CHAPTER IV

RESULTS AND DISCUSSION

Generally, the preparation of polyglycerols from glycerol can be carried out in the presence of homogeneous catalysts, such as NaOH. The catalyst can increase the rate of reaction and results in the products containing diglycerol, triglycerol, higher degree of glycerol oligomers and also unreacted glycerol. However, there are several advantages from using homogeneous catalysts, for examples, the downstreams catalysts separation and product selectivity. The product is required further processes to separate impurities and catalysts. The use of heterogeneous or solid catalysts can possibly avoid these drawbacks. It has been report that, at high temperature, high conversion of higher polyglycerols can be obtained by using alkali oxide (Robert *et al.*, 1998). The use of solid catalysts have several advantages such as ease of catalysts and products separation, reuse and recycle which result in lower production cost and safer environments.

4.1 Effect of Catalyst in Glycerol Dimerization

In this study, the catalytic activities of some heterogeneous catalysts were compared with homogeneous catalysts in terms of total glycerol conversion, diglycerol selectivity, and diglycerol yield. The representative of homogeneous catalysts were NaOH, KOH and $Ca(OH)_2$, while the heterogeneous catalysts were CaO, MgO, and ZrO_2. The reaction temperature and time were fixed at 250°C and 4 hours. After polymerization of glycerol, the products are the mixtures of glycerol, diglycerol, triglycerol, higher glycerol oligomers and catalysts.

To evaluate the catalytic activity, the catalysts were tested for the polymerization of glycerol. The experimental conditions were set as following. The amount of catalyst used is 2.5 mol% at the reaction temperature 250 °C, under inert nitrogen atmosphere, pressure = 500 mmHg. The reactions time was 4 hours and the mixture was stirred by a stirrer at speed 500 rpm The HPLC chromatograms of the

polyglycerols products obtained from these experiments are shown in Appendix A. The summarized results are showed in Table 4.1.

Table 4.1 Glycerol conversion, diglycerol selectivity and yield from homogeneous and heterogeneous catalytic polymerization of glycerol

No.	Catalyst	Glycerol Conversion (wt%)	Diglycerol Selectivity (wt%)	Diglycerol Yield (wt%)
1	-	5.7	25.4	1.4
2	KOH	71.1	43.7	31.1
3	NaOH	65.5	52.4	34.3
4	$Ca(OH)_2$	22.3	67.3	15.0
5	ZrO_2	55.7	36.8	20.5
6	CaO	37.7	70.5	26.6
7	MgO	9.9	73.9	7.3

As shown in Table 4.1, the conversion of glycerol and yield of diglycerol from the blank test (run no.1) are relatively low even though it is performed at high temperature (250 °C) and sufficient reaction time (4 hours). However, when the catalysts are added, the conversion of glycerol and yield of diglycerol are significantly increased. This indicates that the catalysts considerably affect the conversion of glycerol.

Among the tested homogeneous catalyst, KOH exhibited the highest conversion of glycerol at 71.1% and diglycerol yield at 31.1%. However, the yield of diglycerol if NaOH is used is the highest (34.3%). For $Ca(OH)_2$, the yield of diglycerol of 15% is obtained.. In the case of homogeneous catalysts, $Ca(OH)_2$ gave the lowest amount of diglycerol whereas NaOH give the highest amount of diglycerol. Therefore, NaOH was selected for further study to compare with the heterogeneous catalyst. .

The preliminary results from solid catalysts indicated that solid catalysts such as CaO can be used for making di-glycerol from glycerol with high selectivity.

Without optimization, the diglycerol selectivity of 70.5% is obtained if CaO is used as a catalyst, but the yield of diglycerol is obtained about 26.6%. For the zirconium oxide, it is also active (55.7% conversion), however, it is possible that acrolein is also formed from the dehydration of glycerol. Among the tested solid catalysts, MgO gives the lowest conversion and diglycerol yield.

