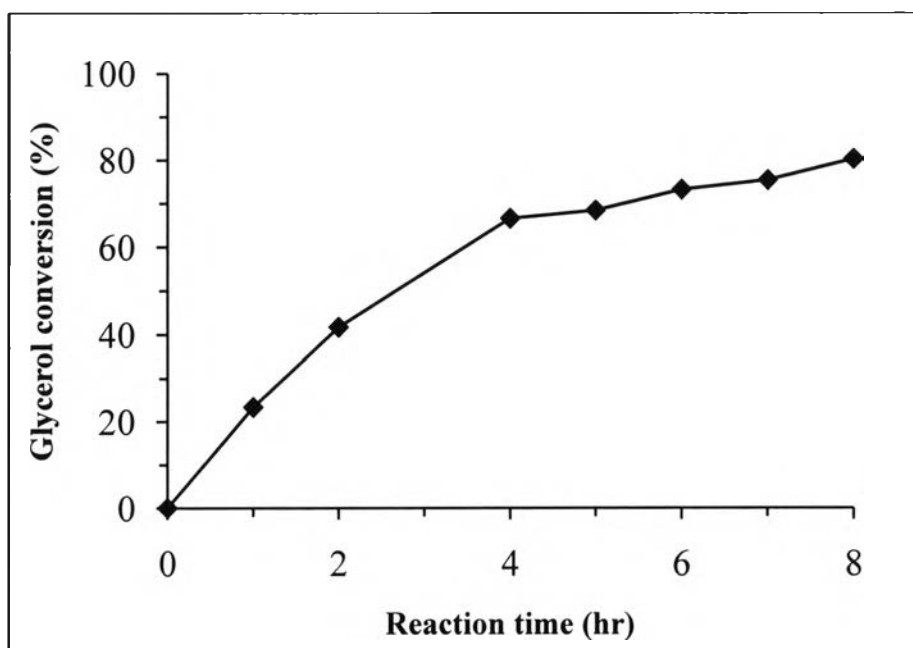


## CHAPTER IV

### RESULTS AND DISCUSSION

#### 4.1 Effect of Reaction Time on Etherification of Glycerol

To study the effect of reaction time on polyglycerol production, the reaction time of glycerol etherification by using alkaline earth oxide as the catalysts was varied up to 8 hrs. Figure 4.1 shows the glycerol conversion at different time when using 2 wt.% of CaO as a catalyst at 240°C under inert nitrogen atmosphere. As expected, the conversion of glycerol increased with reaction time and the maximum conversion could be raised up to 80.25% after 8 hours of reaction time.

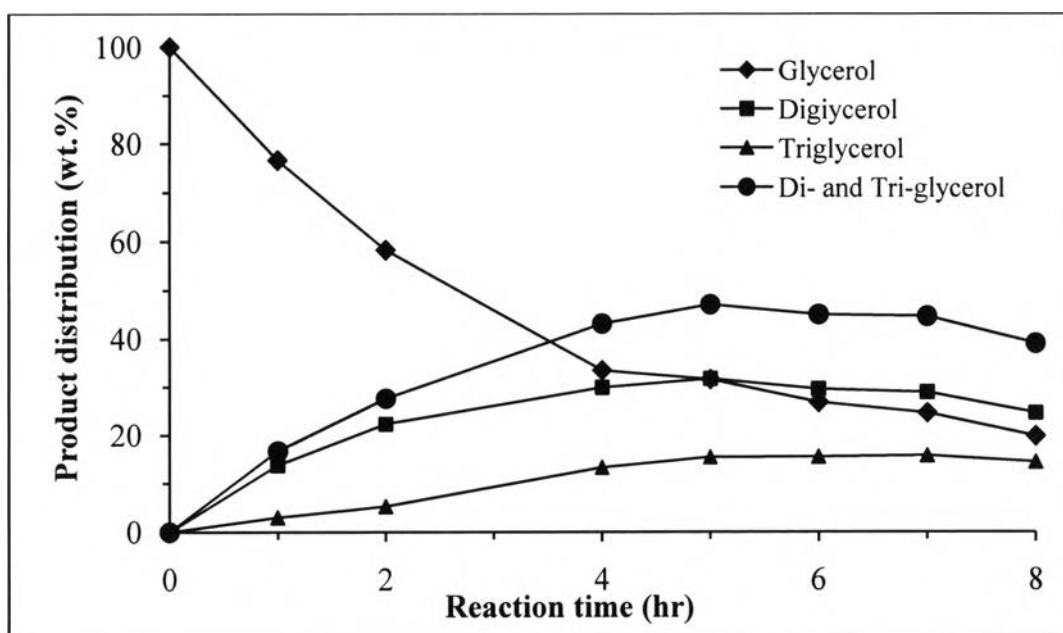


**Figure 4.1** The glycerol conversion for CaO as a function of reaction time at 240°C under inert nitrogen atmosphere in the presence of 2 wt% of catalyst.

