurate, Methyl Linoleate, Methyl Linolenate, Methyl Myristate, Methyl Oleate, and Methyl Palmitate , and all of them were purchased from Fluka.

#### **3.2 Instruments**

##### 3.2.1 Reactor

Reactor used to produce biodiesel is Parr series reactor (300 ml) equipped with programmable PID temperature controller.

### 3.2.2 High Pressure Liquid Chromatography (HPLC)

Perkin Elmer Series 200 high pressure liquid chromatography was used to analyze biodiesel products. The column used was Zorbax Eclipse XDB- C18 column (4.6 mm x 250 mm x 5 $\mu$ m).

## 3.3 Methodology

### 3.3.1 Characterization of Vegetable Oils

Characterization of vegetable oils was provided by Thailand Institute of Scientific and Technological Research. The crude palm kernel oil and crude coconut oil were analyzed based on their density at 27°C. Standard methods were used to obtain kinematic viscosity (ASTM D-445), free fatty acid content (AOCS Cd 3a-63), moisture content (AOCS Aa 3-38) and acid composition (AOCS Ce1-62).

### 3.3.2 Preparation of Catalysts

#### 3.3.2.1 *Zirconium Oxide (ZrO<sub>2</sub>)*

Zirconium oxide used in this thesis was obtained from Riedel-deHaën and used as received.

#### 3.3.2.2 *Zinc Oxide (ZnO)*

Zinc oxide used in this thesis was received from Fluka and used without further purification.

#### 3.3.2.3 *Sulphated Stannous Oxide (SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub>)*

Sulphated Stannous Oxide was prepared by using the method outlined by Chavan *et al.* (1996). Stannous chloride (22.56 g) was dissolved in 200-ml distilled water to get a clear solution. Aqueous ammonium hydroxide (25 ml) was gradually added into this solution until pH is 8. The yellowish solid was precipitated out. The yellowish precipitate was then filtered and washed well with distilled water, dried at 110°C for 12 hours to get stannous hydroxide. This dried hydroxide powder was then equilibrated with 25 ml of 2 N H<sub>2</sub>SO<sub>4</sub> for 2 hours. It was then dried and calcined at 500°C for 4 hours.

#### 3.3.2.4 Sulphated Zirconia ( $\text{SO}_4^{2-}/\text{ZrO}_2$ )

Sulphated Zirconia used in this thesis was prepared by the method outlined by Miao and Gao (1997). Zirconium oxide powder was immersed in a 0.5 M  $\text{H}_2\text{SO}_4$  solution for 30 min, then filtered and dried at  $110^\circ\text{C}$  for 24 hours to form the sulphated sample ( $\text{SO}_4^{2-}/\text{ZrO}_2$ ). Finally, it was calcined at  $500^\circ\text{C}$  for 2 hours.

#### 3.3.2.5 KL zeolite Impregnated with $\text{KNO}_3$ ( $\text{KNO}_3/\text{KL zeolite}$ )

The impregnation method (Zhu *et al.*, 1996), using an aqueous solution of  $\text{KNO}_3$  was used to prepare 21% $\text{KNO}_3/\text{KL zeolite}$  which was found to exhibit the highest basic strength. The KL zeolite (40 g) was impregnated with  $\text{KNO}_3$  solution and followed by drying at  $100^\circ\text{C}$ . The  $\text{KNO}_3/\text{KL zeolite}$  was then calcined at  $600^\circ\text{C}$  for 2 hours.

