CHAPTER IV
RESULTS AND DISCUSSION

Diglycerol can be prepared from glycerol in the presence of homogeneous base catalysts, such as Na_2CO_3. The catalyst can increase the rate of reaction and the yield of diglycerol, triglycerol and higher degree of glycerol oligomers. However, there are several disadvantages from using homogeneous catalysts, for example, product selectivity and the downstreams catalysts separation. Moreover, the product is often required further processes to separate impurities and catalysts. The use of heterogeneous or solid catalysts can possibly avoid these drawbacks. 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 Type in Glycerol Dimerization

The effect of catalyst type was first studied at the reaction temperature 240 °C under inert nitrogen atmosphere and the catalyst loading 2.0 wt%. The mixture was agitated by a stirrer at speed 500 rpm and the reactions time was varied at 1, 2, 3, 4 and 5 hrs. The results of glycerol conversion, diglycerol selectivity and diglycerol yield are summarized in Figure 4.1, Figure 4.2, and Figure 4.3, respectively.

As shown in Figure 4.1 and Figure 4.3, the conversion of glycerol and yield of diglycerol from the blank test were low even though it was performed at high temperature (240°C) and sufficient reaction time (5 hrs). However, if there is catalyst present in the system, the conversion of glycerol and yield of diglycerol are significantly increased. These results indicated that the catalysts considerably enhanced the conversion of glycerol and yield of diglycerol. As expected, the conversion of glycerol also increased with reaction time. It was interesting to note that, for CaO, the glycerol conversion is relatively constant after 2 hr. By comparing the glycerol at 5 hrs reaction time, Na_2CO_3 gave 90% conversion, followed by SrO, BaO, CaO and MgO for 83%, 82%, 72% and 61% conversion, respectively.

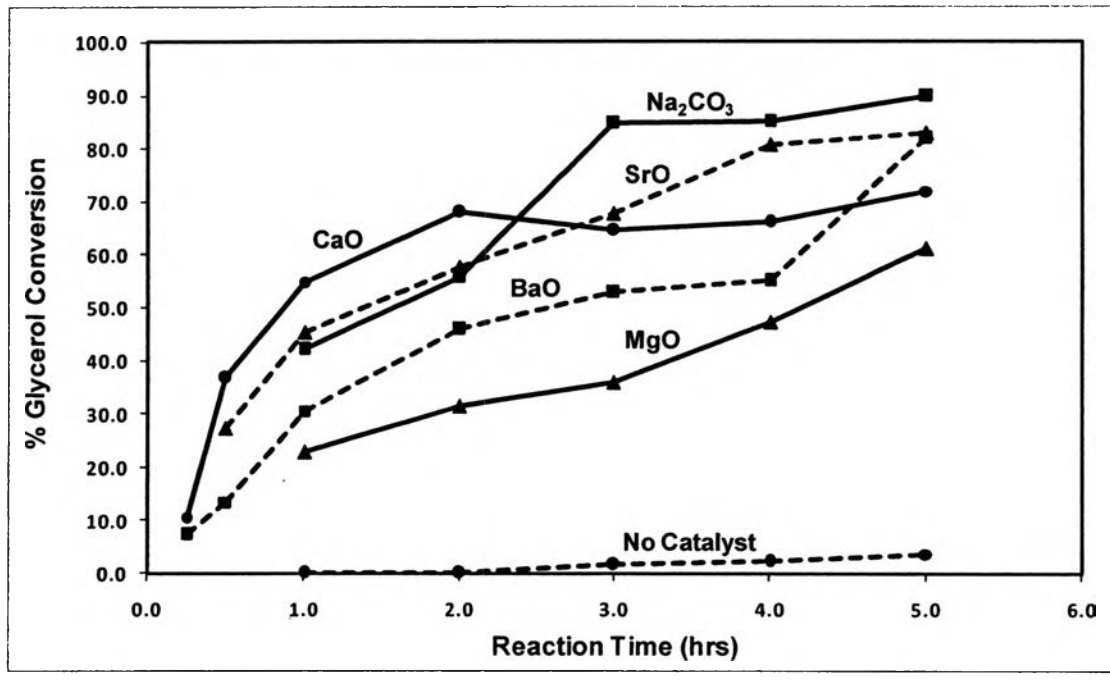

Figure 4.1 The relation between glycerol conversion and reaction time at 240°C and 2 wt% loading of catalysts.