At the beginning of reaction, diglycerol was formed as the major product while the higher polymerization degree of polyglycerols started to dominate at higher glycerol conversion. This is due to the fact that diglycerol can also react with glycerol or diglycerol to form tri- and tetraglycerol and so on. Nevertheless, it was

necessary to focus on maximizing di- and tri-glycerol productions as the most recently used in applications.

Interestingly, the maximum summation of weight percent of di- and tri-glycerol were observed at 5 hours of reaction time as shown in Figure 4.2. It was necessary to keep in mind that the product distribution also involved the content of unreacted glycerol. However, the activity of CaO catalysts dropped after the reaction time 5 hours. This could be due to the less selectivities in di- and tri-glycerol over CaO catalysts at higher reaction time. Subsequently, the reaction time at 5 hours was chosen as the optimum condition for further studying in the next section.

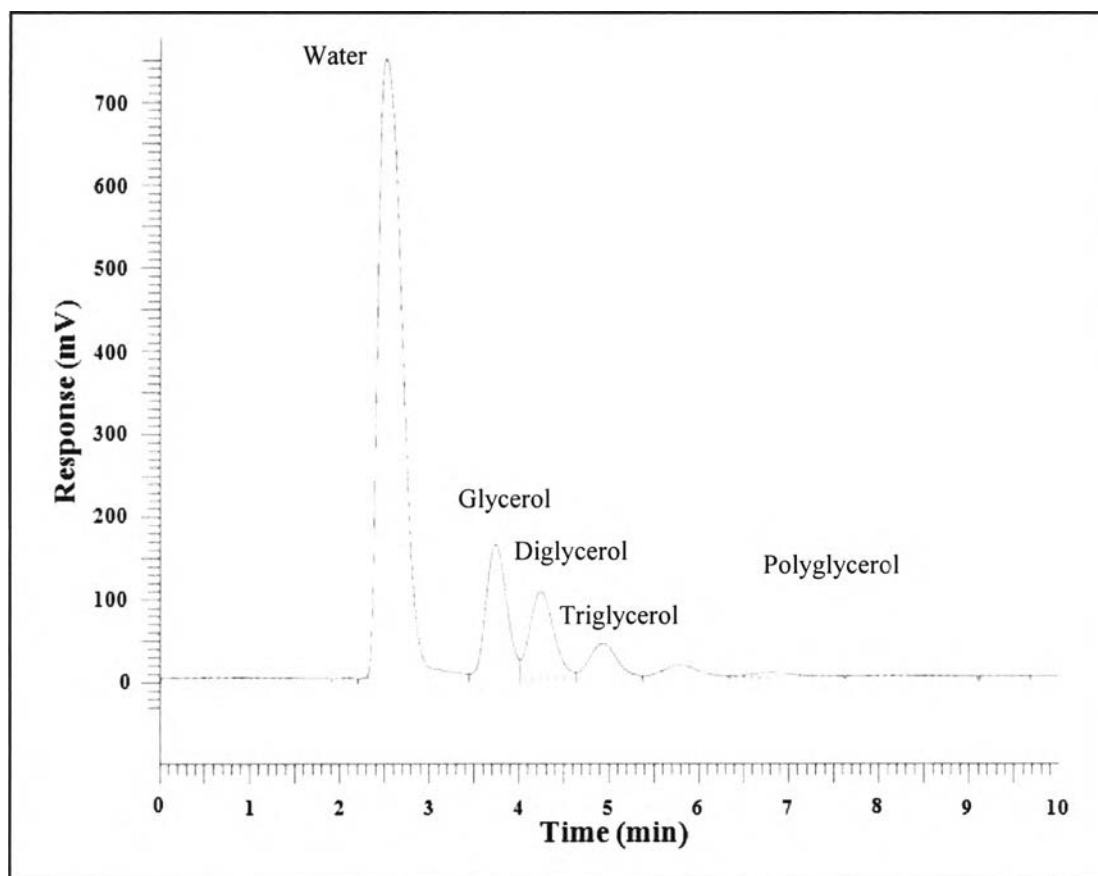


**Figure 4.2** The product distribution for CaO at 240°C under inert nitrogen atmosphere in the presence of 2 wt% of catalyst.

