CHAPTER III
EXPERIMENTAL

3.1 Materials

The catalyst used in this research is calcium oxide (96.0% (AR)) was obtained from UNILAB.The etherification of glycerol has been carried out using glycerol bidistilled (99.5% W/V) from BDH .And the esterification process, triglycerol purchased from Sigma-Aldrich was used to represented polycerol from the etherification step react with oleic acid (maximum limit of impurities) from Panreac.

3.2 Equipment

3.2.1 Reactor

A 250-ml three-necked flask equipped with a reflux condenser, a thermometer and a sampling port was used in the experiment. The custom made furnace to fit with the three-necked flask was used to supply heat and the temperature was digitally controlledby a temperature controller equipped with a thermo couple. The nitrogen gas was continuously purged the system to provide the inert atmosphere during reaction and to carry the water that is form during the raction out from the reaction. The magnetic stirrer was used to provide agitation. The experimental set-up was shown in Figure 3.1

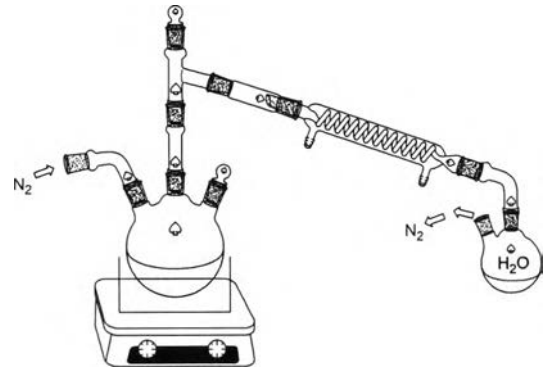
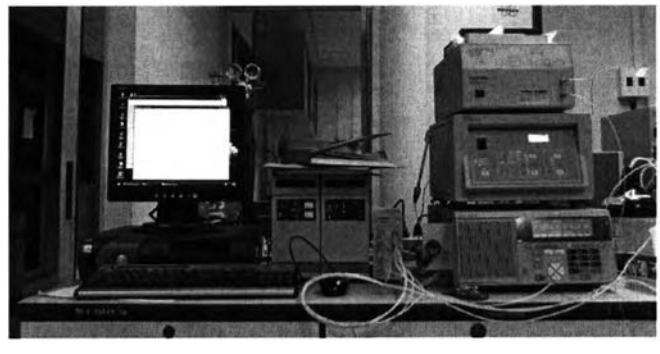


Figure 3.1 Experimental set-up used for synthesis polyglycerols.

3.2.2 High Performance Liquid Chromatography (HPLC)

The Perkin Elmer Series 200 high pressure liquid chromatography with refractive index Series 200 detector was used to analyze diglycerol product samples. The chromatographic column was ZORBAX SAX (4.6 mm×150 mm×5 μm). The mobile phase was acetonitrile/water mixture (80:20 vol/vol) at a flow rate 1.0 ml/min.The SHIMADZU LC-20 AD high pressure liquid chromatography with SHIMADZU SPD-20A uv/vis detector was used to analyze polyglycerol ester product samples. The chromatographic columns were2 LiChrospher 100 Diol (4 mm×250 mm×5 μm) in series.The mobile phase is a mixture of 2-propanol-water (60:40, v/v) at a flow rate 0.2 ml/min. and 40°C. High Performance Liquid Chromatography (HPLC) were shown in Figure 3.2

(a)



(b)

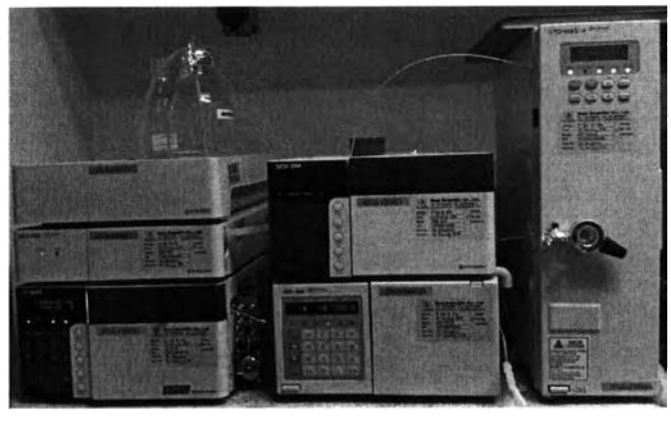


Figure 3.2 High Performance Liquid Chromatography (HPLC).(a)The Perkin Elmer Series 200 HPLC;(b)The SHIMADZU LC-20 AD HPLC.