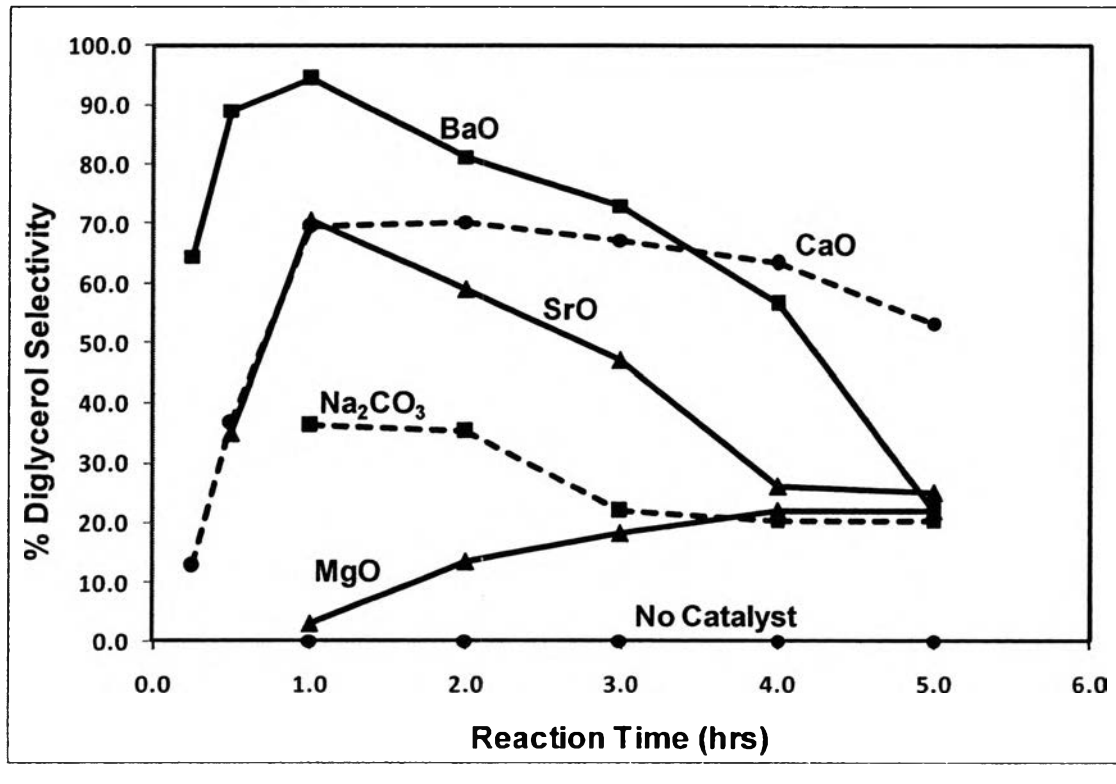

Figure 4.2 The relation between selectivity toward diglycerol and reaction time at 240°C and 2 wt% loading of catalysts.