#### 4.1.1 High Performance Liquid Chromatography Analysis (HPLC)

In order to determine the component of polyglycerol produced from the first step, the HPLC was used and the result was shown in Figure 4.3. The intensities of observed peak were represented into three main components—glycerol, diglycerol, and triglycerol—corresponding to the retention time at 3.74, 4.24, and 4.93 min., respectively. After the retention time at 4.93 min., the two remaining peaks

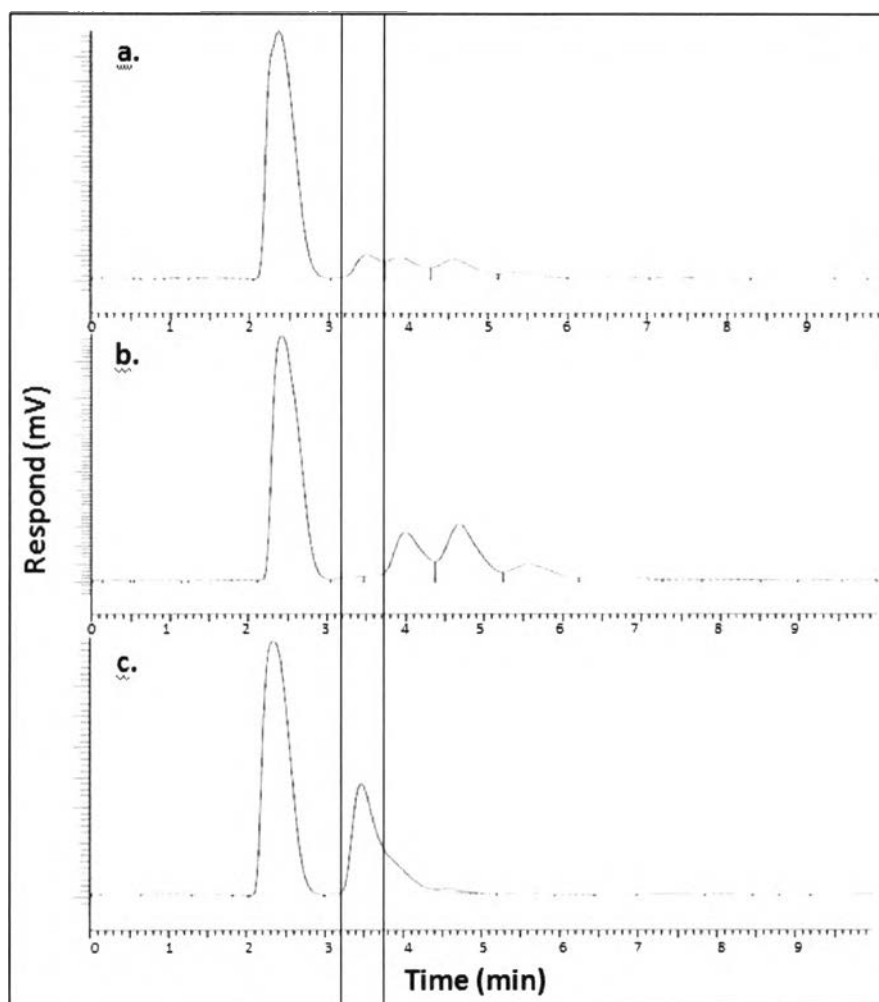
with much weaker signal are referred to polyglycerol. Indeed, the concentration of each component can be related with the area of peak.



**Figure 4.3** HPLC separation of polyglycerol operated for 5 hours of reaction time.

## 4.2 Polyglycerol Purification

The removal of unreacted glycerol was done by using vacuum distillation. The products from previous step contains CaO and must be separated prior to vacuum distillation step. It can be separated by using the centrifuge and filtration. During the vacuum distillation, unreacted glycerol started to come out at 138°C and end up with 200°C. This was agreement with the results of Seiden *et al.* (1976) who proposed that the unreacted glycerol as the remaining reactant in etherification reaction was distilled in the close range of temperature around 149–204°C.



