CHAPTER III
EXPERIMENTAL

3.1 Materials

3.1.1 Chemicals

All chemicals used in the experiment are shown in Table 3.1. They were used without further purification.

Table 3.1 Chemicals used in the research

Name	Source	Purity
Acetonitrile	Lab-Scan	HPLC grade
Calcium Hydroxide	Lab-Scan	96.0% (AR)
Calcium Oxide	Lab-Scan	96.0% (AR)
Diglycerol Standard	Solvay	90.0% (purified)
Glycerol	BDH	99.5% (purified)
Magnesium Oxide	Lab-Scan	96.0% (AR)
Polyglycerol Standard	Solvay	15-30% diglycerol, 35-55% triglycerol,10-25% tetraglycerol, 10% pentaglycerol, 5% higher oligomer
Potassium Hydroxide	Lab-Scan	85.0% (AR)
Sodium Hydroxide	EKA chemical	99.0 % (AR)
Zirconium Oxide	Riedel-deHaen	pure

3.2 Equipment

3.2.1 Reactor

A 500-ml three-necked flask equipped with a reflux condenser, a thermocouple and a sampling port was used in the experiment. The flask was immersed in oil bath with heater. The nitrogen gas passed the reactor to purge air from system. The magnetic stirrer was used to provide agitation. The experimental set-up is shown in Figure 3.1.

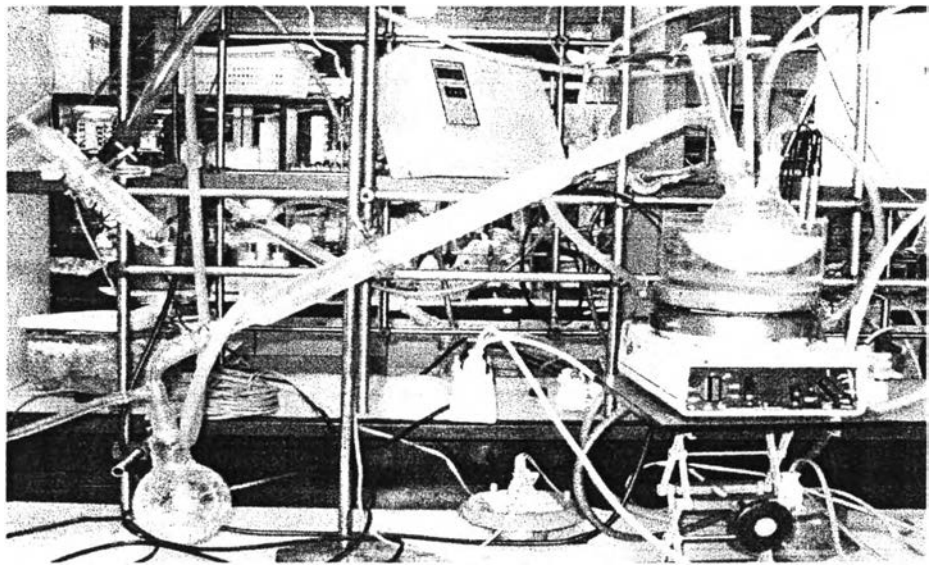

Figure 3.1 Experimental set-up used for synthesis polyglycerols.

3.2.2 High Performance Liquid Chromatography (HPLC)

The Perkin Elmer Series 200 high pressure liquid chromatography was used to analyze polyglycerols samples. The column used was PL-SCX column (4.6 mm x 150 mm x 8μm) with refractive index detector. The mobile phase was acetonitrile/water mixture (90:10 vol/vol) at a flowrate 0.5 ml/min. The column temperature used was at room temperature. The pump pressure was used operated in the range of 300 to 600 psi. Samples were diluted with mobile phase (1 g sample in 100 ml) and the injection volume was 20 μl.

3.2.3 Brookfield Viscometer

The viscosities of polyglycerols were measured by Brookfield Digital Rheometer Model DV- III. Temperature was controlled by water bath temperature. Spindle 21 was used to measured viscosity of polyglycerols.

3.3 Methodology

3.3.1 Polymerization of Glycerol Using Homogeneous Catalysts

One hundred grams of glycerol was weighed and placed in a 3-neck round bottom flask. The flask was moved in oil bath and then heated at temperature 150°C under nitrogen atmosphere. After 30 minutes, the desired amount of catalyst was weighed and mixed with glycerol in the reactor. The reaction was carried out until it reached the desired reaction time. The reactor was then cooled down to room temperature. Both heating and cooling times of the reactor were less than 30 minutes.