Many of the investigated solid catalysts show high potential to be used as the heterogeneous catalysts for the dimerization of glycerol. Although they give a little lower amount of diglycerol when compare to homogeneous catalyst, catalyst separation step will be simplified when heterogeneous catalyst is used. They could replace the homogeneous catalyst in the polymerization of glycerol. Among the tested solid catalysts, it is found that zirconium oxide catalyst is the most active, but less selective solid catalyst. Magnesium oxide catalyst is not very active, but quite selective. Nevertheless, these catalysts were not studied further because they favored the formation an undesirable by-products such as acrolein which is mainly obtained by double dehydration of glycerol. Since the calcium oxide shows good activity and selectivity for the diglylcerol synthesis, it is selected for further study

4.1.1 Potassium Hydroxide

William (1949) patented potassium hydroxide as one of the homogeneous catalyst for the production of polyglycerols from glycerol. Therefore, potassium oxide was used in this study. The results showed that the conversion of glycerol is high as compared to the other catalyst studied..

4.1.2 Sodium Hydroxide

Sodium hydroxide is known to be an effective catalyst for condensation reaction of glycerol (Benjamin, 1941 and William et al., 1949). It was confirmed in this study that NaOH has the potential to catalyze the reaction having the highest diglycerol yield (34.3%) when compared to the other tested catalysts.

4.1.3 Calcium Hydroxide

Calcium hydroxide was used to compare with potassium or sodium hydroxide for the dimerization of glycerol. It was suggested that, by using calcium

hydroxide, the formation of cyclic polyglycerols is greatly reduced (Lemke, 2003). In this work, the $Ca(OH)_2$ gave high selectivity of diglycerol (67.3%) but the conversion is low when compared to the other hydroxide.

4.1.4 Zirconium Oxide

Zirconium (ZrO_2) catalyst possesses both acidic and basic properties. It has been used in several chemical reactions, such as hydrogenation, esterification, and etc. In this study, ZrO_2 exhibits the lowest catalytic activity because it gives the lowest glycerol conversion and diglycerol yield when compare to the other studied catalysts. It can catalyze the conversion of glycerol to 55.7% with 36.8% selectivity of diglycerol, and the diglycerol yield only 20.5%.

4.1.5 Calcium Oxide

Calcium oxide is utilized to prepare diglycerol by reaction between glycerol, calcium oxide and carbon dioxide by Wright (1946). From the condensation results, it can catalyze the reaction to yield diglycerol 26.6% and selectivity of diglycerol is 70.5%.

4.1.6 Magnesium Oxide

Magnesium oxide is considered as basic solid catalyst. It can be easily separated from the product after reaction. From the results, it give the 73.9% of diglycerol selectivity. On the other hand, the glycerol conversion and diglycerol yield are very low at 9.9% and 7.3% respectively.

In order to increase the basicity of magnesium oxide, alkali-doped magnesium oxides were synthesized (Barrault *et al.*, 2002). The addition of lithium gave a more basic solid because lithium ions are smaller in size than magnesium. Therefore, lithium ions were inserted more easily in the framework of MgO and then lead to the creation of oxygen gaps, which are responsible for the strong basicity.

4.2 Effect of Reaction Conditions on Glycerol Dimerization

Both NaOH and CaO were selected for further study as homo- and heterogeneous catalysts for the dimerization of glycerol. First, the amount of catalyst was varied in order to find the optimum amount of catalyst. Second, the reaction temperature was varied to find the optimized reaction time for polymerization. Finally, the reaction time was studied for suitable reaction time in formation diglycerol.

4.2.1 Effect of the Amount of Catalyst

One important variable affecting the glycerol conversion is the amount of catalyst. For homogeneous catalysts, it has been revealed that the amount of catalysts has a strong influence on the conversion of glycerols (Garti *et al.*, 1981 and Lemke, 2003). Therefore, the effect of the amount of NaOH and CaO on dimerization of glycerol was studied. Initially, glycerol was heated in flask at temperature 150 °C for 30 minutes under nitrogen flow. The catalyst was added and vigorously stirrer. The temperature was then raised to 250 °C. The heating period was 15 minutes. The water from the reaction was trapped and measured.

The results of catalytic of NaOH catalyst and CaO catalyst were shown in Figure 4.1 and Figure 4.2, which conversion of glycerol, diglycerol selectivity, and diglycerol yield were plotted as a function of %mol catalyst.