**Figure 4.4** HPLC separation of polyglycerol.(a) the polyglycerol at 5 hours of reaction time; (b) the polyglycerol after distillation; (c) the condensate.

From Figure 4.4, it can be seen that the existence of glycerol can be detected in the interval of 3.2-3.75 minute. According to Figure 4.4 (b), the number of detected glycerol was too weak when compared with Figure 4.4 (a). Based on the calculation, the glycerol was efficiently separated to 85.83% by vacuum distillation; furthermore, the presence of distilled glycerol could also be confirmed in Figure 4.4 (c).

### 4.3 Synthesis of Polyglycerol Ester

Polyglycerol ester was prepared by polyglycerol—product from the etherification step—esterified with oleic acid continuously for 3 hours under the conditions of inert nitrogen atmosphere and the reaction temperature of 180°C. The final products could be classified in the presence of 2 phases layers, as shown in Figure 4.5.



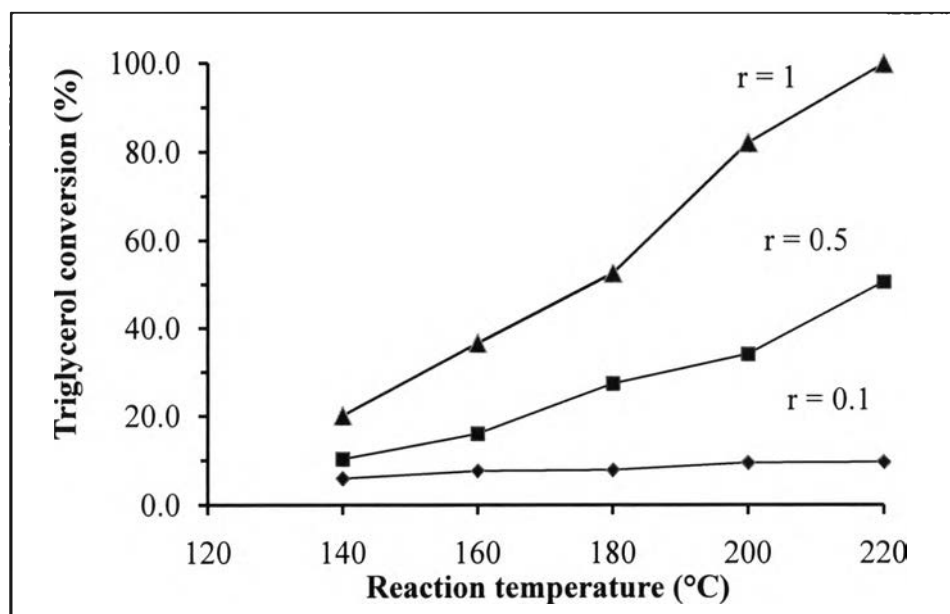
**Figure 4.5** The products from esterification step under the conditions of oleic acid/polyglycerol molar ratio at 0.5, the reaction temperature of 180°C, and 3 hours of reaction time under the inert nitrogen atmosphere.

### 4.4 Effect of Reaction Temperature on Esterification

The reaction temperature was also considered as an important parameter which affects to the triglycerol conversion. In this step, triglycerol obtained from sigma-aldrich was used to esterified with oleic acid for 3 hours under the conditions of inert nitrogen atmosphere in presence of 2wt% of CaO as catalyst. The reaction temperature was varied from 140°C to 220°C. The reactions were done with molar ratio of oleic acid and triglycerol equal 0.1, 0.5, and 1.0.

The effect of temperature on this esterification reaction was shown in Figure 4.6. The results showed the effect of temperature on triglycerol conversion of three ratio of oleic to triglycerol molar ration ( $r$ ) at temperature 140, 160, 180, 200 and 220°C and 3 hour reaction time, The triglycerol conversion increased because reaction temperature could increase the rate of reaction. This is due to the esterification reactions are endothermic in nature as well might be due to the

increased ability of triglycerol conversion with an increase in the operation temperature. For the reaction temperature at 220°C provides highest of triglycerol conversion of three ratio.



