



CHAPTER IV

RESULTS AND DISCUSSION

4.1 Effect of Catalyst Type on the Etherification of Glycerol

The effect of catalyst type was first studied at 240°C under inert nitrogen atmosphere in the presence of 2 wt% of catalyst. Figure 4.1 shows the glycerol conversion for BaO, CaO and MgO as a function of reaction time. As expected, the conversion of glycerol increases with reaction time, and homogeneous catalysts, NaOH and Na₂CO₃ (Table 4.1) are more active than heterogeneous materials. The relative catalytic activities of the alkaline earth oxides indicate the following reactivity order: BaO>CaO>MgO. This order is in accordance with their basicity; that is, BaO>CaO>MgO. By comparing the glycerol at 6 hr reaction time, NaOH gives 81% conversion, followed by Na₂CO₃, BaO, CaO and MgO for 76%, 72%, 68% and 30% conversion, respectively.

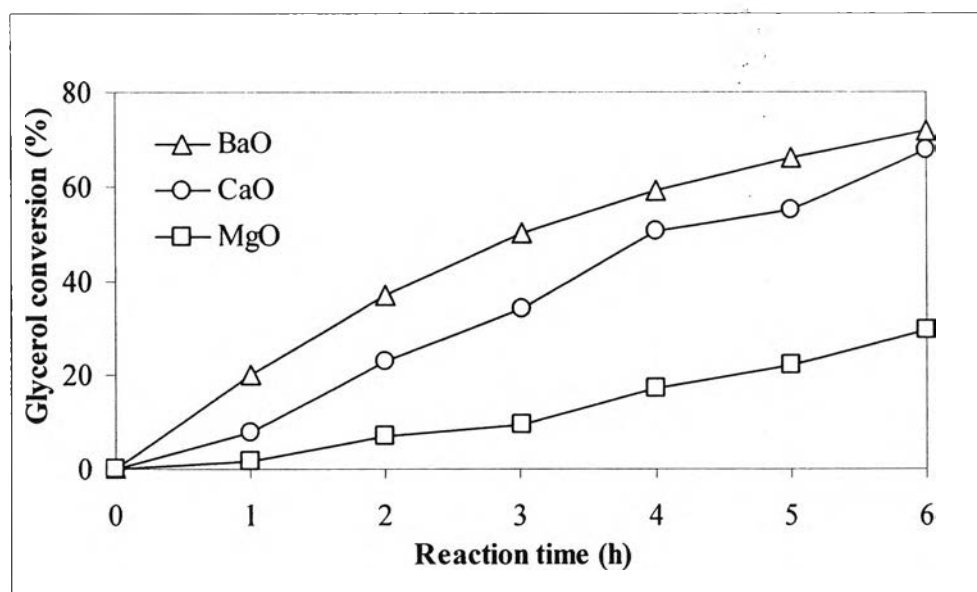


Figure 4.1 The glycerol conversion for BaO, CaO and MgO as a function of reaction time at 240°C under inert nitrogen atmosphere in the presence of 2 wt% of catalyst.

Table 4.1 Glycerol conversion for NaOH, Na₂CO₃, BaO, CaO and MgO (240°C under inert nitrogen atmosphere in the presence of 2 wt% of catalyst)

Types of catalyst	Glycerol conversion at 6 h (%) (12 h)
Homogenous catalyst	
NaOH	81
Na ₂ CO ₃	76(95)
Heterogenous catalyst	
BaO	72(88)
CaO	68
MgO	30

In the case of BaO and Na₂CO₃, the conversion was initially similar at 6 hr but Na₂CO₃, which is a homogenous catalyst gradually reached a final value of about 95% while BaO reached a conversion of about 80% after 12 h of reaction.

In order to explain the difference between the catalysts, base properties of these metal oxide catalysts were examined by TPD of adsorbed CO₂. The results of catalysts characterizations were showed in Figure 4.2. BaO showed desorption peaks at 620°C, accompanied by the shoulder peaks at 570 °C. This demonstrated that BaO possessed of the strong basic sites and CaO had desorption peak at 400 and 350 °C. Finally, MgO showed peak at 330°C. This indicated that MgO had weak basic site. It can be concluded that BaO has highest strength of basic sites, followed by CaO and MgO.

Scanning electron microscope (SEM) has been used to determine the morphology. Figure 4.3-Figure 4.5 show the SEM micrographs of the catalysts. The results show that the particles of BaO were agglomerated and had a large flat shape while the smaller size is observed in CaO. MgO reveals lowest aggregates of smallest particles. This is supported by the BET surface area results (Thanasanvisit, 2008). BaO which has largest size of particles, also has lowest surface area about 0.37 m²/g followed by CaO 3.00 m²/g and MgO 50.05 m²/g, respectively. It is important to mention here that the surface areas of the three materials are also

different and follow the order $\text{MgO} > \text{CaO} > \text{BaO}$. However, although MgO has a larger surface area than the others it is still not so reactive.

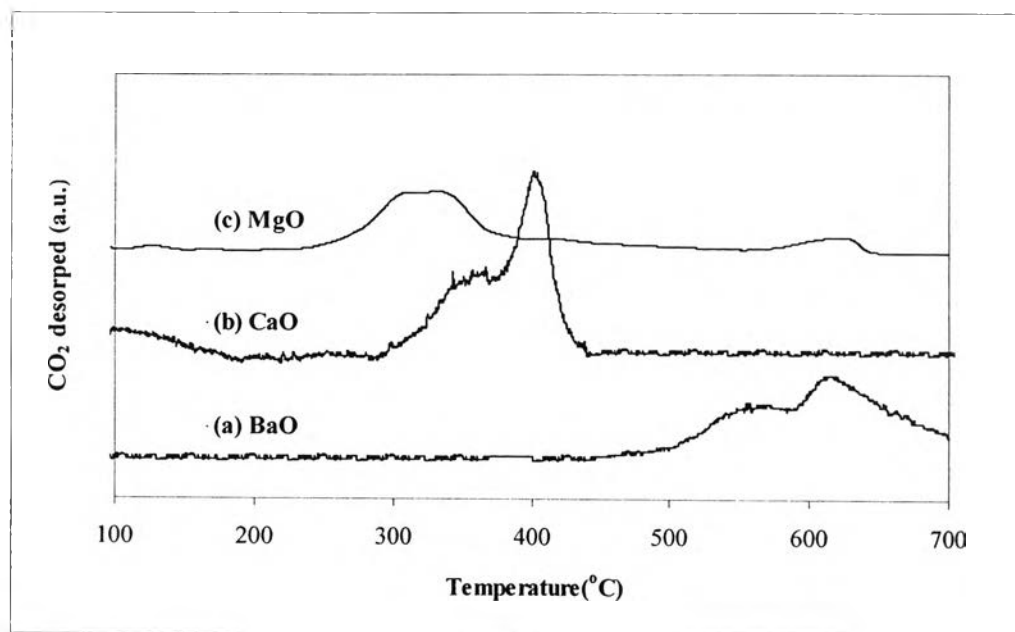


Figure 4.2 CO₂-TPD of metal oxides: (a) BaO; (b) CaO; (c) MgO.

