CHAPTER 3

EXPERIMENTAL METHODS

3.1 Input Material

The input materials used in this study are palm oil and methanol as shown in Table 3.1.

Table 3.1 Input materials

Name	Supplier	Description
Palm oil	Morakot Industry Co.Ltd.	Refined palm olein from pericarp contains 0.0075% butylated hydroxytoluene (BHT) as antioxidant. Edible oil, packed in 1 liter plastic bottle.
Methanol	O.V. Chemical &Supply Co.Ltd.	99.8% purified industrial grade

3.2 Experimental Set up

Cylinder Reactor

A cylinder reactor, as shown in Fig.3.1, was designed and contructed. Details of the design and construction can be found in a literature of Jaipayul (2007). The reactor consisted of a high pressure vessel (1) connected with a pressure gauge (6), a nozzle (7) and pipes (9). The vessel was a 400 ml high pressure vessel, batch type, made of St 35 seamless steel pipe. The vessel structure and the St 35 specifications are given in Fig.3.2 and Table 3.1, respectively. The vessel was heated in an oven (2) with a 2 kW electrical heater (3). Temperature was controlled by a heater-controller (4) and a thermocouple (5). The pressure gauge (6) was the 70547H-51102 Yanma diesel injector tester pressure gauge. The nozzle (7) was the 4JA1 Isuzu diesel fuel injector and used as a sample releasing valve. When the vessel pressure was over the nozzle limit, the nozzle valve then opened and sample could be released and kept in the cylindrical container (8) and the bottle container (13). Photographs of the experimental set up are in Appendix D.

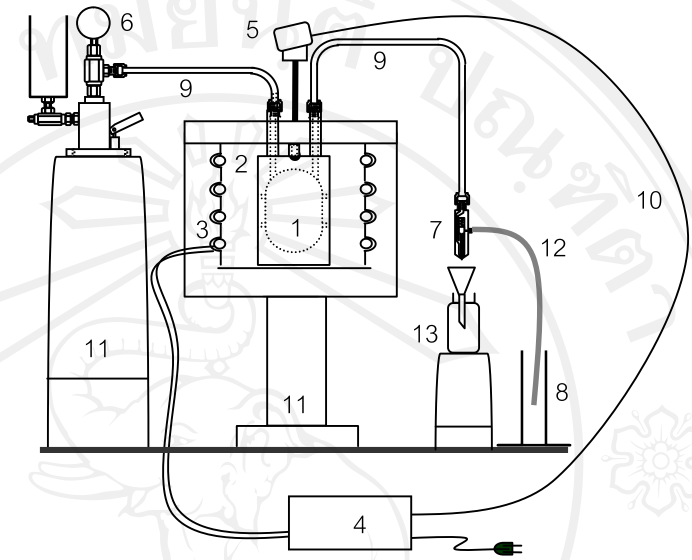

Fig.3.1 Cylinder reactor

1. high pressure vessel, 2.oven, 3.electrical heater, 4.heater-controller, 5.thermocouple, 6.pressure gauge, 7.nozzle, 8.cylindrical container, 9. pipe, 10. signal wire, 11. stand, 12. sample tube, 13. bottle container

Table 3.2 Specification of the St 35 Seamless Steel Pipe

% Carbon:	0.18
Ultimate strength:	340-440 kg/mm^2
tensile strength:	235 kg/mm^2
Equivalent material:	ASTM A53-S

High Pressure Vessel

The high pressure vessel as shown in Fig. 3.2 had a cylindrical body with two necks. The body had 100 mm outside diameter, 180 mm height and 400 ml capacity. The internal space was a capsule shape. The neck had 105 mm height, 13.0 ml outside diameter, and 4.0 mm wall thickness. The male connectors attached on the top of the necks were those used in a standard diesel fuel system. The thermocouple port was at the top of the body. A photograph of the high pressure vessel is in Appendix D

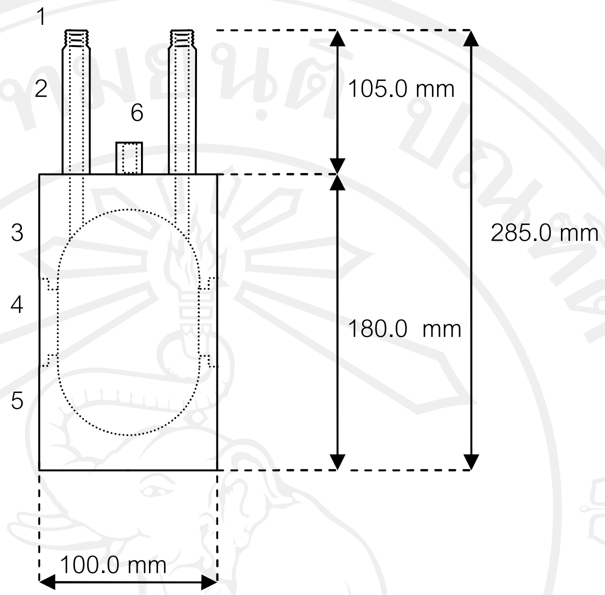

Fig. 3.2. High Pressure Vessel 1. male connector, 2. neck, 3.upper part of body, 4. middle part of body, 5. lower part of body, 6. thermocouple holder.