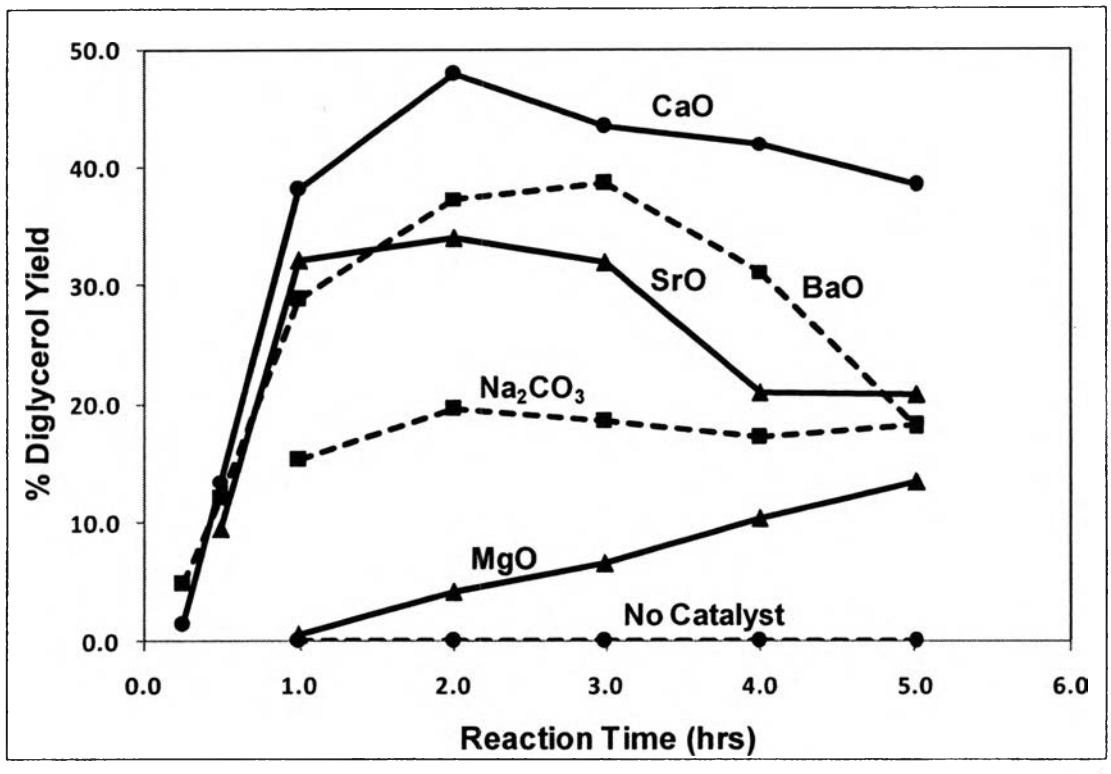

Figure 4.3 The relation between yield of diglycerol and reaction time at 240°C and 2 wt% loading of catalysts.

By comparing the activities of these catalysts at the same reaction time, the results in Figure 4.1 can be explained that glycerol conversion of CaO, SrO and BaO catalysts are higher than MgO propably due to the fact that the basic strengths of CaO, SrO and BaO are higher than that of MgO (from temperature-programmed desorption (TPD), the basic strengths are in order BaO > SrO > CaO > MgO). In case of CaO and BaO, the results did not agree with the basic strength. This may be affected from the number of basic sites and BET surface area of CaO higher than BaO. (For the number of basic sites : (MgO (26.7 μmol/g) > CaO (18.7 μmol/g) > SrO (11 μmol/g) > BaO (5.39 μmol/g)) and for BET surface area : (MgO (50.05 m^2/g) > SrO (4.78 m^2/g) > CaO (3.00 m^2/g) > BaO (0.37 m^2/g))

From Figure 4.1-4.3, at 1 hr reaction time, BaO can convert 31% of glycerol with high selectivity 94% toward diglycerol resulting in the total diglycerol yield of 29%. Moreover, CaO provided higher total diglycerol yield (38%) and higher conversion of glycerol (55%) but much less selectivity of diglycerol (69%) than BaO. This indicated that CaO was effective not only condensation of glycerol, but also of

diglycerol or higher degree, therefore the selectivity towards diglycerol was much less than BaO. At 1 hr, the selectivity toward diglycerol was 94% for BaO, 70% for CaO, and 71% for SrO, which are higher than Na_2CO_3 and MgO (only 36% and 3%, respectively). Moreover, the yields of diglycerol from BaO, CaO, and SrO were 29%, 38%, and 32%, respectively, which were all higher than the yield from Na_2CO_3 and MgO, which were merely 15% and 1%, respectively.

It was also observed that, from Figure 4-2, several catalysts (BaO, SrO and CaO) illustrated the maximum selectivity at 1 hr reaction time. This was due to the fact that diglycerol could also react with glycerol or diglycerol to form tri- and tetraglycerol and so on. Therefore, the selectivity toward diglycerol was dropped if the reaction was longer.

For the zirconium oxide (ZrO_2), it possessed both acidic and basic properties. It has been used in several chemical reactions, such as esterification, and etc. In this study, ZrO_2 was active catalyst (62% conversion), but it took very long reaction time (12 hrs) to catalyze the reaction, comparing to other studied catalysts. Its diglycerol selectivity and diglycerol yield were 42% and 26%, respectively.