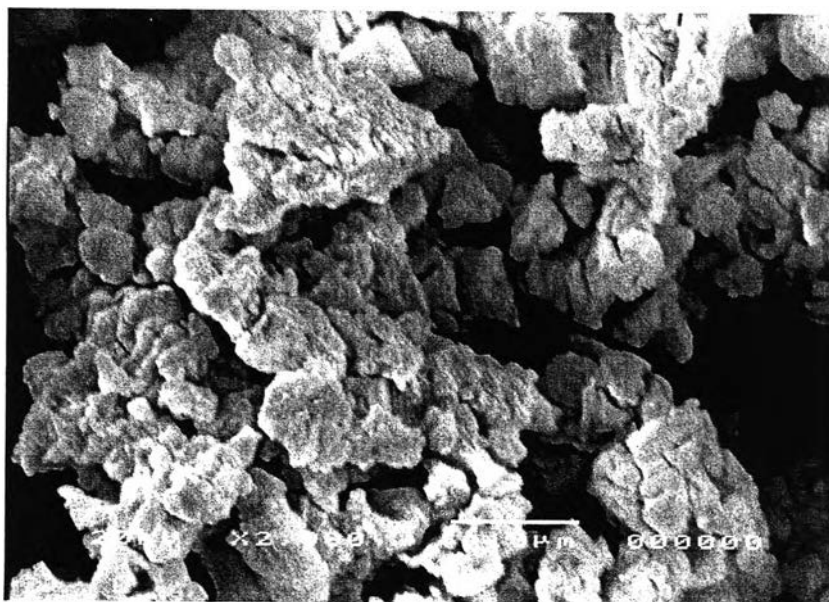


Figure 4.3 SEM image of BaO.

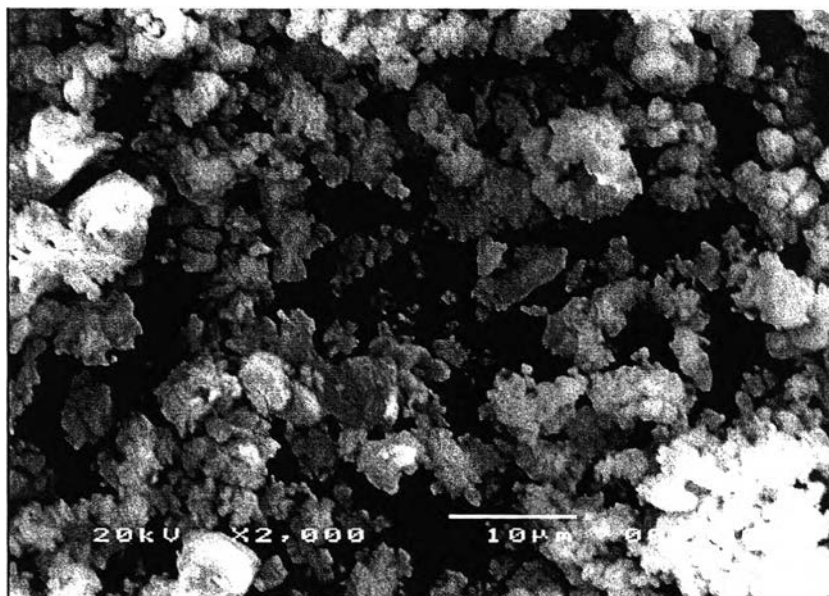


Figure 4.4 SEM image of CaO.

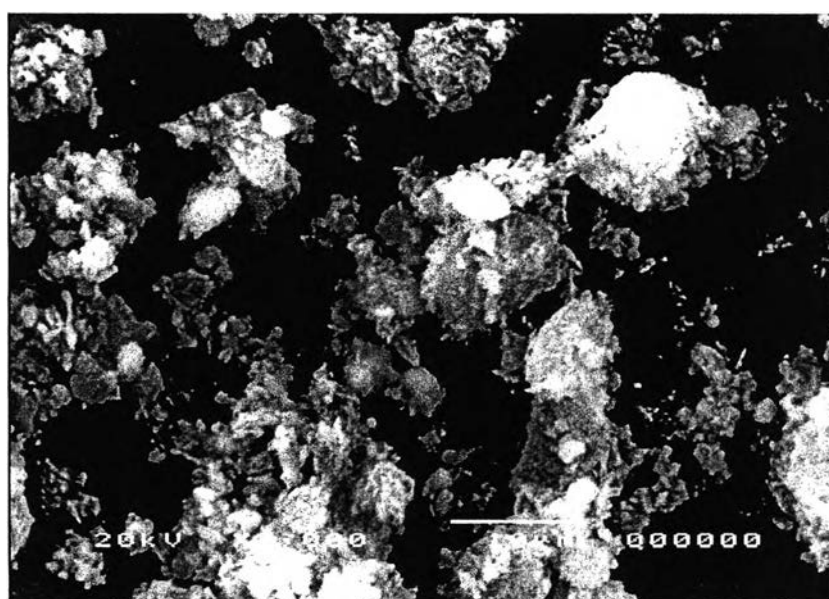


Figure 4.5 SEM image of MgO.

At the beginning of reaction diglycerol is formed as the major product, while the higher polyglycerols start to dominate at higher glycerol conversion. It is also observed that, from Figure 4.6, several catalysts (Na_2CO_3 , BaO , CaO) illustrate the maximum diglycerol concentration (39, 34, 31% respectively) at 4 hr reaction time. The high basicity not only catalyzes glycerol to diglycerol, it also increases ability of glycerol to form triglycerol as shown in Figure 4.7 and Figure 4.8. This is due to the fact that diglycerol can also react with glycerol or diglycerol to form tri- and tetraglycerol and so on. Therefore, the selectivity toward diglycerol is dropped if the reaction is prolonged. Figure 4.7 summarizes the selectivity of diglycerol for each catalyst applied. The diglycerol selectivity is defined as a ration of weight of diglycerol to weight of product (except remaining glycerol) according to Equation (4.1).

$$\text{Diglycerol Selectivity (wt \%)} = \frac{\text{Weight of diglycerol}}{\text{Weight of product}} \times 100 \quad (4.1)$$

It follows from Figure 4.8 that diglycerol selectivity of 100% is achieved only at low glycerol conversion up to 20% and the selectivity declines with higher glycerol conversion. At 80% conversion, 20% selectivity to diglycerol are obtained.

