

CHAPTER III

EQUIPMENTS AND EXPERIMENTAL PROCEDURES

3.1. Effect of co-solvents

3.1.1. Equipments

First, the effect of co-solvents was studied in a 250-mL batch reactor (Parr Instrument Company, model 4576), equipped with a mechanical stirrer and internal cooling. The reactor was heated with an external electrical heater. The maximum pressure and temperature values of the equipment were 50 MPa and 500°C, respectively. The temperature of the reactor was measured with a j-type thermocouple and controlled at $\pm 5^\circ\text{C}$ for a set time. The pressure of the reactor was measured with a pressure gauge and transducer.

As the highest ME content obtained from the 250-mL reactor was slightly lower than expected, the effect of co-solvent was studied in a smaller batch tube reactor, whose dimension was 9.525 mm O.D., 0.213 mm thickness and 200 mm length. The total volume was 5.5 mL. The reactor was heated by immersion in a fluidized sand bath and the temperature was measured by a k-type thermocouple.

3.1.2. Materials

Crude palm kernel oil (PKO) was supplied by Chumporn Palm Oil Industry, PCL. The sample was warmed and filtered prior to use. Commercial grade methanol, hexane (mixture of C6 isomers containing more than 65% n-hexane) and tetrahydrofuran (THF) were used with no further purification. All standard methyl esters for gas chromatograph calibration and methyl undecanoate (internal standard) were supplied by Fluka. Analytical grade carbon disulfide (CS_2), which was used as a dilution solvent for the gas chromatograph, was supplied by Merck.

3.1.3. Experimental procedure

3.1.3.1. The 250-mL reactor

The reaction vessel was charged with a given amount of vegetable oil, methanol and co-solvent and was then heated to the desired temperature. The reaction time and stirring speed were fixed at 10 min and 500 rpm, respectively, for every experiment. At the end of the reaction, the reactor was quenched in an ice-water bath to about room temperature and pressure. The content in the reaction vessel was weighed and put in a

rotary evaporator to remove the solvent phase (co-solvent and methanol). The oil phase was left to settle for at least 8 hours in a separatory funnel to ensure complete separation. Two liquid phases were obtained; ester (top layer) and crude glycerol (bottom layer). The ester layer was then analyzed for ME content.

3.1.3.2. The 5.5-mL reactor

The reaction vessel was charged with a given amount of PKO, methanol and co-solvent and was immersed in a fluidized sand bath at the designed temperature and was shaken manually from time to time to ensure uniform mixing. The reaction time was held constant at 10 min. At the end of the reaction, the reactor was then quenched in an ice-water bath to stop the reaction. The solvent phase was then evaporated by warming in a water bath at 80°C for 2 hours. Glycerol was separated by centrifuging at 4000 rpm for 10 min. The ester (top layer) phase was then analyzed for %ME content.

3.1.4. Analysis of methyl esters

For the ME content measurement, a gas chromatograph (Varian Model CP-3800), equipped with a capillary column coated with polydimethylsiloxane (30 m x 0.25 mm x 0.25 μ m, DB-1, J&W Scientific) and an FID detector, was used with helium as carrier gas. The ester product and the known amount of internal standard was diluted with CS₂ before injection and standardized by the internal standard method. The temperature of the injection port and detector were 250°C and 280°C, respectively. The column oven was held at 110°C for 2 min and then raised to 260°C at 15°C/minute. The final temperature was held constant for 10 min.

The ME content was calculated from their content in the biodiesel product as analyzed by GC. The content (or purity) was defined as a ratio of the weight of methyl esters, as obtained from GC, to the total weight of the biodiesel product.

For the GC-MS analysis, a Shimadzu Model GCMS-QP2010 gas chromatograph coupled with a mass spectrometer and equipped with a capillary column coated with polydimethylsiloxane (30 m x 0.25 mm x 0.25 μ m, DB-1ms, J&W Scientific) was used with helium as carrier gas. The biodiesel sample was diluted in CS₂ before injection. The injection port, ion source and interface temperature were 250, 200 and 230°C, respectively. The molecular weight scan range was 50-800 m/z and 3 min of solvent cut time. The column was held at 90°C for 5 min and then raised to 260°C at 20°C/minute. The final temperature was held constant for 10 min.