To compare the effect of basicity of homogeneous catalyst, the mol% of NaOH and Na_2CO_3 were fixed to compare the glycerol conversion between NaOH and Na_2CO_3. From the Figure 4.4, the results showed that the activity of NaOH is higher than Na_2CO_3 because the basic strength of NaOH (basicity (pK_b) = -2.43) higher than that of Na_2CO_3(basicity (pK_b) = 3.67). Moreover, the results showed that the diglycerol selectivity of Na_2CO_3 is higher than NaOH.

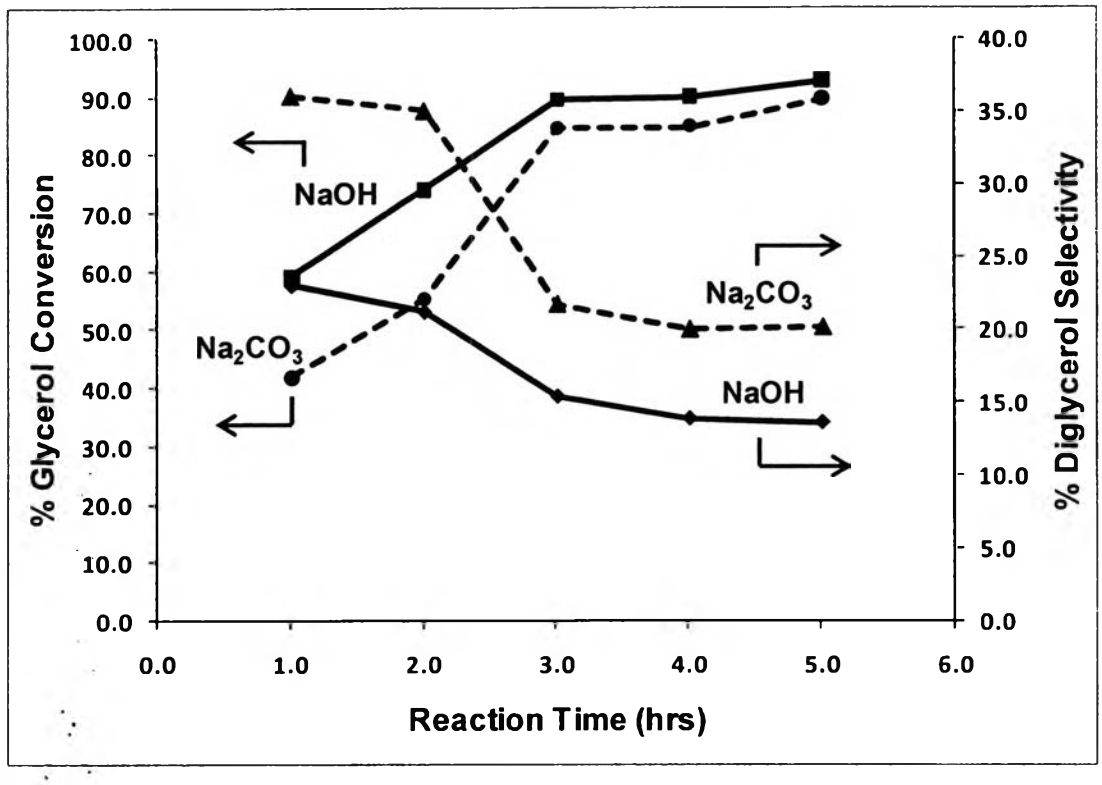

Figure 4.4 The relation between glycerol conversion, diglycerol selectivity and reaction time at 240°C and 2 wt% loading of NaOH and Na_2CO_3.

4.2 Effect of Reaction Conditions on Glycerol Dimerization

Among the tested catalysts, CaO and BaO provided the highest diglycerol yield and diglycerol selectivity. Then the CaO and BaO were selected for further study in this section.

4.2.1 Effect of the Catalyst Loading

One important variable which affect to the glycerol conversion was the amount of loaded catalyst. Therefore, the effect of the amount of CaO and BaO on dimerization of glycerol was studied. Initially, glycerol was heated in flask at temperature 150°C for 30 minutes under nitrogen flow. The temperature was then heated to 240°C, and the catalyst was added while the reactants was stirred. The reaction was allowed for 1 hour.