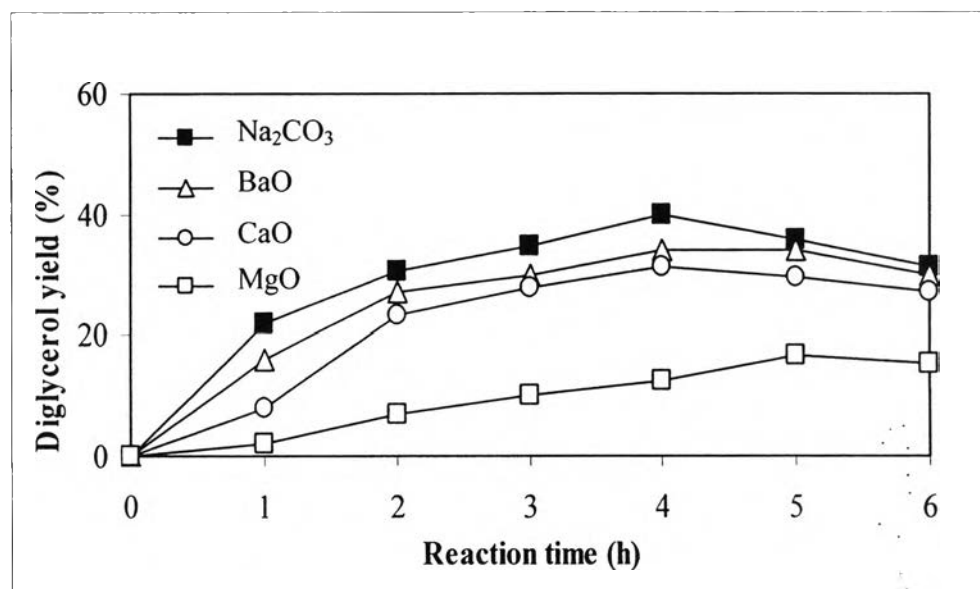


Figure 4.6 The diglycerol yield for Na₂CO₃, BaO, CaO and MgO as a function of reaction time at 240°C under inert nitrogen atmosphere in the presence of 2 wt% of catalyst.

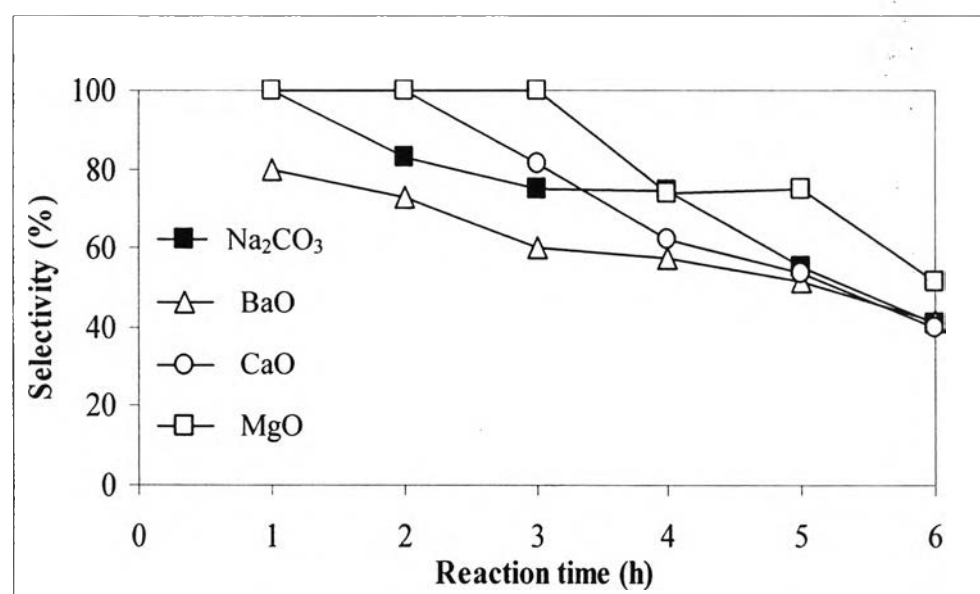


Figure 4.7 The diglycerol selectivity for Na₂CO₃, BaO, CaO and MgO as a function of reaction time at 240°C under inert nitrogen atmosphere in the presence of 2 wt% of catalyst.

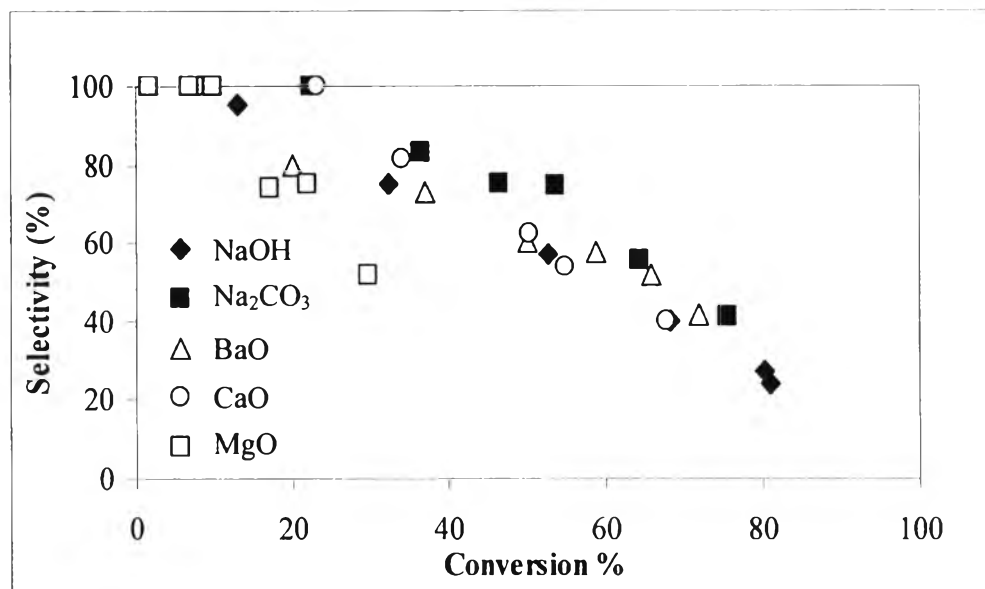


Figure 4.8 The diglycerol selectivity for NaOH, Na₂CO₃, BaO, CaO and MgO as a function of the glycerol conversion at 240°C under inert nitrogen atmosphere in the presence of 2 wt% of catalyst.

4.2 Effect of Reaction Temperature on the Etherification of Glycerol

The reaction temperature was varied from 220°C to 250°C. The effects of temperature on this etherification reaction are shown in Figure 4.9 and Figure 4.10 for BaO and in Figure 4.11 and Figure 4.12 for CaO. It can be seen that the temperature affects not only the rate of reaction but also the concentration of the formed diglycerol. This is due to the etherification reactions are endothermic in nature as well as it might be due to the increased ability of glycerol to form diglycerol and longer chain during the reaction with an increase in the operating temperatures. The higher operating temperatures were not further investigated because glycerol can lead to the formation of undesired product at high temperature such as acrolein.