3.2. Effect of additional parameters and scale-up reactor optimization

3.2.1. Equipments

3.2.1.1. The scale-up reactor

A coiled tubular reactor made from stainless steel (SUS316 tubing of 9.525 mm O.D., 0.138 mm-thickness) was employed. The reactor received oil/hexane mixture and methanol, preheated separately in a coiled preheater made from stainless steel (SUS316 tubing of 3.175 mm O.D., 0.094 mm thickness). Both reactor and preheater were immersed in a molten salt bath. The molten bath was electrically heated and controlled by a temperature controller (Sigma Model SF48). Temperature sensors were equipped at reactor inlet, molten salt bath and heater. The inlet was connected with a high pressure pump (Thar technology Model P-50 and P-200), while the outlet was connected to a cooling coiled tube immersed in a cooling bath. The outlet was equipped with a Tee type filter (140 μ m), a pressure sensor (Kyowa Electronic Instruments Model PGM-500KE) and a back pressure regulator (Go-regulator Model BP-66). The inlet pressure was monitored by high pressure pump software and outlet pressure was monitored by Hengstler Process Indicator Model 0735A60000. Complete experimental setup is shown in Figure 3.1.

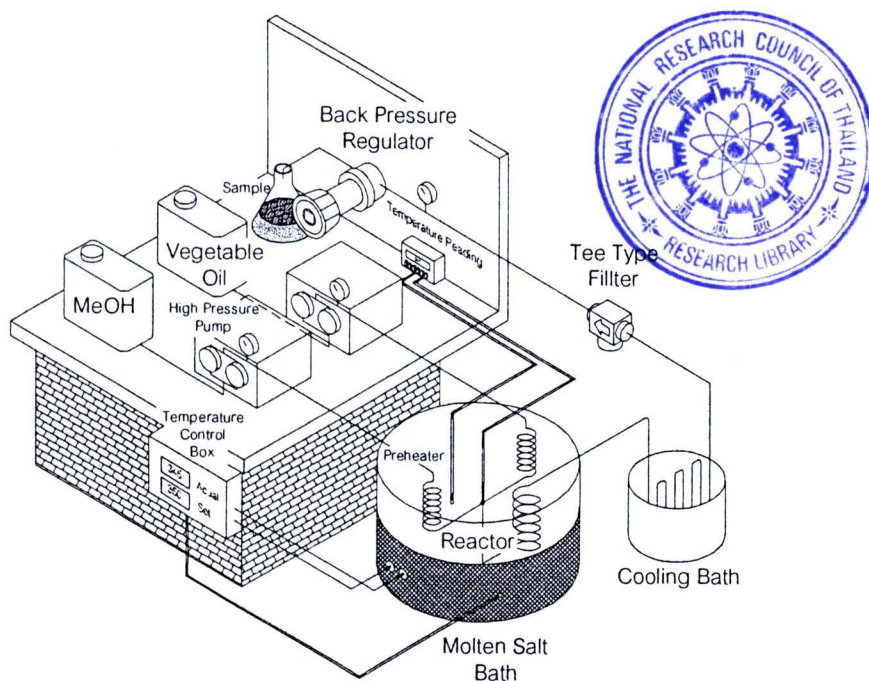


Figure 3.1 Schematic diagram of scale-up tubular reactor for biodiesel production with SCM.

3.2.1.2. The 250-mL and 5.5-mL reactors

The 250-mL and 5.5-mL batch reactors are described in section 3.1.1.

3.2.2. Materials

Palm kernel oil (PKO) sample was warmed and filtered prior to use. Commercial grade methanol and hexane (mixture of hexane isomers contain more than 65% of n-hexane) were used with no further purification. Standard mixture methyl esters that has composition refer to Lauric oil were supplied by Restek. A mixed molten salt consisted of NaNO_3 , NaNO_2 and KNO_3 (1:5:6 weight ratio) was used as a heating medium for both the preheaters and the reactor.

3.2.3. Experimental procedure

3.2.3.1. The scale-up reactor

The methanol and vegetable oil mass flow rate was measured by weighting method at the outlet high-pressure pumps before feeding the reactants into the reactor. The molten salt bath was first heated to designed temperature before feeding the reactants, after inlet and outlet flow rate were approximately equal; the back pressure regulator was then closed to increase the system pressure. When the system reached steady state, as noticed from a constant ME content over 90 min, the product was collected. The liquid product was weighed and put in a rotary evaporator to remove solvent phase. Oil phase was left to settle for several hours in a separatory funnel, preferably overnight, to ensure complete separation. Two liquid phases were obtained, ester (top layer) and crude glycerin (bottom layer). The ester layer was measured for %ME content.

3.2.3.2. The 250-mL and 5.5-mL reactor

The experimental procedure described in Section 3.1.3.1 and 3.1.3.2 were used to study the effect of reaction time on ME content, temperature gradient between reactor wall and bulk fluid and effect of contaminants in crude PKO.

