CHAPTER III

MATERIALS & METHODS

3.1 Materials and chemicals

Purified palm oil samples used in this study was manufactured by Chumporn Palm Oil Industry Public Company Limited. Palm fatty acid was suppled by Thai V.O. Fuels Company Limited. Methanol and hexane analytical grade and were from Fisher scientific, UK, and sulfuric acid was purchased from Carlo ERBA. Methyl ester standard (methyl palmitate, methyl stearate and methyl oleate) were purchased from Wako Chemicals, USA. Commercial sulfated zirconia catalyst and zirconium oxide used for the preparation of the catalysts were purchased from Aldrich.

3.2 Preparation of catalysts

Sulfated zirconia (SO_4^{2-}/ZrO_2) catalyst was prepared from the impregnation of H_2SO_4 over commercial zirconium oxide (ZrO_2) precursor (particle size: < 100 meshes or 149 microns). The ZrO_2 was immersed in 0.1 mol/liter of H_2SO_4 at 70 °C for 30 minutes, which was then dried at 110 °C for 24 hours, and calcined for 2 hours. In this work, three different SO_4^{2-}/ZrO_2 catalysts were prepared at various conditions as shown in the Table 3.1.

Table 3.1 Preparation conditions of SO_4^{2-}/ZrO_2 catalysts

Catalyst	Zirconium oxide (g)	Sulfuric acid (ml)	Calcined temperature (°C)
SZ1	40	18	500
SZ2	40	30	500
SZ3	40	30	900

The characterization of the prepared SO_4^{2-}/ZrO_2 catalysts were carried out to determine the specific surface area and the amount of sulphur element of this solid catalyst by Brunauer-Emmett-Teller (BET) and X-ray fluorescent spectrometer (XRF), respectively.

3.3 Supercritical methanol transesterification and esterification reaction

The production of biodiesel from purified palm oil and palm fatty acid in supercritical methanol was carried out in a batch type reactor with SO_4^{2-}/ZrO_2 catalysts. A schematic diagram of the system employed was shown in Figure 3.1, which consisted of an electric furnace and an 8.8 ml stainless steel reactor, having the maximum allowable reaction pressure of 200 MPa (AKICO, Japan). Prior to the experiment, the temperature of the heating furnace (T_1) at the location of the furnace adjacent to the reactor was controlled at 200-300 °C. The effects of different operating conditions including mass ratio of SO_4^{2-}/ZrO_2 catalysts to reactants, reaction temperature, reaction time, and molar ratio of methanol to reactants, were determined on the yield of methyl esters produced, and the effect of catalyst recycling was also investigated. To carried out the reaction, the purified palm oil or palm fatty acid was mixed with methanol at a specific molar ratio of 6:1-42:1 (methanol to purified palm oil) and 3:1-12:1 (methanol to fatty acid), respectively. The SO_4^{2-}/ZrO_2 catalyst was then added in the concentration range of 0-1 wt %. The reactor was then placed in the furnace heater which caused the temperature T_1 to drop by 4-5 °C. The system was allowed to heat up for 1-2 min until the set temperature T_1 was reached. After the set point temperature at T_1 was reached, the reaction temperature T_2, at the center of the reactor, was also measured. There was approximately 8-9 °C difference between the steady state temperature at T_1 and T_2, thus if the 300 °C set point temperatures, the actual reaction temperatures at T_2 was approximately 290 °C, which was reached to approximately 15 minute (heating time), at which point the reaction was allowed to continue for a period of 0–15 min.

After the reaction, the vessel was removed from the heater and placed into a water bath to stop the reaction. The reaction products were discharged from the reactor and were centrifuged, it formed three phases. The top phase was a mixture of methyl ester (biodiesel) and a small amount of unreacted methanol which was removed by evaporation, the middle phase was glycerol and/or water, and the lower phase was solid SO_4^{2-}/ZrO_2 catalyst. The obtained biodiesel was analyzed by gas chromatography (GC).

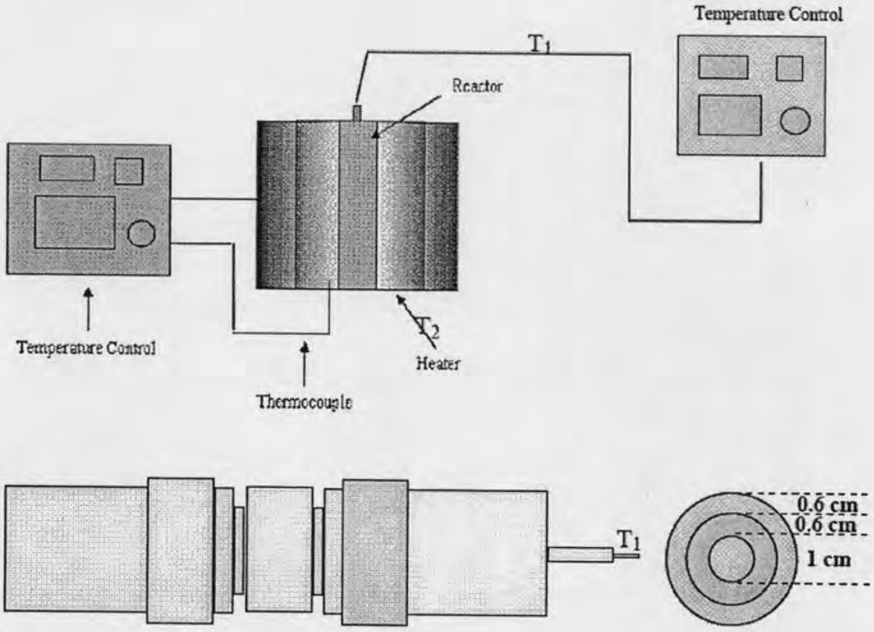

Figure 3.1 Schematic diagrams of apparatus for biodiesel production in supercritical methanol.

3.4 Methyl ester analysis

The fatty acid methyl esters (FAMEs) analysis was carried out using GC (Shimadzu 2010 model) with a flame ionization detector (FID) in which one microliter of the sample was injected into column. The GC consists of a capillary column (DB-WAX, Carbowax 20 M, 30 m, 0.32 mm ID, 0.25 μm). The injector, detector, and column temperatures were at 250, 260 and 200 °C respectively. Pressure was 64.1 kPa and linear velocity was 25 cm/sec. Thecarrier gas was helium (He) and the make-up gas was nitrogen (N_2). The samplewas prepared by adding 0.05 ml of FAMEs to 5 ml of n-hexane and methyl heptadecanoate was used as an internal standard. The methyl ester yield was estimated from the ratio of the quantity of FAMEs to that of the reactants (purified palm oil or palm fatty acids):

$$\%\ \text{yield of methyl ester} = \frac{W_{ME}}{W_F} \times 100 \qquad (3.1)$$

where W_{ME} and W_F are weights of methyl ester (g) and the feed reactant (g), purified palm oil or palm fatty acid, respectively.