**Figure 4.6** The effect of reaction temperature on the triglycerol conversion in various molar ratio of oleic acid and triglycerol (r).

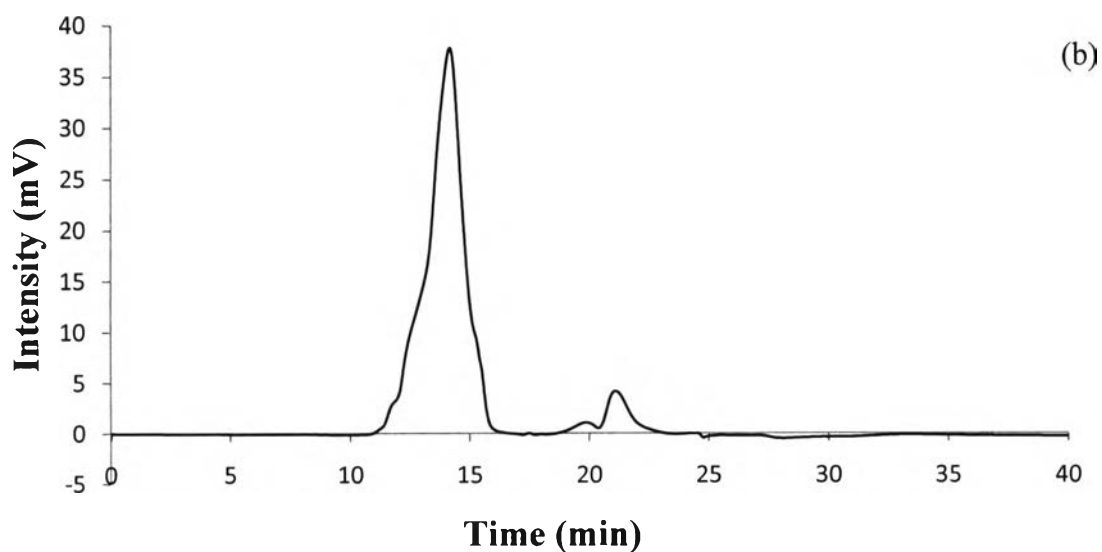
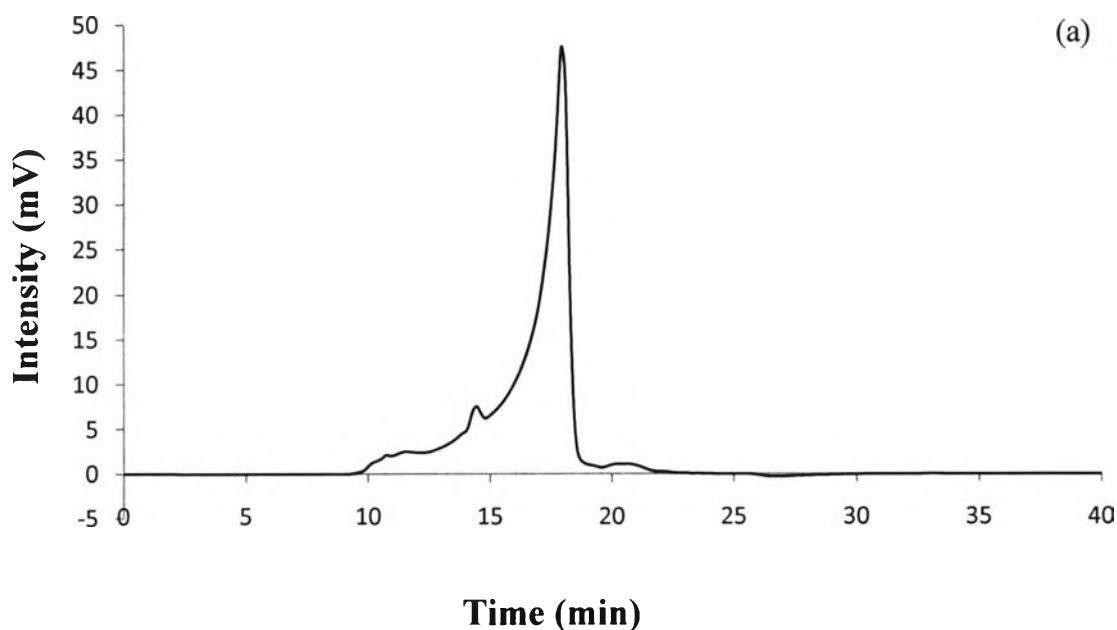
#### 4.5 Effect of Oleic Acid-Polyglycerol Molar Ratio on Esterification