The catalytic results of CaO and BaO catalyst were shown in Figure 4.5 and Figure 4.6. The conversion of glycerol, diglycerol selectivity, and diglycerol yield were plotted as a function of amount of catalyst.

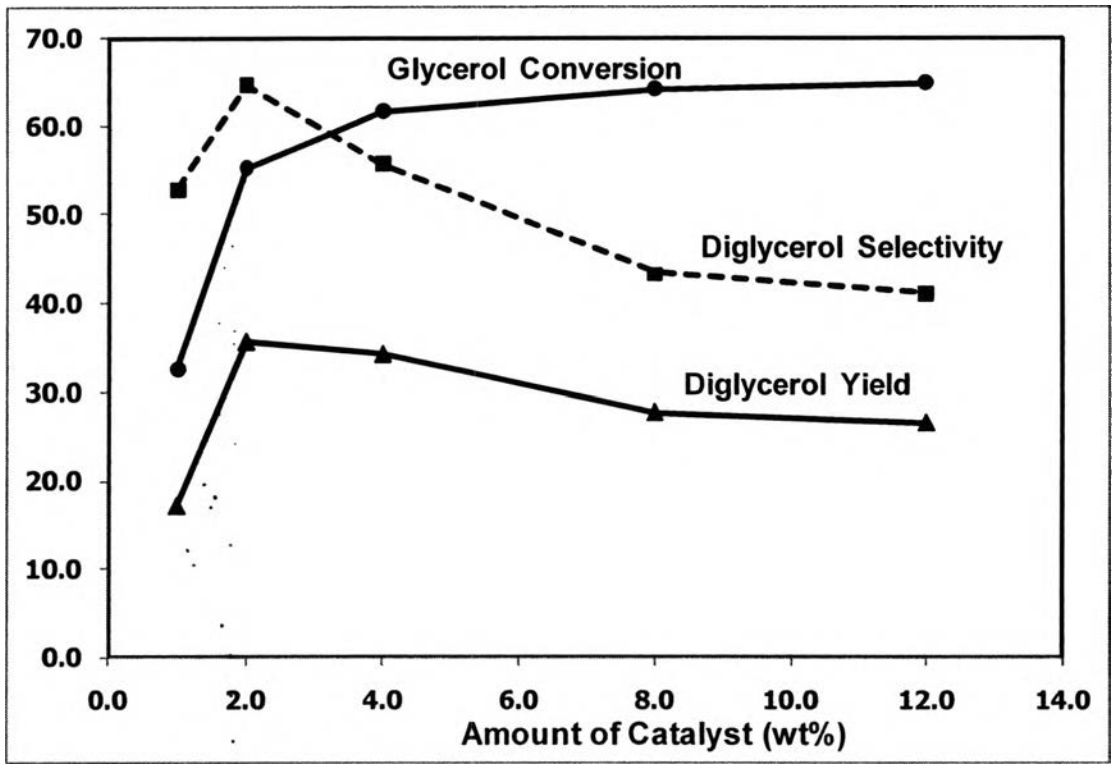

Figure 4.5 The relation between glycerol conversion, diglycerol selectivity and yield and the amount of CaO catalyst at 240°C and 1 hr.

From Figure 4.5, as the amount of CaO catalyst increased, the conversion was increased. However, if the amount of CaO catalyst higher than 2 wt%, the conversion was relatively constant, while the diglycerol selectivity was significantly decreased. This can be explained by the fact that higher degree of glycerol oligomers were formed. Moreover, the total diglycerol yield was also decreased for the CaO loading more than 2 wt%. The conversion and diglycerol yield at 2 wt% of catalysts and reaction time 1 hour were 55% and 36%, respectively.

The effect of the amount of BaO catalyst was shown in the Figure 4.6. The glycerol conversion and diglycerol selectivity were significantly increased when the amount of catalyst was increased from 1 wt% to 2 wt%. However, the diglycerol selectivity was significantly decreased when amount of BaO was added beyond 2

wt%. The total diglycerol yield was slightly decreased with increasing amount of catalyst after BaO was loaded more than 2 wt%.