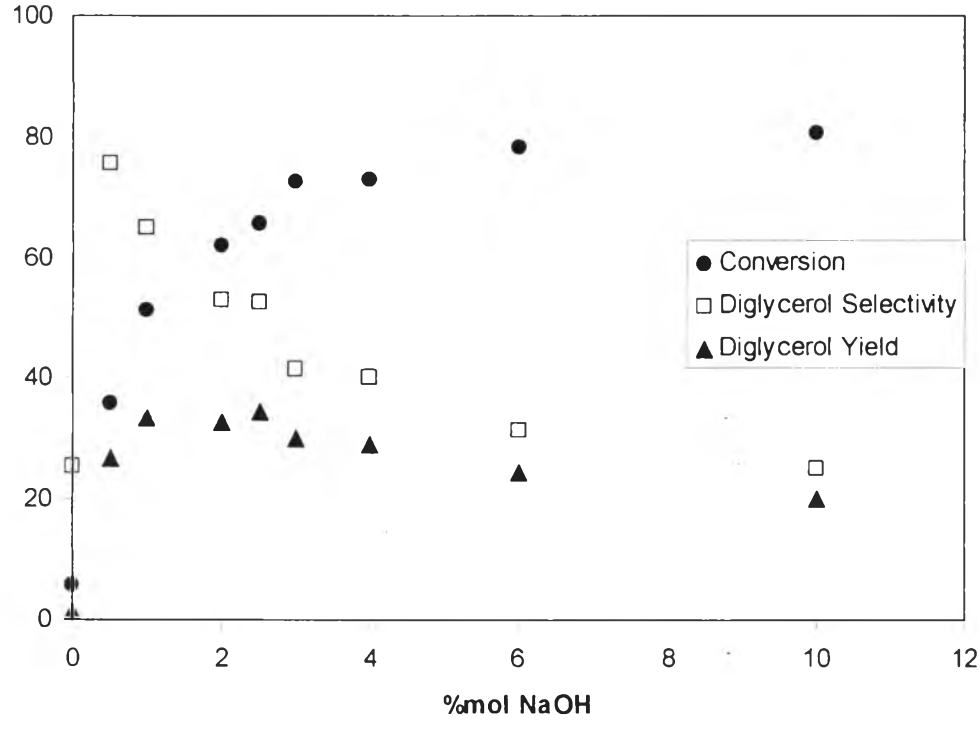

Figure 4.1 Effect of the amount of NaOH in the dimerization of glycerol.

Figure 4.1 showed the results of catalytic of NaOH catalyst. It was obvious that, by increase the amount of catalyst, the conversion is higher. But, if the catalysts is more than 0.5% mol NaOH, the conversion is not increased much. The diglycerol selectivity is significantly decreased with the amount of catalyst. This probably can be explainded by the fact that higher degree of polyglycerols are formed at higher catalysts concerntration. However, the total diglycerol yield at more than 2 mol% NaOH is slightly decreased. The optimum conversion and diglycerol yield at about 60% were obtained at 2 mol% catalysts. It is interesting to note that the conversion of glycerol is significantly increased when the amount of catalyst is increased from 0 to 2 mol%. From the results, 2 mol% of NaOH is sufficient enough to catalyzed the polymerization of glycerol to diglycerol. When more than 2 mol% of NaOH are added, the glycerol conversion increases since glycerol can convert to diglycerol, triglycerol, tetraglycerol and higher oligomers, resulting in the significantly decrease of diglycerol selectivity. Barrault *et al.* (2002) studied activity and selectivity of some catalysts in glycerol polymerization. They

found that homogenous catalyst is more active and the less selective catalyst; the distribution of polyglycerols being rather large. This result is in agreement with the results from NaOH.