The homogeneous catalysts were sodium hydroxide, potassium hydroxide and calcium hydroxide. The polymerization reactions were studied by fixing the reaction temperature 250 °C for 4 hours under nitrogen atmosphere and stirrer speed of 500 rpm. The conditions used are shown in Tables 3.2. Parameters such as amount of catalyst, reaction time, and reaction temperature were examined. The conditions used are listed in Table 3.3, Table 3.4 and Table 3.5.

3.3.2 Polymerization of Glycerol Using Heterogeneous Catalysts

The investigation of heterogeneous catalysts was done by fixing the reaction temperature at 250 °C, for 4 hours under nitrogen atmosphere and speed 500 rpm. The conditions used are shown in Tables 3.2. The heterogeneous catalysts were zirconium oxide, magnesium oxide and calcium oxide. The catalysts were studied further in the effect of the amount of catalyst, reaction time and reaction temperature. The conditions used are listed in Table 3.3, Table 3.4 and Table 3.5.

Table 3.2 Condition used for types of catalyst (250 °C, 4 h)

Experiment No.	Catalyst	Amount of Catalyst (% mole catalyst)
1	None	2.5
2	NaOH	2.5
3	$Ca(OH)_2$	2.5
4	KOH	2.5
5	ZrO_2	2.5
6	ZnO	2.5
7	MgO	2.5
8	CaO	2.5

Table 3.3 Condition used for amount of catalyst (250 °C, 4 h)

Experiment No.	Amount of Catalyst (% mole catalyst)
9	0.0
10	0.5
11	1.0
12	2.0
13	2.5
14	3.0
15	4.0
16	6.0
17	10.0

Table 3.4 Condition used for reaction time (2.5 mol% catalyst, 250 °C)

Experiment No.	Reaction time (h)
18	2
19	4
20	6
21	8

Table 3.5 Condition used for reaction temperature (2.5 mol% catalyst, 4 h)

Experiment No.	Reaction temperature (°C)
22	200
23	220
24	240
25	260

3.3.3 Polglycerols Analysis

Analysis of the products were performed by high-performance 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). PL-SCX column (4.6 mm x 150 mm x 8μm) was used and the mobile phase was acetonitrile/water mixture (90:10 vol/ vol) at a flowrate of 0.5 ml/min. The column temperature used was at ambient temperature (27°C). The pump pressure was operated in the range of 300 to 600 psi. The polyglycerols samples were diluted with acetonitrile/water mixture (90:10 vol/ vol) and the injection volume was 20 μl.

The amount of glycerol and diglycerol were quantified by comparing the RID signal for each glycerol and diglyceorl of the HPLC chromatogram of polyglycerols product with the RID signal of each glycrol and diglycerol standard. In order to see the purity of product samples, the glycerol conversion is defined as

following. In the first step, the weight of glycerol used calculated from the approximately one gram of sample (from experimental part) subtract with the remaining of glycerol that calculate from HPLC chromatogram (from peak area convert to amount of glycerol in grams). This value takes to calculate glycerol conversion following with equation 3.1.

$$\text{Glycerol conversion (wt\%)} = \frac{\text{Weight of glycerol used}}{\text{Weight of sample (approximately one gram)}} \times 100 \qquad (3.1)$$

Next step, the weight of diglycerol (calculate by convert peak area of HPLC chromatogram to the amount of diglycerol in gram), the weight of the sample (approximately one gram) and the weight of product (except remaining glycerol) that calculate from the HPLC chromatogram of product which were used to calculate diglycerol selectivity and diglycerol yield following equation 3.2 and 3.3.

$$\text{Diglycerol selctivity (wt\%)} = \frac{\text{Weight of diglycerol}}{\text{Weight of product (except remaining glycerol)}} \times 100 \qquad (3.2)$$

$$\text{Diglycerol yield (wt\%)} = \frac{\text{Weight of diglycerol}}{\text{Weight of sample (approximately one gram)}} \times 100 \qquad (3.3)$$

3.3.4 Viscosities of Polyglycerols Products

Viscosities of glycerol, diglycerol, and polyglycerols standard were measured based on density at 60°C by Brookfield viscometer.