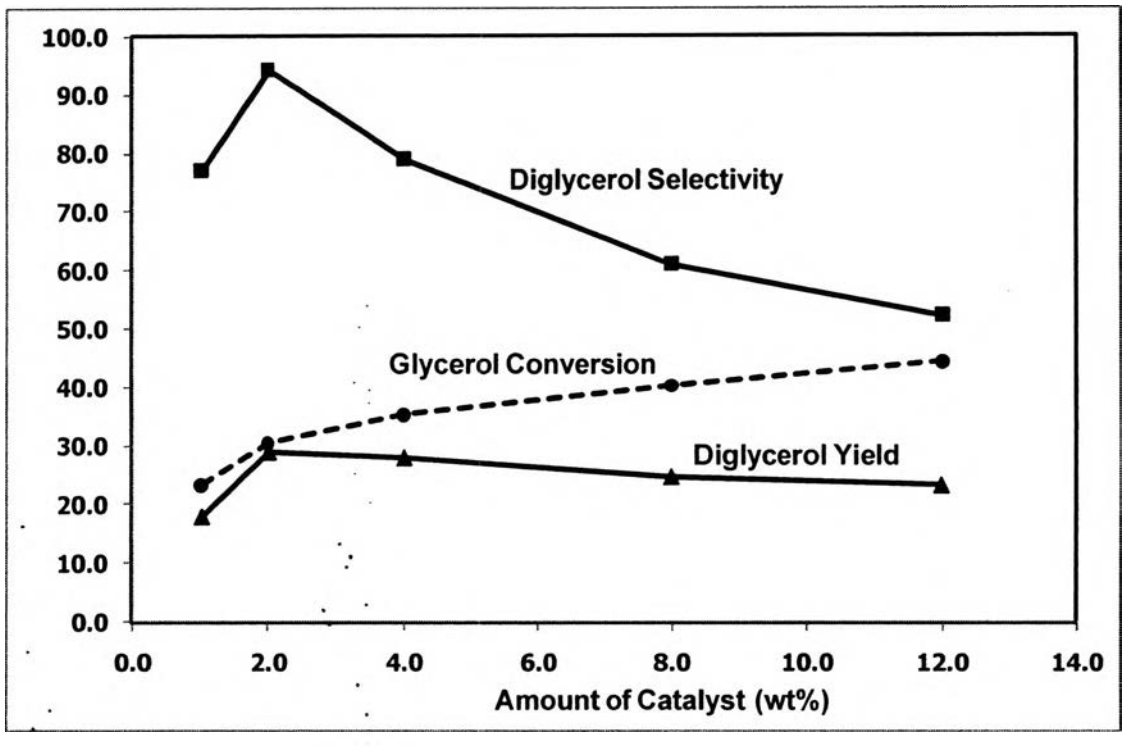

Figure 4.6 The relation between glycerol conversion, diglycerol selectivity and diglycerol yield compare with amount of catalysts of BaO at 240°C and 1 hr.

From Figure 4.6, it was interesting to note that the conversion of glycerol was significantly increased when the catalyst loading was increased from 0 to 2 wt%. Apparently, 2 wt% of catalysts was effective to catalyse the condensation of glycerol to diglycerol. However, if more than 2 wt% of catalysts was added, the glycerol conversion slightly increased while the diglycerol selectivity significantly decreased. This can be explained that glycerol can convert to diglycerol, triglycerol, and higher oligomers, resulting in the significantly decreased of diglycerol selectivity.

It was also observed that BaO catalyst provided higher diglycerol selectivity than CaO catalyst, but, CaO gave higher total yield of diglycerol than BaO.

4.2.2 Effect of Reaction Temperature on Glycerol Dimerization

The reaction temperature was also considered as an important parameter which affects to the diglycerol yield. In this study, the effect of reaction temperature was studied in the range of 220°C to 260°C. The reactions were carried out with the fixed amount of catalyst (2 wt%), under nitrogen atmosphere and the stirrer speed of 500 rpm.