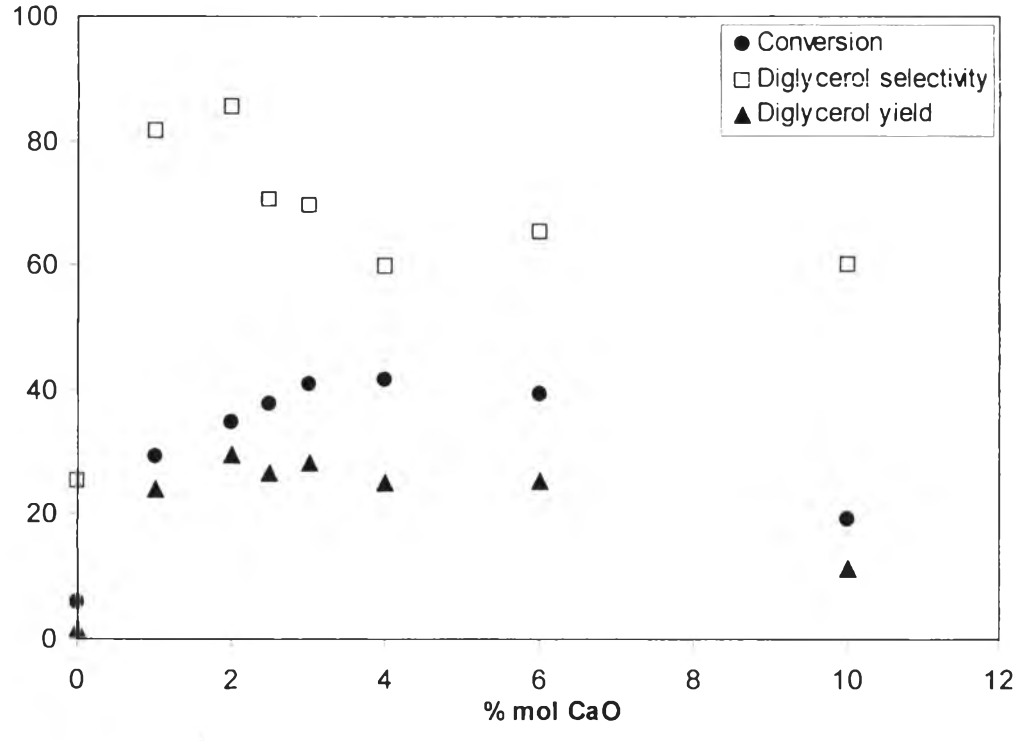

Figure 4.2 Effect of the amount of CaO in the dimerization of glycerol.

The effect of the amount of CaO catalyst is shown in the Figure 4.2. The conversion of glycerol is increased up from around 30% to around 43% when the amount of catalyst is increased from 0.5 mol% to 4 mol%. However, the diglycerol selectivity (about 85%) is significantly decreased when amount of CaO was added beyond 2 mol%. The diglycerol yield was slightly decreased with increasing the amount of catalyst after CaO was added over than 2 mol% and the diglycerol yield is greatly drop when the CaO content is 10%. Furthermore, it is observed that CaO is agglomerated if it is added more than 2%. This probably causes CaO to be less effective.

When compared between CaO and NaOH as a catalyst for the polymerization of glycerol, at 2% mol catalyst, NaOH exhibited higher conversion

than CaO whereas CaO exhibited diglycerol selectivity higher than NaOH. The results reported in this figure show that NaOH is a more active but less selective catalyst. The distribution of polyglycerols products from NaOH is rather large while CaO is more selective toward diglycerol, but the less active than NaOH.

4.2.2 Effect of Reaction Temperature on Glycerol Dimerization

The reaction temperature is also considered as one of the most important variable affecting the polyglycerols yield. It was reported that, at temperature lower than 200 °C, the reaction proceeds too slowly (Garti *et al.*, 1981 and Stuhler, 1985). Glycerol will be decomposed at temperature higher than 280 °C and the amount of acrolein will increase significantly. In this study, the effect of reaction temperature is studied in the range of 200 to 260 °C . The reactions were carried out with the fixed amount of catalyst (2.5 mol%), under nitrogen atmosphere and the stirrer speed of 500 rpm.