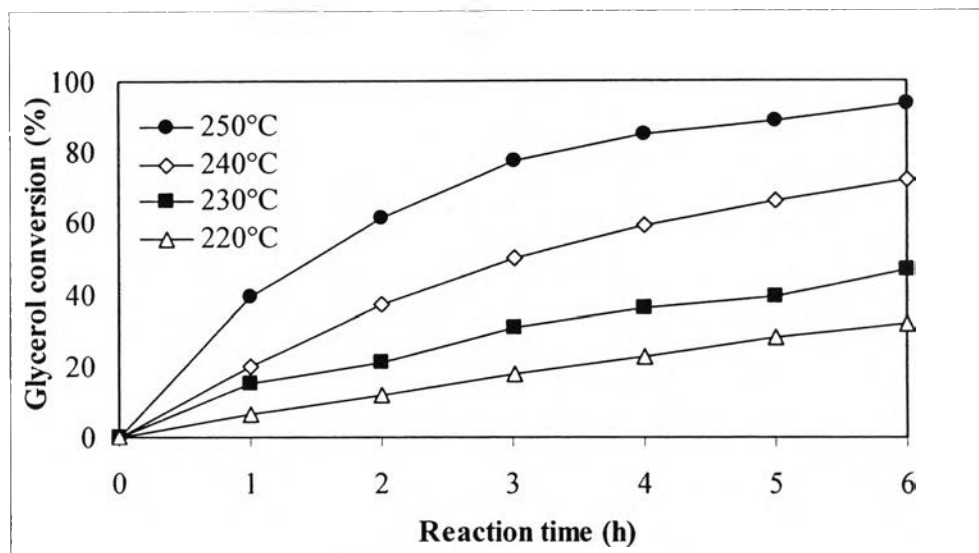


Figure 4.9 The glycerol conversion of BaO for reaction temperature at 220, 230, 240, 250 °C as a function of reaction time under inert nitrogen atmosphere in the presence of 2 wt% of catalyst.

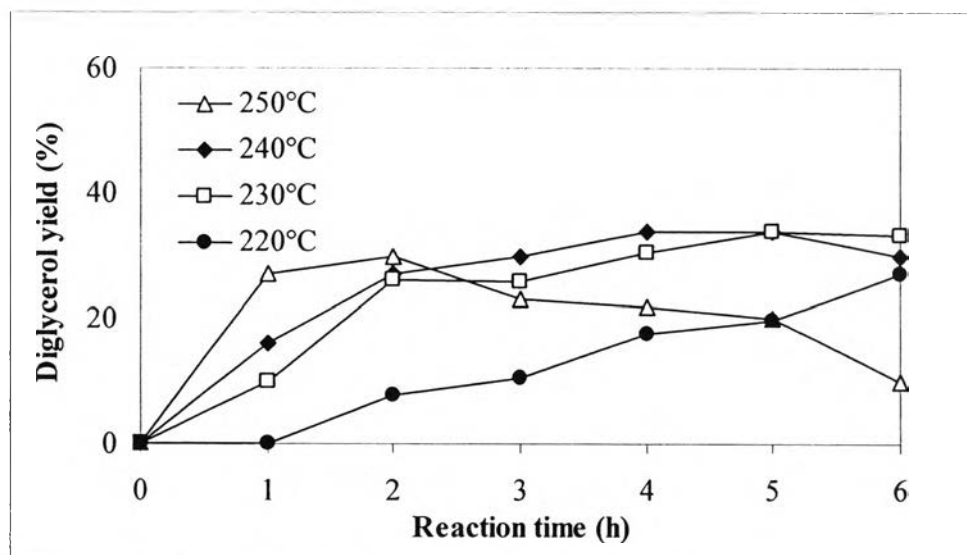


Figure 4.10 The diglycerol yield of BaO for reaction temperature at 220, 230, 240, 250 °C as a function of reaction time under inert nitrogen atmosphere in the presence of 2 wt% of catalyst.

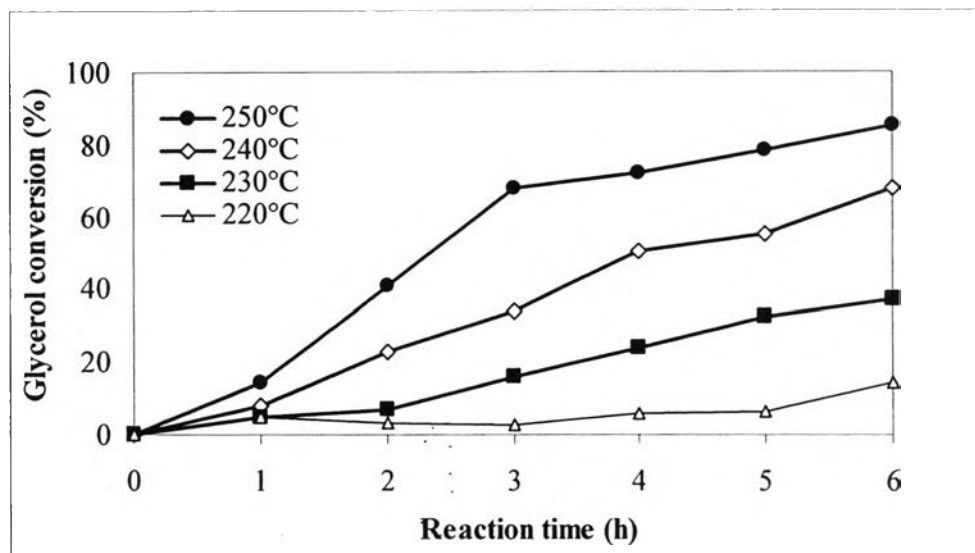


Figure 4.11 The glycerol conversion of CaO for reaction temperature at 230, 240, 250 °C as a function of reaction time under inert nitrogen atmosphere in the presence of 2 wt% of catalyst.

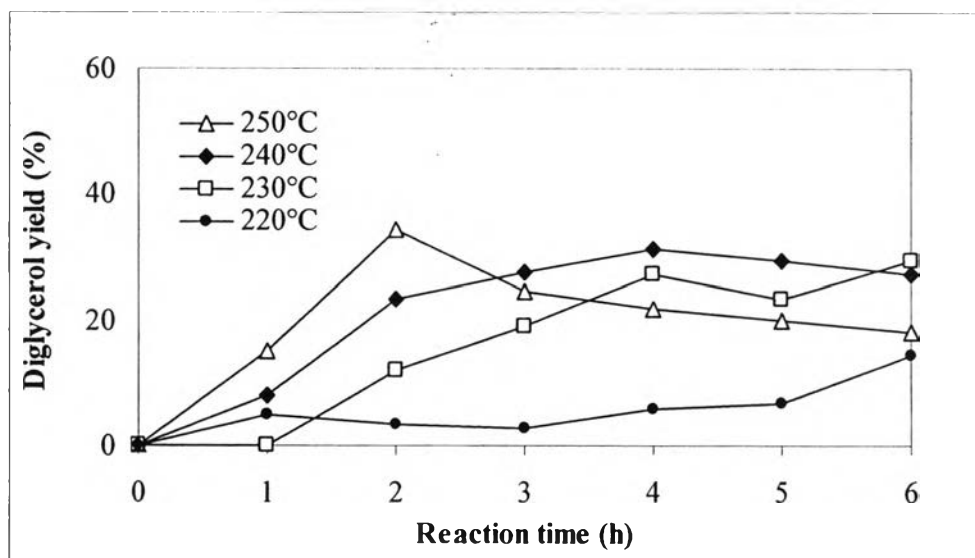


Figure 4.12 The diglycerol yield of CaO for reaction temperature at 230, 240, 250 °C as a function of reaction time under inert nitrogen atmosphere in the presence of 2 wt% of catalyst.