The effect of reaction temperature for the CaO was shown in Figure 4.7. The results showed that, at temperature 220, 230, and 240°C with 1 hour reaction time, the glycerol conversion, diglycerol selectivity and diglycerol yield increased because reaction temperature could increase the rate of reaction. For the reaction temperature above 240°C, the diglycerol selectivity and diglycerol yield significantly decreased with temperature because glycerol could convert to diglycerol or higher oligomers. Therefore, the temperature at 240°C, provides conversion of glycerol 55%, diglycerol selectivity 65%, and diglycerol yield 36%.

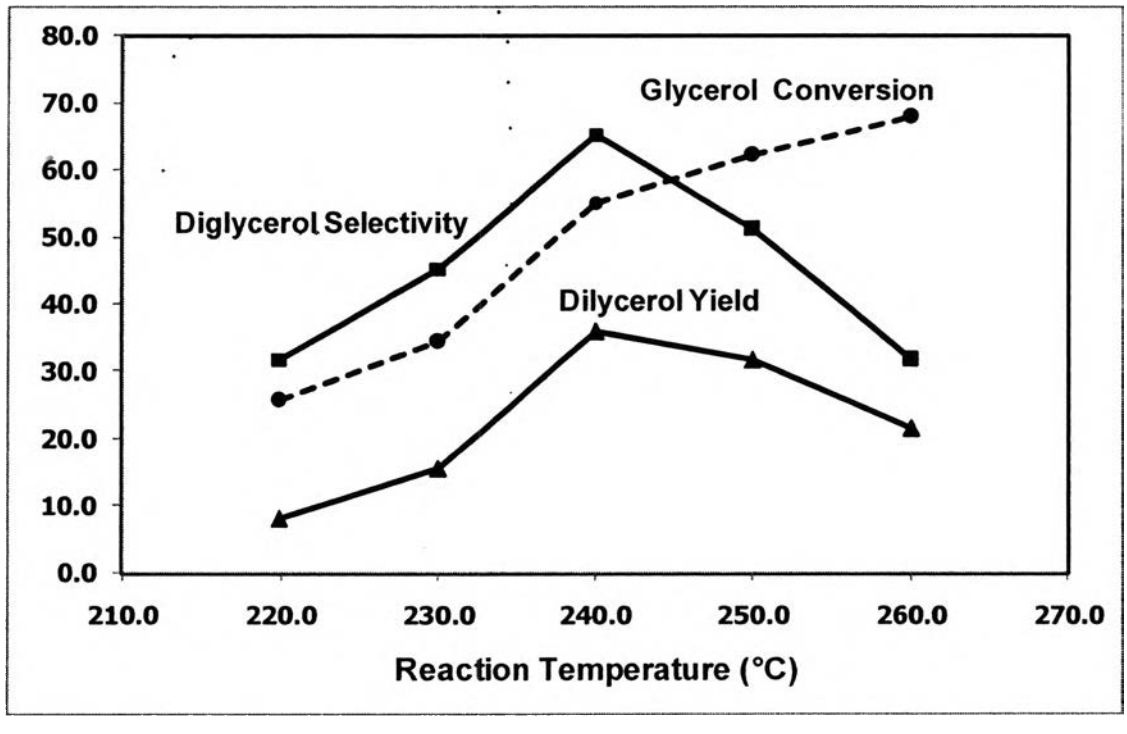

Figure 4.7 The relation between glycerol conversion, diglycerol selectivity and diglycerol yield compare with reaction temperature of CaO at 2 wt% of catalysts and 1 hr.

The effect of reaction temperature in BaO was shown in Figure 4.8. The results showed the similar trends as observed in the case of CaO catalyst. The conversion of glycerol significantly increased at temperature higher than 220°C whereas diglycerol selectivity and diglycerol yield increased with temperature but they decreased if temperature is higher than 240°C. Moreover, glycerol conversion, diglycerol selectivity and diglycerol yield were obtained about 33%, 81% and 27%, respectively, when BaO was used.