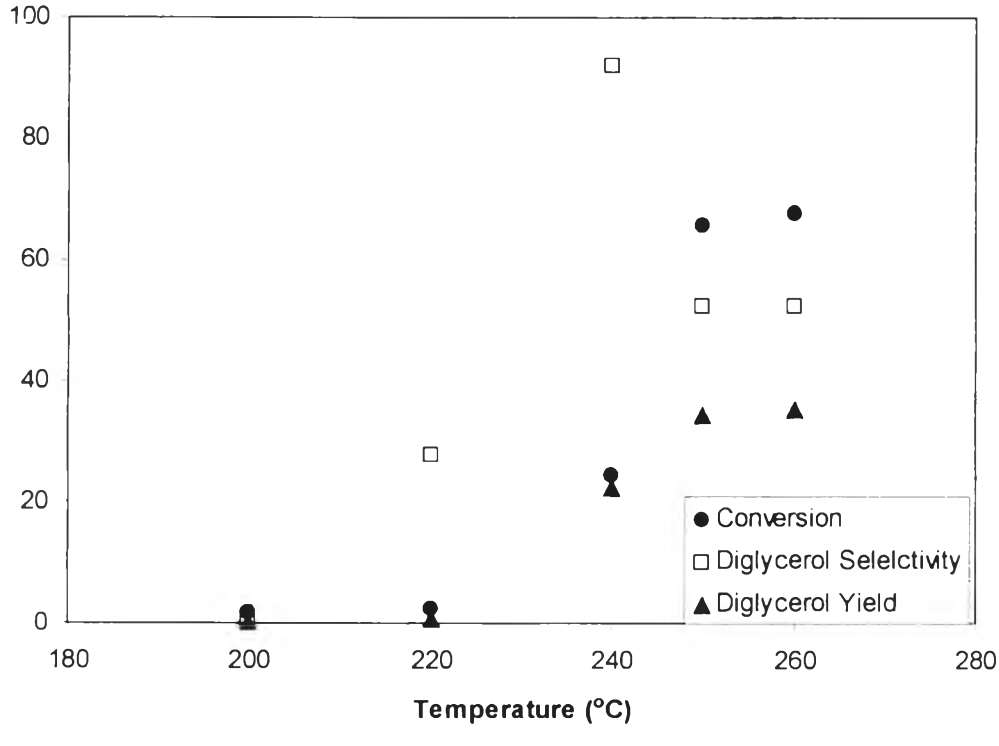

Figure 4.3 Effect of the reaction temperature for glycerol dimerization with NaOH

The effect of reaction temperature for the NaOH catalyzed dimerization of glycerol is shown Figure 4.3. It can be seen that, at temperature 200 and 220 °C after 4 hours, the conversion of glycerol and yield of diglycerol are very low. For the reaction temperature above 220 °C, the conversion of glycerol and yield of diglycerol increases significantly with temperature. The optimum temperature was found to be at 250 °C, providing optimum conversion of glycerol and selectivity of diglycerol at about 60%. Moreover, the conversion of glycerol, selectivity and yield of diglycerol are relatively constant at temperature 250 and 260 °C.