#### 3.3.2.6 Zirconia-Supported Potassium Nitrate ( $\text{KNO}_3/\text{ZrO}_2$ )

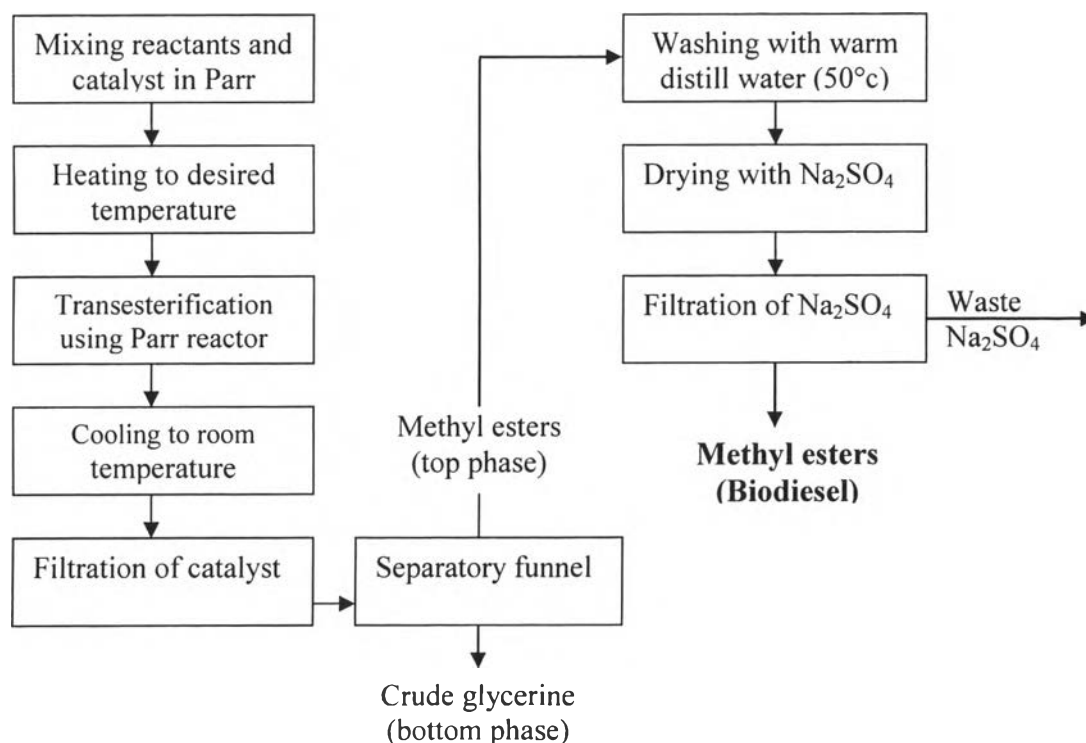
Zirconia-supported potassium nitrate was prepared using the method outlined by Wang *et al.* (2000). The 20% $\text{KNO}_3/\text{ZrO}_2$  was prepared by grinding 40 g of  $\text{ZrO}_2$  with 8 g of  $\text{KNO}_3$  and followed by adding distilled water of 24 ml. The paste was kneaded and then dried at  $110^\circ\text{C}$  for 12 hours. Finally, the 20% $\text{KNO}_3/\text{ZrO}_2$  was calcined at  $600^\circ\text{C}$  for 2 hours.

### 3.3.3 Transesterification of Vegetable Oils using Heterogeneous Catalyst

Seventy grams of vegetable oil was weighed and placed in a Parr series reactor. The desired amount of catalyst and methanol was weighed and mixed with oil in the reactor. The reactor was placed in heater and then heated to the desired reaction temperature. The reaction was carried out until it reached the desired reaction time and the reactor was then cooled down to room temperature. Both heating and cooling times of the reactor were less than 15 minutes. After cooling, the catalyst was separated from the product mixture by using suction flask. The product mixture was then placed in a separatory funnel and was allowed to stand overnight to ensure the separation of the methyl esters and the glycerol phase. The glycerol phase (bottom phase) was removed and placed in a separate container. Afterwards the methyl esters phase (top phase) was washed with warm distilled

water (50°C) until the water layer is clear (Karaosmanoğlu *et al.*, 1996). Finally, the methyl esters product (biodiesel) was dried by adding sodium sulfate (25% based on the weight of washed methyl esters product). The schematic diagram of the biodiesel production by heterogeneous catalytic transesterification. is shown in Figure 3.1.