Nozzle

The nozzle as shown in Fig. 3.3 had a needle which pushed against the main gate by the spring force. When the sample pressure was over the spring pressure, the needle was then lifted up and the sample was released through the main gate. The excessive sample then went back into nozzle chamber to lubricate the needle and the spring before released through the return pipe. Table 3.2 shows the nozzle specification.

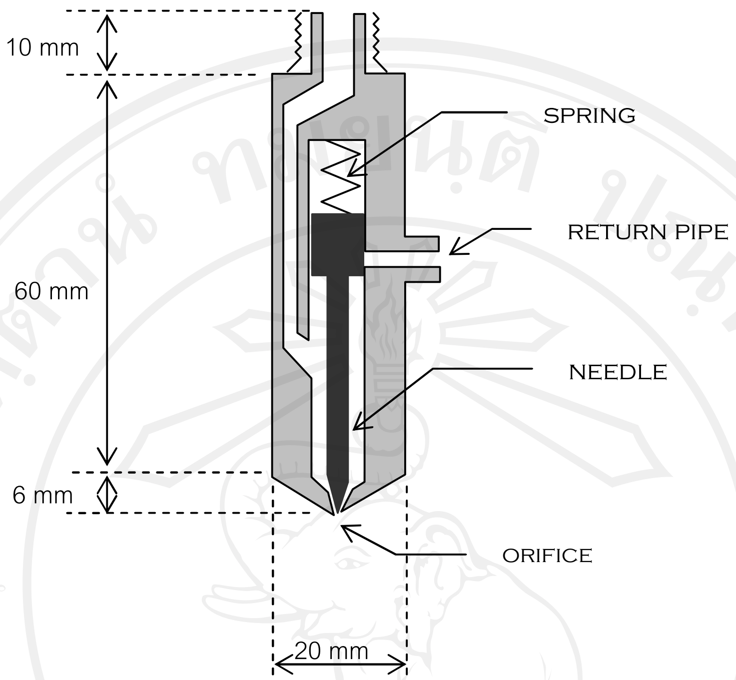

Fig.3.3 Nozzle

Table 3.3 Nozzle Specification

Injection type: high pressure solid, single spring, hole with 4 orifices
Injection opening pressure : 185 kg/cm^2 (2631 psi , 18.143 MPa)
Holder model : 48-3230H
Engine model application : 4JA1 Isuzu, 2500 CC, direct injection,

3.3 Experimental Procedure

Two experimental programs were carried out; methanolysis of palm oil and kinetic of reaction

3.3.2 Methanolysis of Palm Oil

The methanolysis of palm oil were divided into two parts; 1) Temperature survey tests and 2) Fixed temperature tests. Both parts carried out in the cylinder reactor. The reactor was modified so that product will not be released during the running of the process, but it remained in the reactor for cooling down to the room temperature in several hours. Samples were analyzed by gas chromatography-mass spectrometry (GC-MS) and biodiesel yields were reported.

Temperature Survey Tests

Five tests were carried out at molar ratio of methanol-to-oil 43:1, at various temperatures and holding time as listed in Table 3.4. The aim was to find the most suitable condition that gave maximum biodiesel yield.

Table 3.4 Methanolysis Temperature Survey Tests

Temperature	Holding time	molar ratio of methanol-to-oil
150 °C	55 min	43:1
300 °C	10 min	43:1
300 °C	35 min	43:1
350 °C	35 min	43:1
400 °C	35 min	43:1

Input materials (methanol and palm oil) were loaded into the vessel of the cylinder reactor. The volumes of materials used for each test were 64 ml methanol and 36 ml palm oil. It equivalented with 43:1 molar ratio of methanol-to-oil. After that, the reactor was heated. The temperature rose from room temperature to the target temperature and be held at this temperature in accordance with the holding time, before cooled down to the room temperature. Pressure and temperature evolutions were recorded every 10 minutes. After cooling, the product was removed for further analysis by gas chromatography-mass spectrometry. The biodiesel yield was reported in terms of percentage yield based on peak area.

Fixed Temperature Tests

To evaluate the effect of molar ratio of methanol-to-oil and holding time on the biodiesel yield, at a determined temperature which gave the highest yield from the previous survey tests.

