# CHAPTER III

# MATERIALS AND METHOD

## 3.1 Chemicals

Palm fatty acid samples used in this study was provided by Burapha Munkong Co. Ltd, Thailand. Methyl ester standard (methyl palmitate, methyl stearate and methyl oleate) were obtained from Wako Chemicals, USA. Commercial grade methanol (95%) was purchased from Thailand and analytical grade hexane (99.9%) was from Fisher scientific, UK.

## 3.2 Experimental

### 3.2.1 Supercritical methanol esterification reaction in batch reactor

A batch type reactor was used for production of biodiesel from palm fatty acid in supercritical methanol. A schematic diagram of the system employed was shown in Figure 3.1, which consisted of an electric furnace and a 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 250-300 °C. The reactor was then charged with calculated amount of liquid methanol and palm fatty acid with a molar ratio of 1:1 to 1:12. The reactor was then placed in the furnace heater which caused the temperature $T_1$ to drop by 1-2 °C. The system was allowed to heat up for 1-2 min until the set temperature $T_1$ was reached, at which point the reaction was allowed to continue for a period of 10–80 min. After the set point temperature at $T_1$ was reached, the reaction temperature $T_2$, at the center of the reactor, was also measured and the temperature profile at $T_2$ is shown in Figure 3.2. There was approximately 8 °C difference between the steady state temperature at $T_1$ and $T_2$, thus for the 250 and 300 °C set point temperatures, the actual reaction temperatures at $T_2$ were 242 °C and 292 °C, which were reached in approximately 15 minute.

After each 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 allowed to settle and separate into three phases. The top phase was the unreacted methanol which was removed by evaporation. The remaining phases consisting of the upper phase and the lower phase were methyl ester (biodiesel) and water, from which the methyl ester product was drawn for GC analysis.

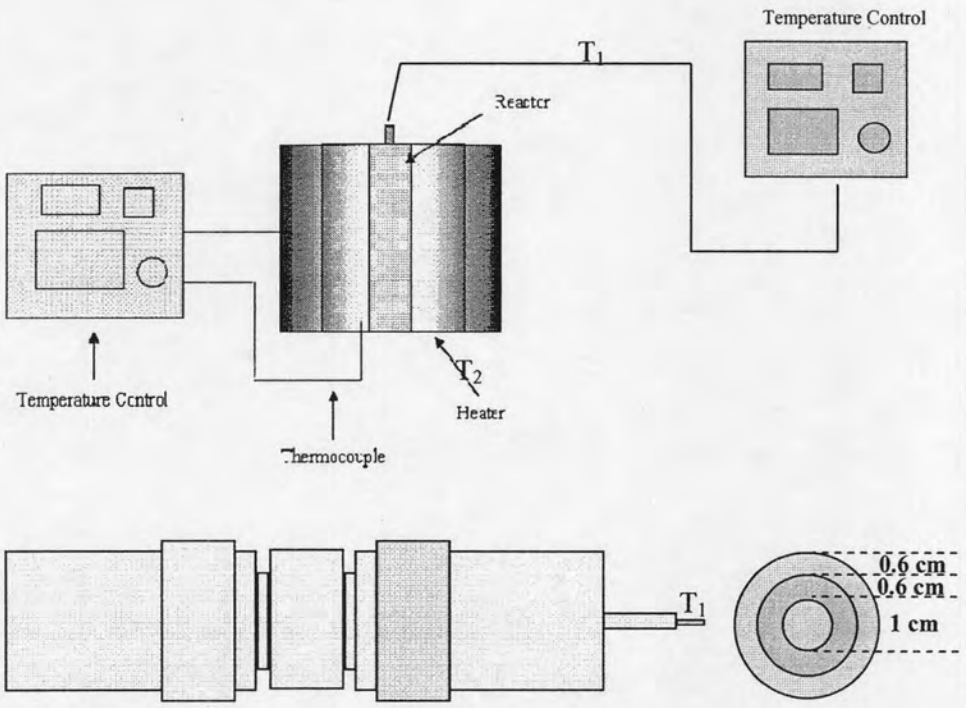


Figure. 3.1 Schematic diagram of apparatus for biodiesel production in supercritical methanol.