3.2.3 Viscosity Meter

The Brookfield viscosity meter, Model DV-III was used to analyze viscosity of polyglycerol ester product samples with spindle no. 27.

3.3 Methodology

3.3.1 Polyglycerol Synthesis

50.0 g of glycerol is weighed and placed in a 3-neck round bottom flask. The flask is then heated to temperature of 150°C under nitrogen atmosphere. After 30 minutes, the flask is heated to temperature of 240°C and 2.0 g of catalyst and mixes with glycerol in the reactor. The investigation of heterogeneous catalysts is done under nitrogen atmosphere and stirrer speed is set to 500 rpm. The reaction is carried out until it reaches the desired reaction time. The reactor is then cooled down to room temperature. The catalysts are studied in the effect of the reaction time (1, 2, 3, 4, 5 hrs).

3.3.2 Polyglycerol analysis

Analysis of the products is performed by using high-performance liquid chromatography (HPLC), a Perkin Elmer Series 200 LC-pump and a refractive index Series 200 detector. The system is controlled by a computer with a software package (Perkin Elmer Turbochrom Navigator). ZORBAX SAX column (4.6 mm×150 mm×5 μm)is used and the mobile phase is acetonitrile/water mixture (4:1 vol/vol) ata flow rate 1.0 ml/min. The column temperature is at ambient temperature of 27°C. The pump pressure is operated in the range of 300 to 600 psi. The polyglycerols samples are diluted with water and the injection volume was 20 μl.

The amount of glycerol and diglycerol are quantified by comparing the RID signal for each glycerol and diglycerol of the HPLC chromatogram of polyglycerols product with the RID signal of each glycerol and diglycerol standard.

The glycerol conversion is defined as shown in Equation (3.1). In the first step, the weight of glycerol used is calculated from the approximately 50.0 g of sample (from experimental part) subtract with the remaining of glycerol that is obtain from HPLC chromatogram (convert peak area to amount of glycerol in grams).

$$\text{Glycerol conversion (wt \%)} = \frac{\text{Weight of glycerol used}}{\text{Weight of starting glycerol}} \times 100 \quad (3.1)$$

The selectivity is defined as a ratio of weight of each component, which was determined by using HPLC, to weight of product (except remaining glycerol) as shown in Equation (3.2).

$$\text{Selectivity of each component (wt \%)} = \frac{\text{Weight of each component}}{\text{Weight of product}} \times 100 \quad (3.2)$$

3.3.3 Polyglycerol Purification

The synthesised polyglycerol is diluted with by the distilled water of 50wt.%, and then centifuged at 12,000 rpm for 20 minutes to separate the used catalysts at the frist step. The remaining must be filter by PTFE membrane filters, 47 mm, 0.45 μm. The unreatced glyceol and water can be separated by vaccum distillation.

3.3.4Polyglycerol Esters Synthesis

Polyglycerol that was prepared in the previous process is used to mix with fatty acid in reactor under nitrogen atmosphere and stirrer speed of 500 rpm for 3 hours. The reaction is carried out until it reaches the desired reaction time. The reactor is then cooled down to room temperature. The productsare studied in the dependence of the reaction temperature and fatty acid:polyglycerol molar ration

3.3.5Polyglycerol Esters Analysis

Analysis of the products is performed by using high-performance liquid chromatography (HPLC),SHIMADZU LC-20 AD was used to analyze polyglycerol ester product samples. The chromatographic column were 2LiChrospher 100 Diol (4 mm×250 mm×5 μm) in series. The mobile phase are methanol and a mixture of 2-propanol-water (60:40, v/v) at a flow rate 0.2 ml/min. The column temperature is at temperature of 40°C. The polyglycerols samples are diluted with 2-propanol-water (85:15, v/v) and the injection volume was 20 μl.The

viscosity of products was analyzed by viscosity meter, BROOKFIELD MODEL DV-III.