The investigation of possible heterogeneous catalysts was studied by fixing the reaction temperature at 200°C, reaction time at 4 hours, 50 bars under nitrogen atmosphere and stirrer speed of 350 rpm. The conditions used are shown in Table 3.1 and Table 3.2. Experiment run No. 1-7, for both palm kernel oil and coconut oil, were done to investigate the possibility of solid catalysts ( $ZrO_2$ ,  $ZnO$ ,  $SO_4^{2-}/SnO_2$ ,  $SO_4^{2-}/ZrO_2$ ,  $KNO_3/KI$  zeolite, and  $KNO_3/ZrO_2$ ) as the heterogeneous catalysts for the transesterification of vegetable oils.



**Figure 3.1** Schematic diagram of the biodiesel production by heterogeneous catalytic transesterification.

**Table 3.1** Condition used for palm kernel oil (200 °C, 50 bars under N<sub>2</sub>)

Experiment No.	Catalyst Type	Amount of Catalyst (% based on weight of oil)	Methanol : Oil Molar Ratio
1	None	3	6:1
2	ZrO <sub>2</sub>	3	6:1
3	ZnO	3	6:1
4	SO <sub>4</sub> <sup>2-</sup> /SnO <sub>2</sub>	3	6:1
5	SO <sub>4</sub> <sup>2-</sup> /ZrO <sub>2</sub>	3	6:1
6	KNO <sub>3</sub> /KLzeolite	3	6:1
7	KNO <sub>3</sub> /ZrO <sub>2</sub>	3	6:1

**Table 3.2** Condition used for coconut oil (200 °C, 50 bars under N<sub>2</sub>)

Experiment No.	Catalyst Type	Amount of Catalyst (% based on weight of oil)	Methanol : Oil Molar Ratio
1	None	3	6:1
2	ZrO <sub>2</sub>	3	6:1
3	ZnO	3	6:1
4	SO <sub>4</sub> <sup>2-</sup> /SnO <sub>2</sub>	3	6:1
5	SO <sub>4</sub> <sup>2-</sup> /ZrO <sub>2</sub>	3	6:1
6	KNO <sub>3</sub> /KLzeolite	3	6:1
7	KNO <sub>3</sub> /ZrO <sub>2</sub>	3	6:1

#### 3.3.4 Biodiesel Analysis

Analysis of biodiesel products was performed by high pressure liquid chromatography (HPLC) using a Perkin Elmer Series 200 LC-pump and a refractive index Series 200 detector and controlled by a PC with a software package (Perkin Elmer Turbochrom Navigator). A Zorbax Eclipse XDB- C18 column (4.6 mm x 250 mm x 5µm) was used and the mobile phase was acetone/ acetonitrile mixture (70:30 vol/ vol) at a flowrate of 0.7 ml/min. The column temperature used

was at ambient temperature (27°C). The pump pressure was operated in the range of 300 to 1000 psi. The biodiesel samples were diluted with acetone (HPLC grade) and the injection volume was 20  $\mu$ l.

The amount of methyl esters for each sample was quantified by comparing the RID signal for each methyl ester of the HPLC chromatogram of biodiesel product with the RID signal of each of methyl ester standard.

In order to see the purity of product samples, the methyl esters content and methyl esters are defined as following. The methyl esters content is defined as a ratio of weight of methyl esters, which was determined by using HPLC, to weight of methyl esters phase (top phase), which may consist of mono-, di- and triglycerides as shown in Equation (3.1).

$$\text{Methyl Esters content (wt\%)} = \frac{\text{Weight of methyl esters (determined by HPLC)}}{\text{Weight of methyl esters phase (top phase)}} \times 100 \quad (3.1)$$

The methyl esters content is defined as a ratio of weight of methyl esters, which was determined by using HPLC, to weight of vegetable oil used as shown in Equation (3.2).

$$\text{Methyl Esters Yield (wt\%)} = \frac{\text{Weight of methyl esters (determined by HPLC)}}{\text{Weight of vegetable oil used}} \times 100 \quad (3.2)$$

The methyl esters content, and methyl esters yield in each experiment were calculated from the content in methyl esters of biodiesel as analyzed by HPLC.