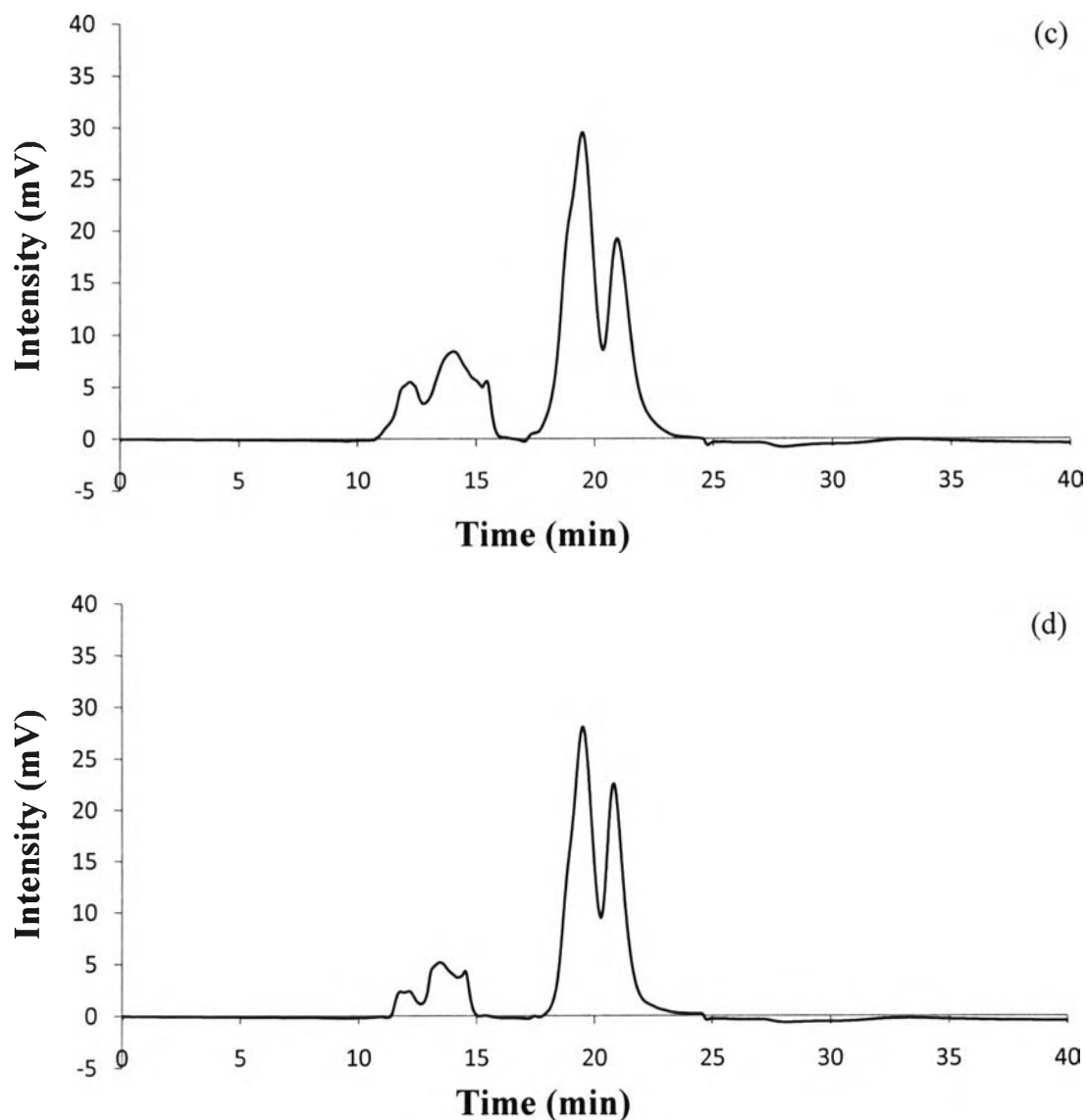
The effect of oleic acid to triglycerol molar ratio (r) was studied at 220°C under inert nitrogen atmosphere in presence of 2wt% of CaO as catalyst for 3 hour. The triglycerol oleate product at r = 0.1 was presented in solid form and r = 0.5 and 1.0 were viscous liquid form.