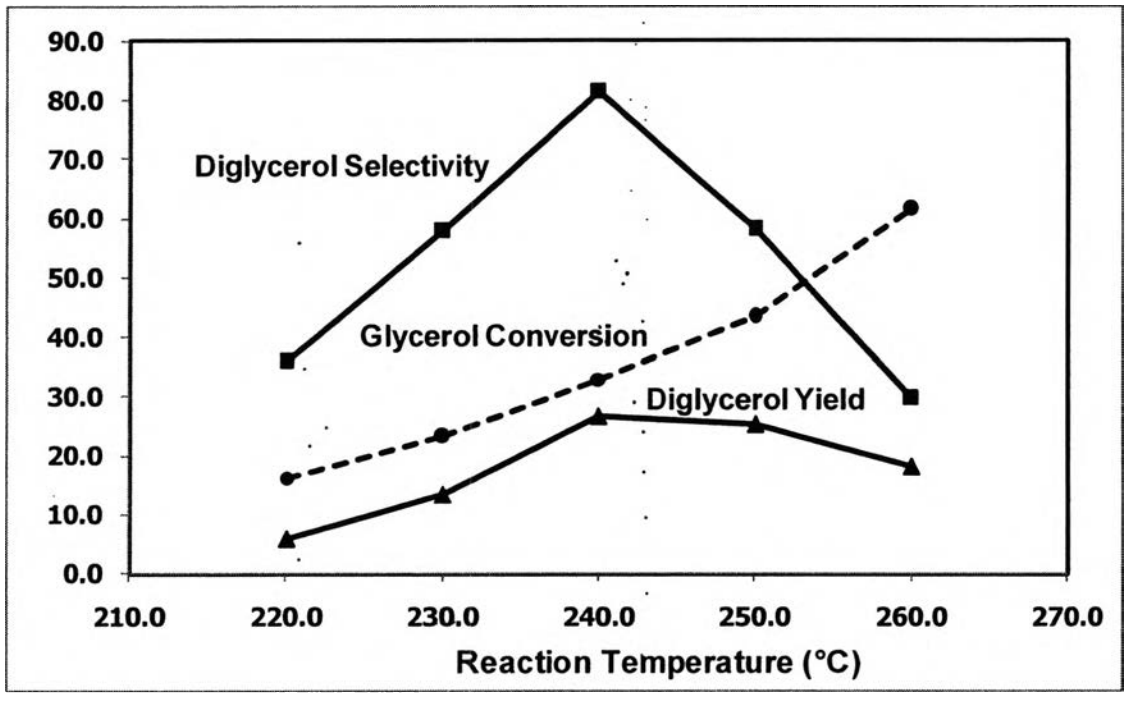

Figure 4.8 The relation between glycerol conversion, diglycerol selectivity and diglycerol yield compare with reaction temperature of BaO at 2 wt% of catalysts and 1 hr.

The results of either CaO or BaO catalyst showed that, at 240°C, BaO catalyst provided higher diglycerol selectivity than CaO catalyst. However, CaO was more reactive and gave higher yield of diglycerol than BaO.

It is interesting to compare the glycerol conversion, diglycerol selectivity and diglycerol yield by CaO and BaO with other reports. From Table 4.1, the results showed that CaO and BaO in this research provided the glycerol conversion and diglycerol selectivity higher than sodium zeolites and sodium silicate of Henkel at the same condition.

Table 4.1 The weight composition(%) of the mixtures obtained by reacting glycerol over zeolites at temperature 513 K (Henkel, 1992).

Catalysts	**Glycerol**	**Diglycerol**	**Triglycerol**	**Other polyglycerols**
Na A	15.4	32.3	20.5	31.8
Na Z	9.5	27.6	20.0	42.9
Na X	9.6	30.9	22.0	37.5
Na silicate	8.5	29.7	23.0	38.8

Table 4.2 also showed that the mesoporous catalysts impregnated with magnesium or cesium catalysts required longer reaction time (8 hrs) and higher reaction temperature (260°C) than CaO and BaO in order to get the same glycerol conversion.

Table 4.2 Etherification of glycerol over mesoporous materials impregnated with magnesium or cesium at temperature 533 K (Barrault, 2004).

Element	Conversion (%)	Selectivity (%) 8 h (24 h)			
impregnated	8 h (24 h)	Diglycerol	Triglycerol	Tetraglycerol	Others
Mg_6	10 (25)	100 (95)	-(5)	-	-
Mg_{25}	80 (-)	65	20	15	Trace
Cs_6	15 (40)	95 (90)	5 (10)	-	-
Cs_{25}	25 (80)	100 (75)	0 (22)	Trace	-