Moreover, the different reaction temperatures show no influence on the diglycerol selectivity as display in Figure 4.13. This means that the temperature increase only the rate of reaction but does not alter the selectivity of diglycerol.

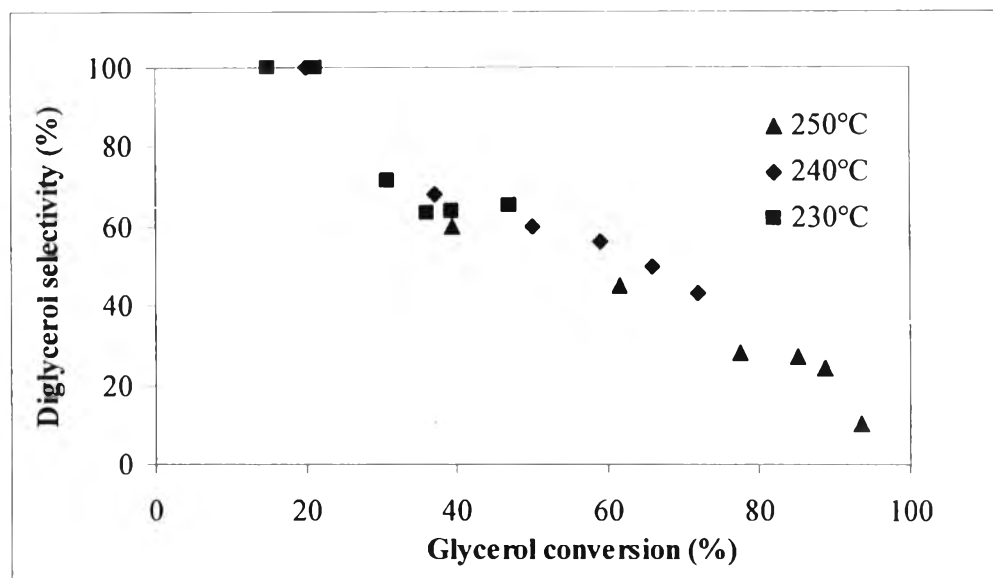


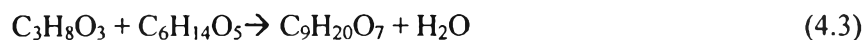
Figure 4.13 The diglycerol selectivity of BaO for reaction temperature at 230, 240, 250 °C as a function of reaction time under inert nitrogen atmosphere in the presence of 2 wt% of catalyst.

4.3 Kinetics and Mechanism

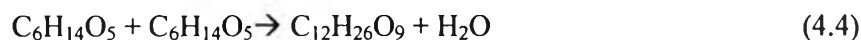
Equation (4.2) describes the stoichiometry of glycerol etherification to diglycerol and equation (4.3) and (4.4) show the further following reaction of the diglycerol to longer molecules. The full reaction model consists of reaction pathways not accessible to an analytical solution of the kinetic equations. However, in this work, the reaction order was determined by integral method at low glycerol conversion. Then, the specific reaction rate constants were evaluated at different temperatures to find out the activation energy.



Glycerol + Glycerol \rightarrow Diglycerol + water



Glycerol + Diglycerol \rightarrow Triglycerol + water



Diglycerol + Diglycerol \rightarrow Tetraglycerol + water

The kinetics investigations started by integrate rate equations for each reaction order. Then the linearized functions of concentration would be plotted with reaction time to find the reaction order. In this method, the suitable order will give a linear relation between the function of concentration and reaction time. For zero order, the glycerol concentration (C_G) versus reaction time for BaO and CaO were plotted as shown in Figure 4.14a and Figure 4.15a. The natural logarithm of concentration ($\ln(C_G/C_{G0})$) as a function of reaction time was used for first order (Figure 4.14b and 4.15b). Finally, second order was investigated by the relation between reciprocal concentration (C_{G0}/C_G) and reaction time (Figure 4.14c and 4.15c). It can be seen that the data in Figure 4.14b and Figure 4.15b which represent for first order tend to be linear more than second order. Therefore, the conversion of glycerol best follows first-order kinetics. This means that first-order kinetics can reasonably represent the data.

The reaction order results were supported by differential method. Figure 4.16 show plots of $[-(dC_G/dt)]$ versus $[C_G]$ on log-log scale where the power obtained is equal to the reaction order. All graphs gave the reaction order close to one (except at 220 °C) which could confirm this reaction is first order.

It could be assume from the reaction that glycerol molecules are attacked by a base (OH^-) at a terminal proton to change the neutral glycerol molecule to an anionic molecule. This anionic glycerol also can attack other glycerol molecule to form diglycerol. Equation (4.5), the large quantity of neutral glycerol can be viewed as constant concentration when comparing with anionic molecule. Therefore, the

reaction depending on only the anionic glycerol concentration is observed as of pseudo first order.

$$r = -k [\text{glycerol}] [\text{glycerol}] \quad (4.5)$$

Where $[\text{glycerol}]$ represents the normal glycerol concentration, $[\text{glycerol}]$ is the concentration of glycerol attacked by OH^- , and k is the rate constant.

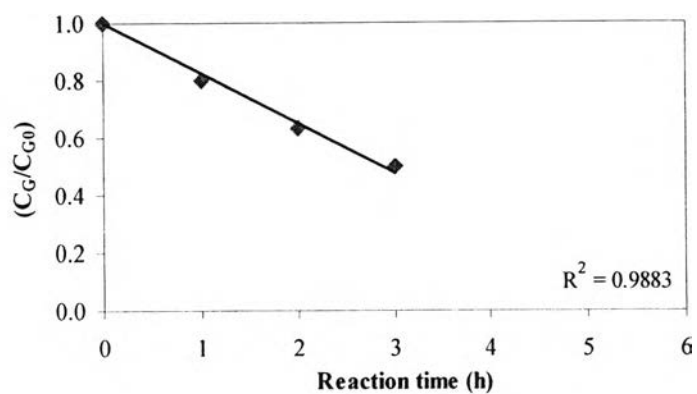
On this basis a pseudo-first-order power law kinetic model was developed for the estimation of kinetic parameters k and E_a . The reaction rate constants of the forward reactions were calculated from experimental data by applying linear regression methods. Kinetic constants were calculated for a series of experiments at a constant temperature (Figure 4.17 and Figure 4.18). The experimental values obtained for the kinetic constants are shown in Table 4.2.