##### 4.5.1 High Performance Liquid Chromatography Analysis (HPLC)

The component of triglycerol oleate products were analyzed by using HPLC, the results were shown in Figure 4.7. Figure 4.7(a) is the HPLC of oleic acid and Figure 4.7(b), (c), and (d) are the HPLC of the triglycerol oleate obtained from the reaction at r = 0.1, 0.5, and 1.0, respectively. The triglycerol monooleate was

expected to be formed when using triglycerol in excess ( $r = 0.1$ ). The HPLC separation result is shown in Figure 4.7(b), it can be seen that the existence of triglycerol monooleate can be detected in the interval of 10.8-16.0 minute. For the products of the triglycerol oleate obtained from higher molar ratio ( $r = 0.5$  and  $1.0$ ). Their HPLC results are shown in Figure 4.7(c) and (d), the area of triglycerol monooleate peak is decreased in higher ratio. They HPLC peaks at around 17.0-24.0 minute were possibly the triglycerol di- or tri-oleate. Moreover, the oleic acid cannot be detected from the triglycerol oleate products. Therefore, the oleic acid was likely to be completely used up in this step.





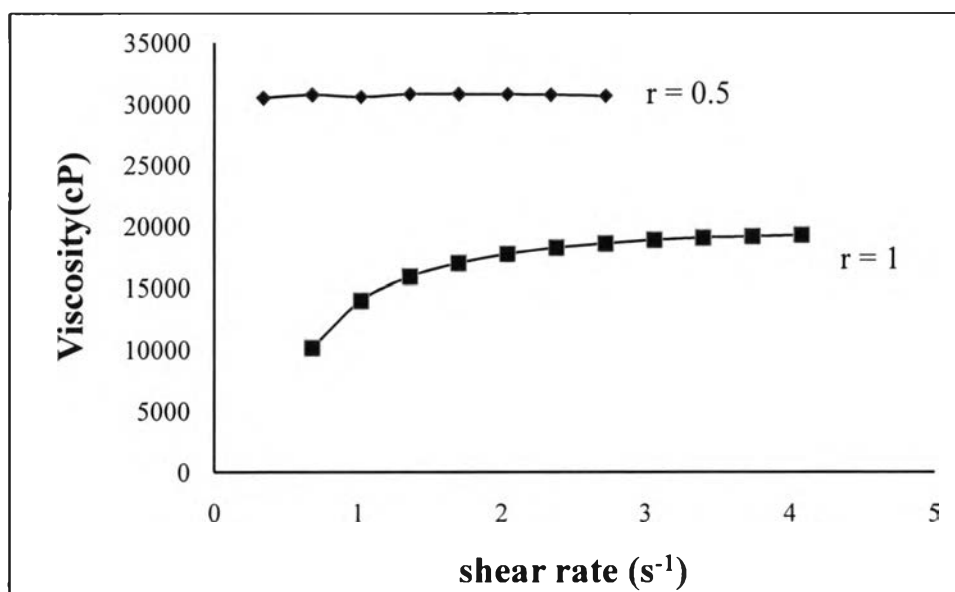
**Figure 4.7** HPLC separation of oleic acid (a) and triglycerol oleate products.(b)  $r = 0.1$  ; (c)  $r = 0.5$ ; (d)  $r = 1$ .

#### 4.5.2 Viscosity of the product

One important property of lubricant is a viscosity. In this work, spindle no. 27 under the room temperature ( $24^{\circ}\text{C}$ ) was used to analyze viscosity of triglycerol monooleate products. The triglycerol oleate were prepared at oleic acid-polyglycerol molar ratio of 0.5 and 1. The viscosity results were shown in Figure 4.8. It can be seen that the viscosity of product at lower oleic acid-polyglycerol molar ratio ( $r = 0.5$ ) was around 30,000 cP higher than viscosity of product at higher oleic



acid-polyglycerol molar ratio ( $r = 1$ ) was around 19,000 cP. Therefore, it can be concluded that the oleic acid-polyglycerol molar ratio could improve of triglycerol oleate's viscosity.



**Figure 4.8** Viscosity of triglycerol oleate product at  $r = 0.5$  and 1.