3.2.3.3. The 5.5-mL reactor to investigate the effect of delay quenching time

The reaction vessel was charged with a given amount of methanol and palm kernel oil at molar ratio of 42:1 was immersed in a fluidized sand bath at 350°C and was shaken manually from time to time. The reaction time was held constant at 10 min The

reactor was then allowed to stand at ambient temperature for varying time then quenched in an ice-water bath. The samples were treated before analyzed employing the same method as described in section 3.1.3.2.

3.2.4. Analysis of methyl esters

The ME content in biodiesel samples were measured by employing the same method described in section 3.1.4.

3.3. Residence time estimation method

3.3.1. Equipments

A coiled tubular reactor (SUS316 tubing of 1/8 in.-o.d., 0.028 in.-thickness and 80 m-length) and two coiled preheaters (SUS316 tubing of 1/8 in.-o.d., 0.028 in.-thickness and 6 m-length) were employed. Both reactor and preheater were immersed in a molten salt bath. The k-type thermocouples were equipped at reactor inlet, outlet and molten salt bath. The inlet was connected with a high pressure pump, while the outlet was connected to cooling bath, an inline filter (0.50 μm), a pressure gauge (Swagelok PG5000) and a back pressure regulator (Go-regulator Model BP-66). The schematic diagram of the reactor is shown in Figure 3.2.

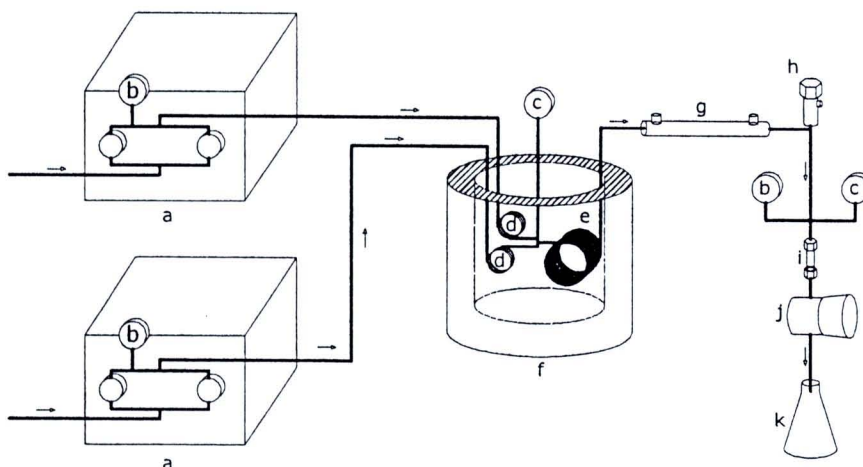


Figure 3.2 Schematic diagram of lab-scale tubular reactor (a) high pressure pump (b) pressure gauge (c) thermocouple (d) preheater (e) reactor (f) molten salt bath (g) double pipe heat exchanger (h) relief valve (i) back-pressure regulator (j) inline filter and (k) sampling flask.

3.3.2. Materials

Commercial grade methanol from I.C.P. Chemicals Co.,Ltd and palm olein oil (major fatty acids composition are palmitic acid 37 %, oleic acid 46 % and linoleic acid 11 %) from Morakot Industries Co., Ltd were used with no further purification. The analytical grade methyl heptadecanoate (99.5 %) and n-heptane (99.5 %) for measurement of ME content in biodiesel were supplied by Fluka and Fisher, respectively.

3.3.3. Experimental procedure

A molten salt bath heated to the reacting temperature was used for temperature control and methanol and vegetable oil mass flow rate was measured by weighting method at the outlet high-pressure pumps before feeding the reactants into the reactor. After temperature stabilization of the bath, palm olein oil and methanol, separately preheated in tubular preheaters made from stainless steel (SUS316 tubing of 1/8-in.-o.d., 0.028-in. thickness and 6 m-length), were pumped into the reactor. Both reactor and preheaters were immersed in a molten salt bath. The K-type thermocouples were set at reactor inlet, outlet and molten salt bath. After the outlet flow was steady, the back pressure regulator was closed to increase the pressure of the system. After system pressure was constant, approximately 3 hours generally required for the system to reach a steady state, three biodiesel products were then sampled at 15 min intervals and analyzed for ME content following the EN14103 standard method.

3.3.4. Analysis of methyl esters

The ME content was measured by EN14103 standard method using Shimadzu Model GC-14B SPL gas chromatograph equipped with auto injector model AOC-17 and DB-WAX capillary column (30 m length, 0.25 mm i.d. and 0.25 μ m thickness) from J&W Scientific. The temperature of the injection port and detector were 250 °C and 300 °C, respectively. The column oven was held at 120 °C for 2 min and then raised to 260 °C at 10 °C/minute. The final temperature was held constant for 5 min.