The rate constants obtained from the model fitting were used to determine activation energies by correlating with temperature according to the Arrhenius equation:

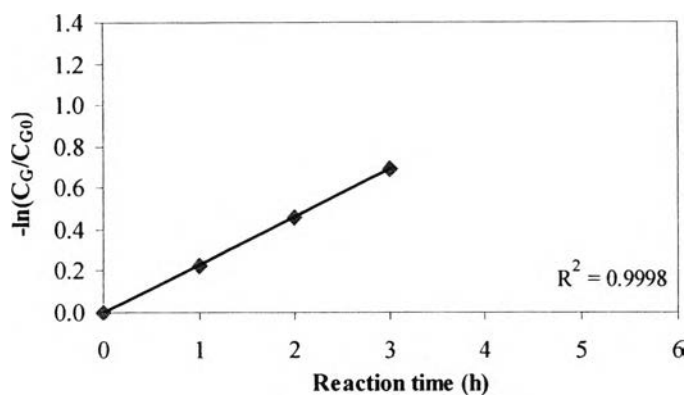
$$\ln(k) = \ln(A) - (E_a/RT) \quad (4.6)$$

Equation (4.6), applying an Arrhenius equation and plotting $\ln k$ versus reciprocal temperature (Figure 4.19), the activation energy obtained was 142.6 and 162.3 kJ/mol for etherification of glycerol using BaO and CaO as a catalyst, respectively. These values agree reasonably well with the basicity of the catalyst that BaO has higher basicity than CaO.

(a)



(b)



(c)

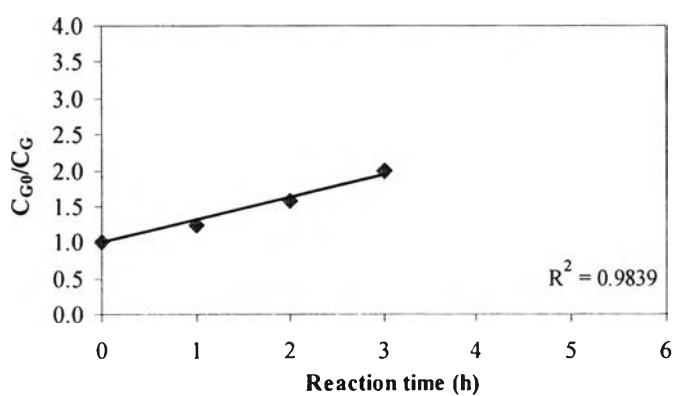
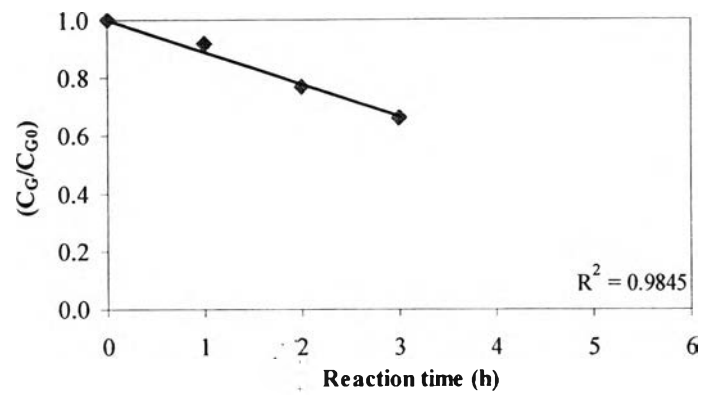
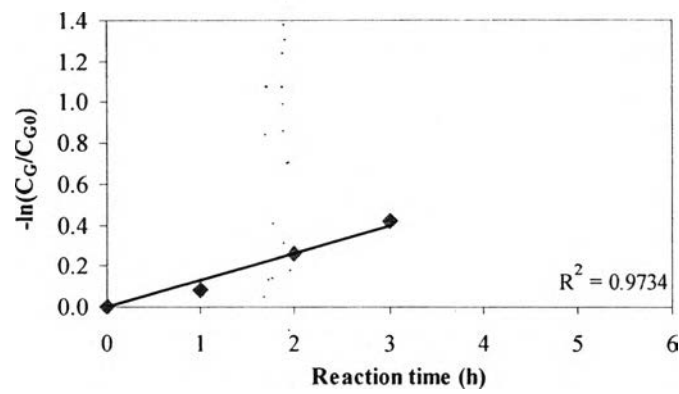


Figure 4.14 The plot of the function of glycerol concentration versus reaction time for 2wt% of BaO at 240°C with zero order (a), first order (b), and second order (c).

(a)



(b)



(c)

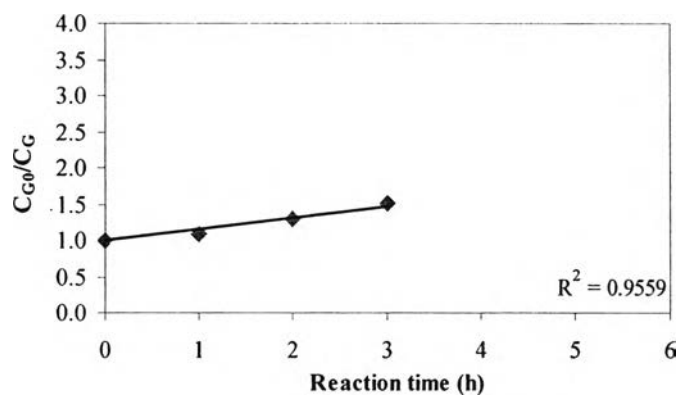


Figure 4.15 The plot of the function of glycerol concentration versus reaction time for 2wt% of CaO at 240°C with zero order (a), first order (b), and second order (c).