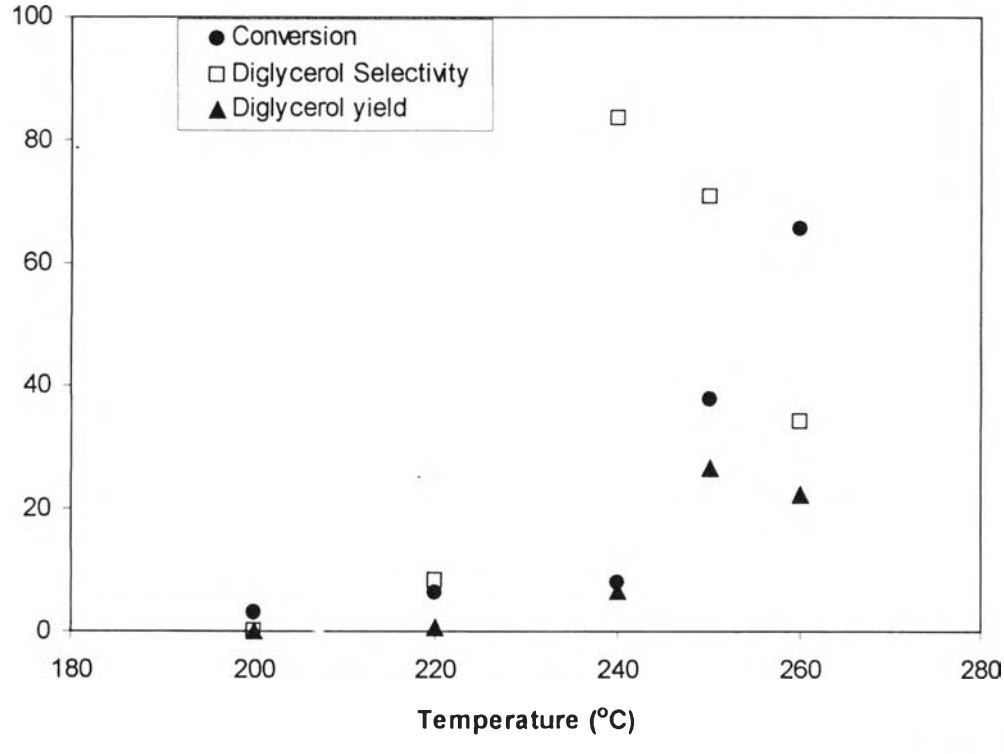

Figure 4.4 Effect of the reaction temperature for glycerol dimerization with CaO.

The effect of reaction temperature in CaO catalyzed dimerization of glycerol is shown in Figure 4.4. The dimerization of glycerol catalyzed by CaO as a catalyst shows the similar trends as in case of NaOH as a catalyst. The conversion of glycerol is increased significantly at temperature higher than 240 °C whereas diglycerol selectivity is decreased. At the temperature 250 °C, both conversion of glycerol and diglycerol selectivity increase to 60 % when CaO was used.

It has been shown that the temperature at 250 °C is an optimized temperature for the dimerization of glycerol by either NaOH or CaO catalyst. The reaction with CaO solid catalyst show higher diglycerol selectivity than that with NaOH homogeneous catalyst. However, NaOH is more reactive and provides higher conversion of glycerol.

4.2.3 Effect of Reaction Time on Dimerization of Glycerol

Garti *et al.* (1981) reported that, for an alkali-catalyzed polymerization of glycerol, the desired degree of polymerization can be otained by varying the reaction time. It is obvious that a shorter reaction time will benefit to the product's economic due to the smaller equipment dimension and, consequently, the lower equipment cost, as well as the energy cost.

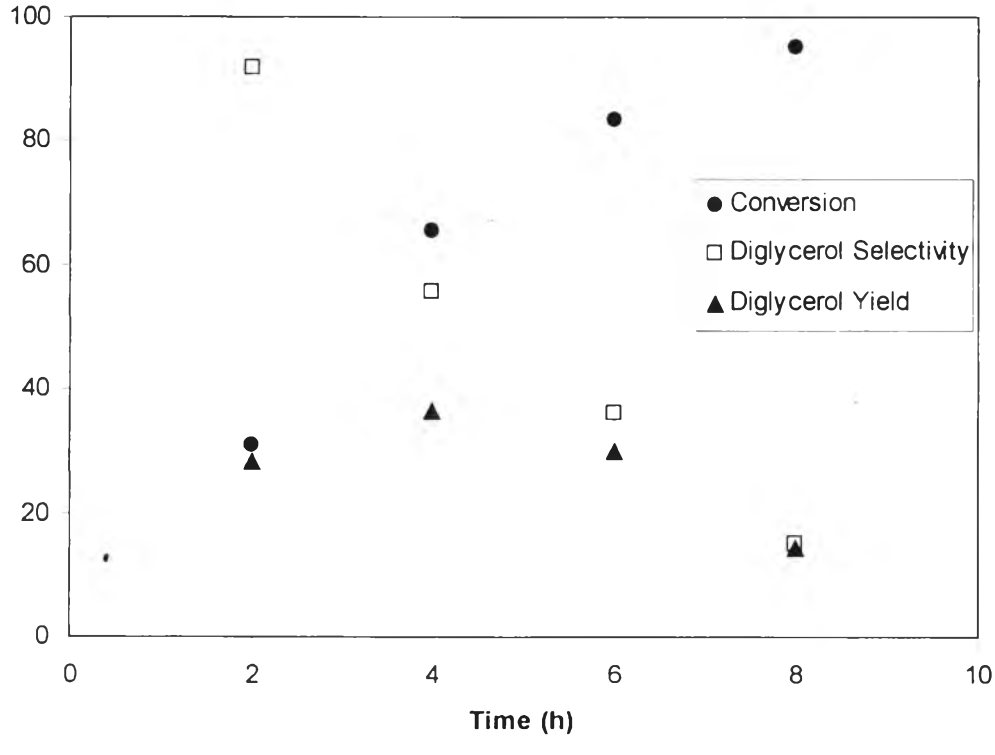

Figure 4.5 Effect of reaction time for glycerol dimerization with NaOH.