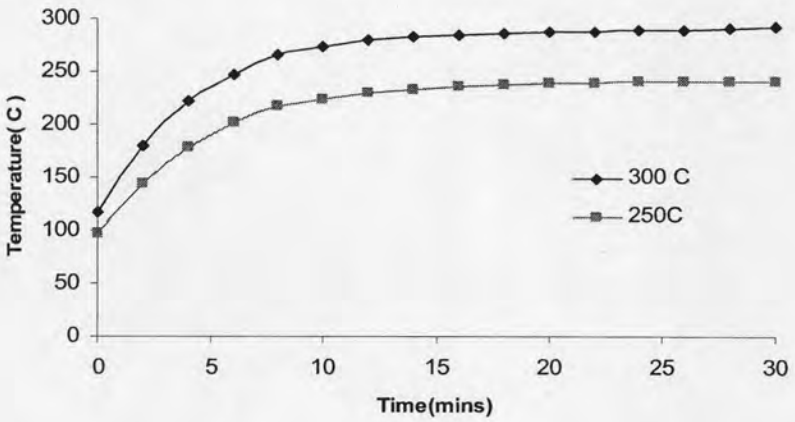


Figure. 3.1 Schematic diagram of apparatus for biodiesel production in supercritical methanol.

### 3.2.2 Conventional esterification in batch reactor

A batch type reactor was used for the conventional production of biodiesel from palm fatty acid in methanol. The schematic diagram of the system employed is shown in Figure 3.3. Palm fatty acid was first melted by heating at 60°C. The calculated weight of palm fatty acids and methanol at the specified molar ratio were charged into the vessel (1,000ml) connected with a condenser as shown in the figure 3.3. For the reaction, 100 g of free fatty acids and calculated amount of methanol at the molar ratio of 1:6 were charged into the reactor. The reaction mixture was then heated to 60 °C. Sulfuric acid was added to the reaction mixture of fatty acid and methanol at 5 wt % of palm fatty acid. The reaction was allowed to take place for a specified reaction time. Note that the addition of the acid caused the temperature to rise to 67 °C. After the reaction, the product was allowed to cool down and separated into three phases. The upper phase was the remaining methanol, the middle phase was methyl ester, and the third bottom phase was water. Water was first removed from the reaction product using a separatory funnel, and the remaining methanol was then removed by evaporation. The product was then neutralized by washing repeatedly with water in a separatory funnel and the remaining water was then removed by a rotary evaporator.

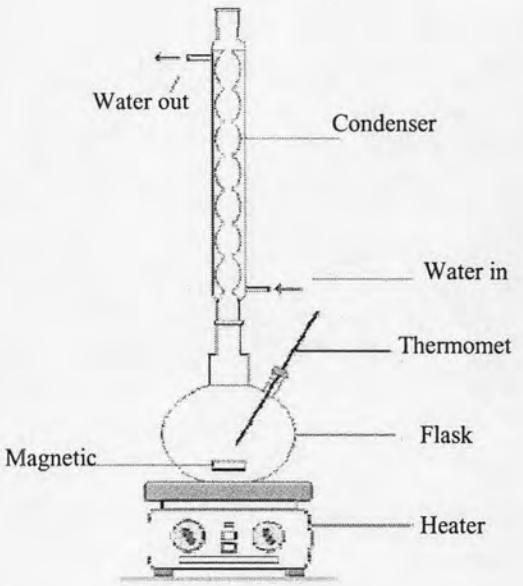


**Figure. 3.3** Schematic diagram of apparatus for acid catalyzed esterifiation.

### 3.2.3 Effect of water on methyl esterification of palm fatty acid

In order to investigate the effect of water on the methyl esterification of palm fatty acid, two sets of experiments will be conducted. In the first set of experiment, the effect of water content (between 0-30 water/fatty acid wt %), on the conversion of fatty acids would be determined at a selected conditions (temperatures, molar ratio methanol and palm fatty acid, and time of reaction), based on the results from experiment 3.2.1.

In the second set of experiment, hydrolysis of fatty acid ester by subcritical water would be investigated. In this experiment, the known amount of methyl fatty acid ester (produced from supercritical methyl esterification of palm fatty acids as described earlier) is hydrolyzed with distilled water at various percentage of water/methyl esters (0-30 wt%) for different reaction times (0-90 min) at the selected temperature based on the results from experiment 3.2.1. After the hydrolysis, the reaction product was analyzed for the concentration of the remaining methyl esters by gas chromatography.

### 3.3 Methyl ester analysis

Analysis of methyl ester in products was carried out using gas chromatography (GC) (Shimadzu 14B, USA) which consists of a column (Rtx 5, 30m, 0.25 mm ID, 0.25 μm) and flame ionization detector (FID). The parameters for the oven temperature was programmed to increase from 150 °C (2 min holding time), to 250 °C (5 min holding time) at the ramping rate of 5 °C/min. Sample were prepared by adding 0.1 ml of oil to 6 ml of n-hexane and ecosane was used an internal standard. Two micro liters of the sample were injected into column.