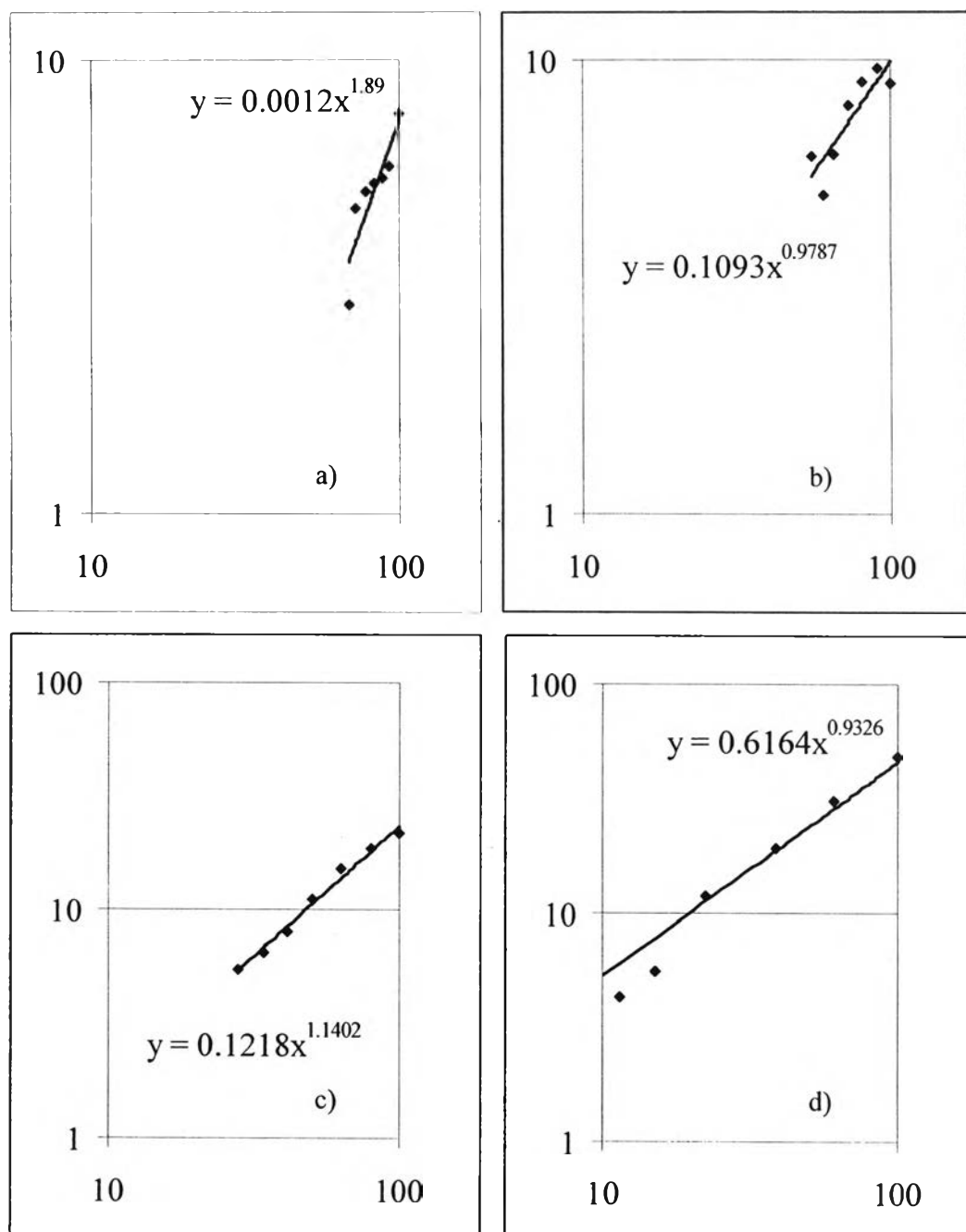


Figure 4.16 Differential method to determine reaction order of BaO at 220°C (a), 230°C (b), 240°C (c), and 250°C (d).

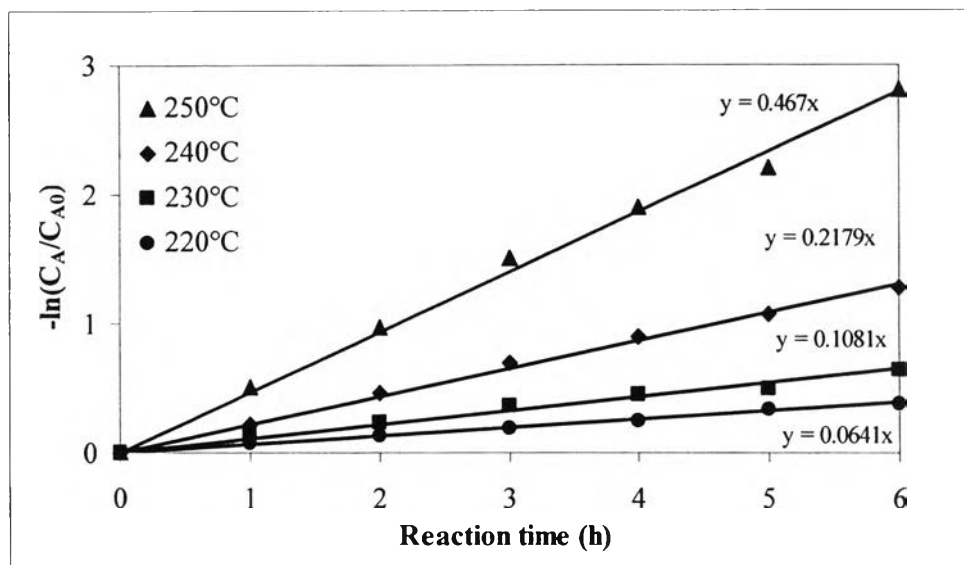


Figure 4.17 The evaluation of the rate constants for the first order reaction at 220, 230, 240, and 250°C of BaO.

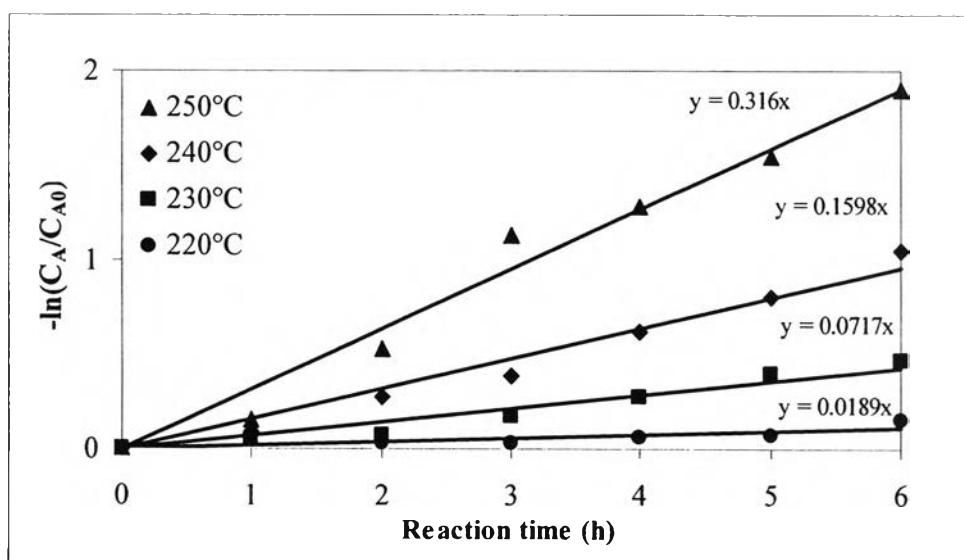


Figure 4.18 The evaluation of the rate constants for the first order reaction at 220, 230, 240, and 250°C of CaO.