Three molar ratios of methanol-to-oil, 8:1, 22:1, and 42:1, were studied. In each run the reactor temperatures were increased from room temperature to a specified one, with a holding time of 0 min, 10 min, 35 min, 70 min and 105 min. After that the reactor then was cooled down to the room temperature. The products were analyzed using gas chromatography-mass spectrometry. Biodiesel yield was reported in terms of percentage yield based on peak area. The most suitable holding time of each molar ratio was determined.

3.3.3 Kinetics of Reaction

This was the most important part of the study. The aim was to determine the reaction rates and activation energies of palm oil methanolysis under the allow ability condition that the reactor could provide. The cylinder reactor was used. Real-time samples (samples that collected during the runs) were collected and analyzed by GC-MS. Data from analysis were used for the calculation of apparent reaction rates and activation energies.

Kinetics Modeling

To perform kinetics modeling of methanolysis, 22 real-time samples were collected from two representative tests at the condition described in Table 3.5. All samples were analyzed by gas chromatography mass spectrometry . The analysis data was reported in terms of methyl esters fraction (x). Reactor temperature and pressure evolutions were periodically recorded. Relationship of the methyl esters fraction (x) and reaction time (t) was determined. The reactor temperature (T) as function of time (t) was also determined.

Table 3.5 Test Condition for the Kinetics Modeling

Test condition	Test 1	Test 2
Molar ratio (methanol:oil)	43:1	43:1
Volume ratio (methanol:oil)	256 ml : 144 ml	256 ml : 144 ml
Temperature range	146-209°C	146-209°C
Pressure range	140-190 atm	140-190 atm
Test period	40 min	40 min
Sampling period	20 min	20 min

Kinetics modeling was carried out using the previous information. The aims were to calculate: 1) the apparent rate constants at various temperatures, 2) the activation energy and the pre-exponential factor according to the Arrhenius equation, and 3) the reaction rate. Two different models were used in the calculations as

- Zero order model: $r = kC_{TG}^{m}C_{MeOH}^{n}$, when, m=n=0

- First order model: $r = kC_{TG}^{m}C_{MeOH}^{n}$,when, m=1, n=0

Results of the calculations were compared with those reported in the literature.

3.4 Sample Analysis

Sample analysis was an important tool for evaluation of the biodiesel yield and the methyl ester fraction (x). Two techniques were used in this study; thin-layer chromatography (TLC) and gas chromatography (GC). The GC gave more reliable result than that of the TLC but the cost of GC is rather expensive. Detail of each technique is described.

Thin-layer Chromatography

Thin-layer chromatography is a technique of sample analysis. The TLC alumimum sheets Siliga gel 60 F_{254}, as described in Table 3.6, is cut from the original size (20x20 cm^2) into a usable size (3x7 cm^2) as in Fig.3.4. After spotting with a sample, the TLC plate is then placed into a solvent tank, Fig.3.5, which containing a mixture of three agents as shown in Table 3.7.

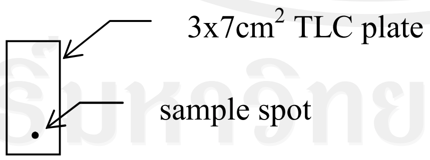

Fig.3.4 TLC Plate Cut into 3x7 cm^2.

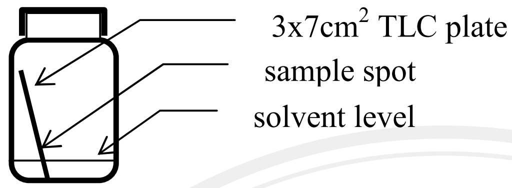

Fig.3.5 Solvent Tank

Table 3.6 TLC Plate Details

Plate Material:	Aluminum sheet
Adsorbent Material:	Silica gel (SiO_2) : Partical size range : 60-200 micron (70-230 mesh ASTM)
Available at :	Merck Company, Germany Product Name: TLC alumimum sheets Siliga gel 60 F_{254} Original size: 20 x 20 cm^2

Table 3.7 Solvent Mixture

Agent	Fraction by volume
n-heptane	90
Ethyl acetate	10
Acetic acid	1

Gas Chromatography

To quantify the methyl esters fraction in samples, gas chromatography is used. It is Hewllet Packard GC-MS model 53-973 gas chromatograph-mass spectrometer. Column and condition of analysis are shown in Table 3.12.

Table 3.8 Column and GC-MS Condition

Column : AT-1MS (100% dimethylpolysiloxane), 30 m x 0.25 mm x 0.25 µm
MS Quadrupole & MS Source Temperature : 150 & 230 °C Injector Temperature: 250 °C
Oven Temperature Program: 130 °C on initial, hold 2 min, 200 °C (5 °C/min) 250 °C (10 °C/min), hold 10 min
Carrier gas: Helium (1.0 ml/min)