The effect of reaction time on glycerol dimerization by NaOH as a catalyst is shown in Figure 4.5. The glycerol conversion, diglycerol selectivity, and

diglycerol yield are plotted as a function of reaction time. The amount of catalyst was at 2.5 mol%, temperature at 250 °C, under nitrogen atmosphere, and the stirrer speed of 500 rpm. Conversion of glycerol was significantly increased with increasing reaction time whereas the diglycerol selectivity was decreased. For the reaction time longer than 4 hours, the diglycerol yield slightly decreased with reaction time. As the reaction time is longer, the glycerol conversion increases since glycerol gradually convert to diglycerol, triglycerol, tetraglycerol and higher oligomer resulting in the significant decrease of diglycerol selectivity. From the result, the optimum time for dimerization of glycerol was found at 4 hours.

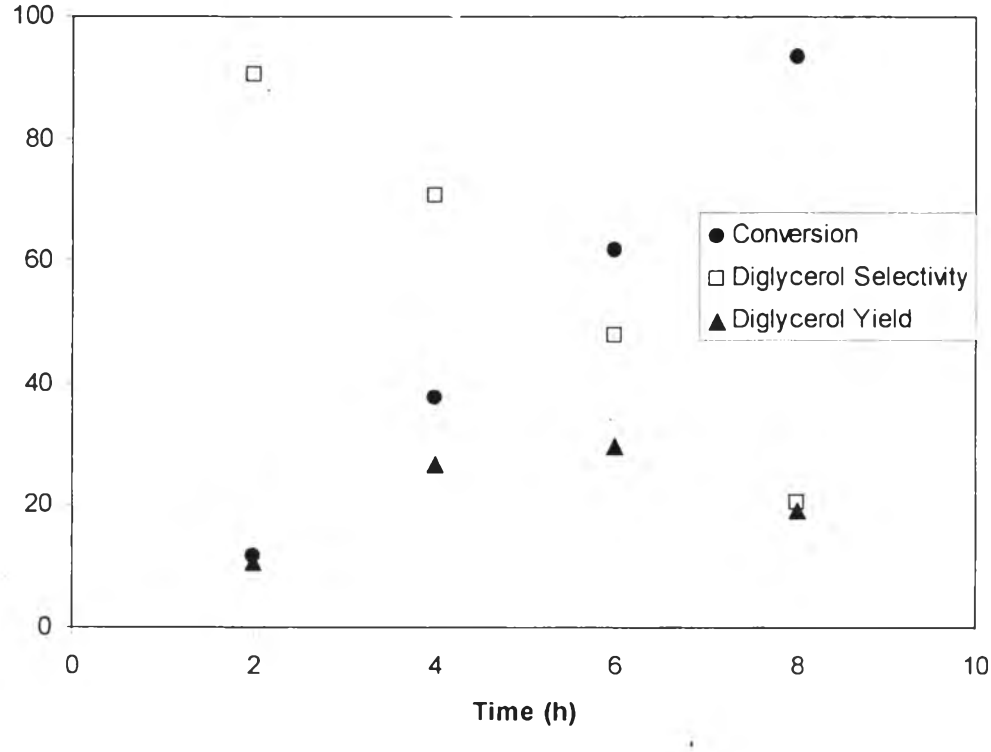

Figure 4.6 Effect of reaction time for glycerol dimerization with CaO.

The effect of reaction time in the dimerization of glycerol by using CaO as a catalyst is shown in Figure 4.6. The results were similar to the NaOH catalyzed reaction. The optimum reaction times for the polymerization of glycerol obtained by using CaO showed at around 6 hours. It is suggested that CaO required reaction time

longer than NaOH for the same conversion. This may be explained by the fact that NaOH catalyst is more reactive than CaO catalyst.