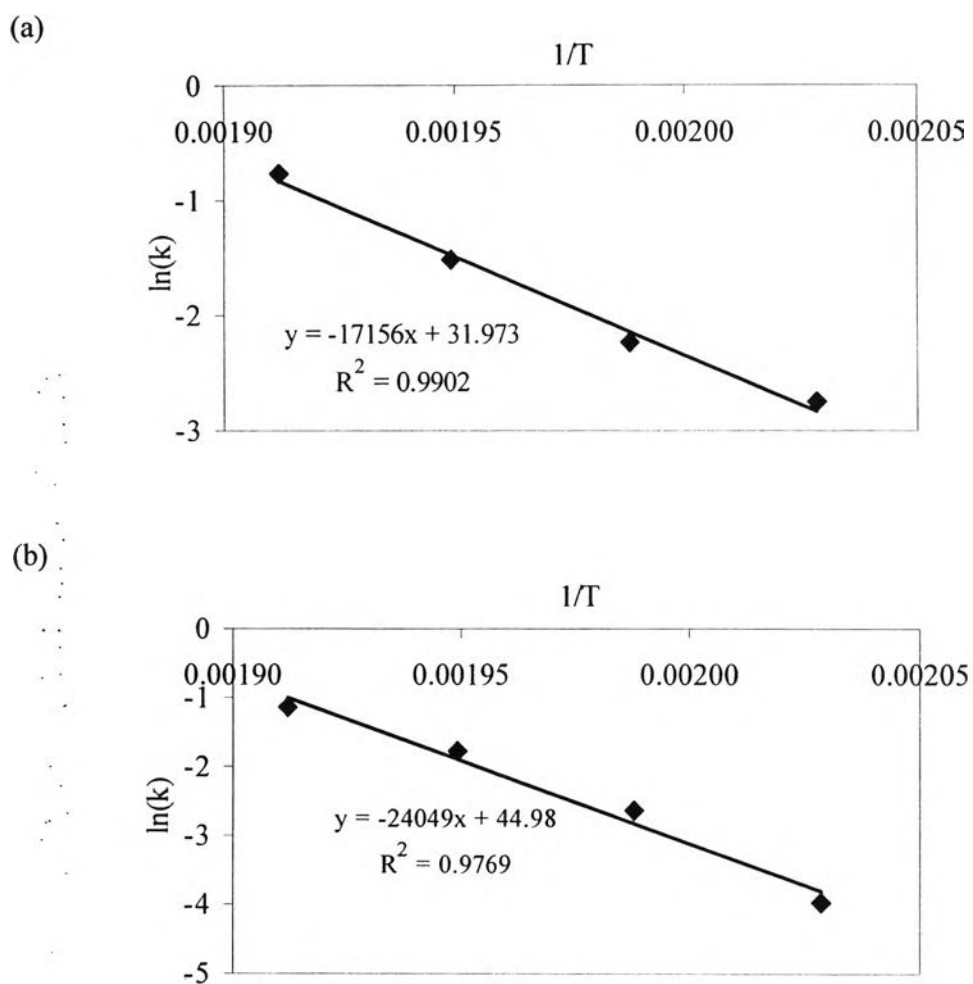


Figure 4.19 Arrhenius plot for etherification of glycerol using (a) BaO and (b) CaO as catalysts.

Table 4.2 Kinetic constant of BaO and CaO

Temperature (°C)	220	230	240	250
k of BaO (h^{-1})	0.064	0.108	0.218	0.467
k of CaO (h^{-1})	0.019	0.072	0.160	0.316

4.4 Pilot Scale Study

In laboratory scale process, the etherification of glycerol was investigated to find the suitable alkaline earth oxides and the operating conditions. CaO which give satisfied activity and has commercial advantages was selected to use further in pilot scale study. An our objective was scaled up to a pilot scale process receiving the real glycerol from biodiesel production. A pilot scale process has been installed at the biodiesel plant as shown in Figure 4.20. The process was initially designed based on laboratory process. The reactor was constructed of a stainless steel cylindrical reactor with a size of 20 kg. The process was heated by four 3,000 watt 3 phases electric coils and was circulated by a 0.5 HP pump. The system was operated at 240°C of 2 wt% CaO loading under nitrogen atmosphere according to the condition from the previous experiments.

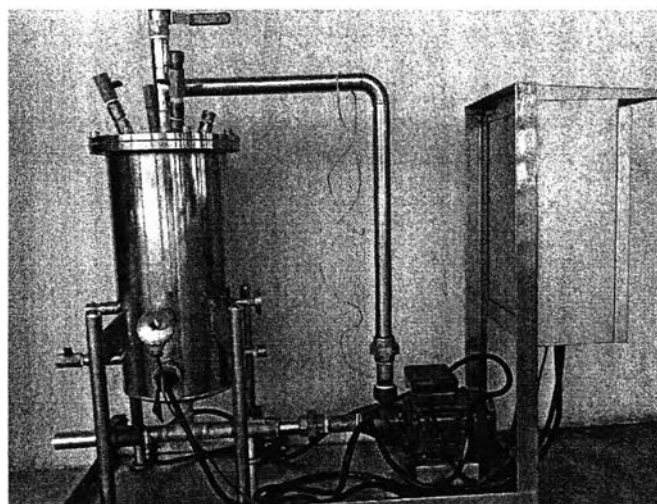


Figure 4.20 The pilot scale reactor.

Figure 4.21 shows the results from pilot scale study. It was observed that trend of concentration for each component is similar to the previous studies. At 6 h of reaction time, the glycerol concentration is about 39 % and diglycerol concentration is 30 %, the rest is triglycerol. However, the glycerol conversion from pilot scale study is still lower than laboratory scale as shown in Table 4.3. This is

possibly due to lower agitation from using pump. Therefore, to improve the process, it may be suggested that the process need longer reaction time than 6 h. Besides, using propeller may be more effective and provide more agitation than pumping. This process uses heterogenous catalyst and is operated at high temperature that can pump damage.

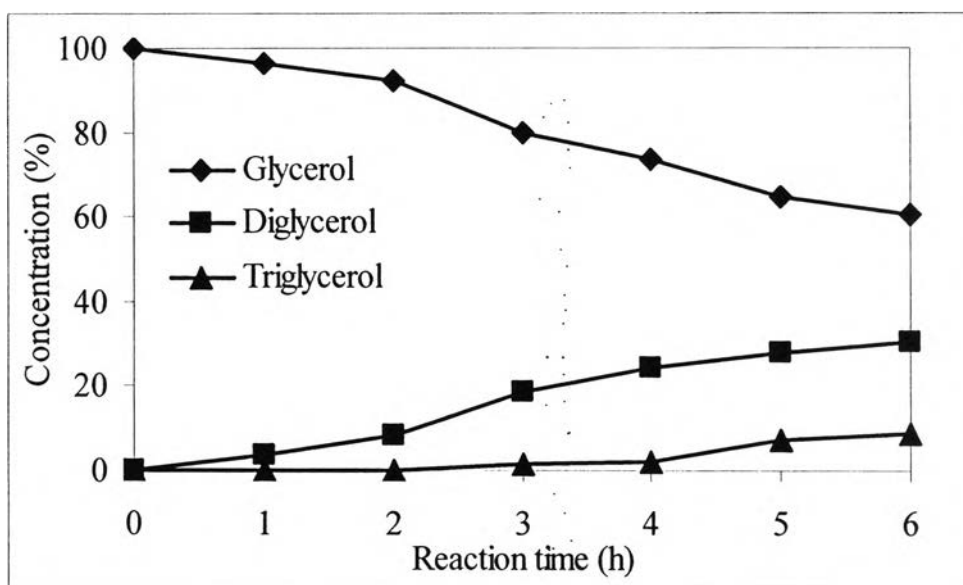


Figure 4.21 The concentration of the glycerol, diglycerol, and triglycerol as a function of reaction time at 240°C of 2 wt% CaO loading under nitrogen atmosphere in pilot scale process.

It can be seen from Table 4.3 that conversion of glycerol and diglycerol yield in the pilot scale study at 6 h of reaction time were parallel with the laboratory scale at 3 h. Therefore, it can be concluded that pathway of reaction is still the same as laboratory but the reaction rate is lower.

Table 4.3 Results from pilot scale study compare to laboratory scale

Experiments	Glycerol conversion (%)	Diglycerol Yield (%)	Diglycerol Selecivity (%)
Pilot (3 h)	20	19	93
Pilot (6 h)	39	30	77
Lab.(3 h)	34	28	81
Lab. (6 h)	68	27	40