

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Synthesis of 1,2-O-Isopropylidene Glycerol

4.1.1 Protection Reaction

In this work, the protection reaction or acetonation was obtained by reacting glycerol with acetone. The *p*-toluenesulfonic acid was used as a catalyst. To monitor glycerol conversion and 1,2-O-isopropylidene glycerol formation, the products from the reaction were analyzed by using Gas Chromatography (GC). The example of GC chromatogram are shown in Figure 4.1.

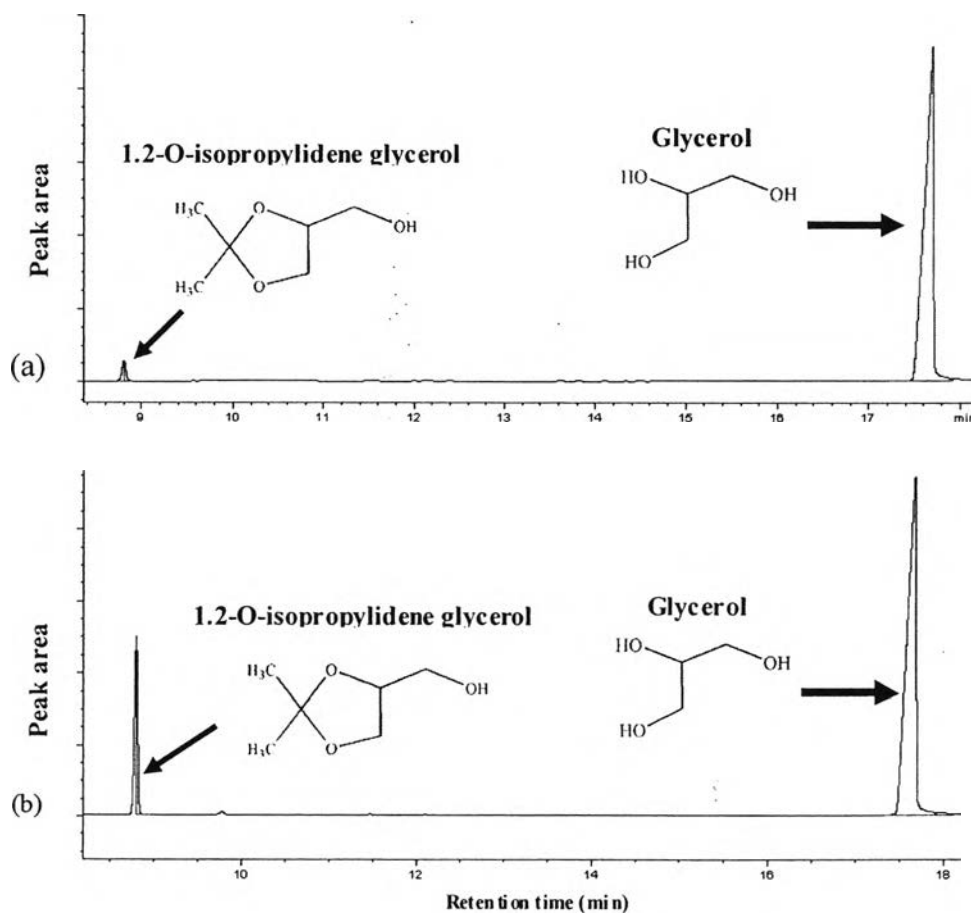


Figure 4.1 GC chromatogram of protection of glycerol: (a) at 6 h reaction time and (b) at 16 h reaction time.

As shown in Figure 4.1, it can be observed that the yield of protected glycerol (1,2-O-isopropylidene glycerol) was increased with reaction time. The synthesis of 1,2-O-isopropylidene glycerol was adapted from the work by Yu and coworkers (2003). But, in this work only two adjacent hydroxy groups on glycerol were protected without using chloroform as solvent and reaction time was extended from 6 h to 16 h. The relation between the reaction time and glycerol conversion was summarized in Figure 4.2. It can be seen that, at 16 h reaction, time the conversion of glycerol is 82.4%.

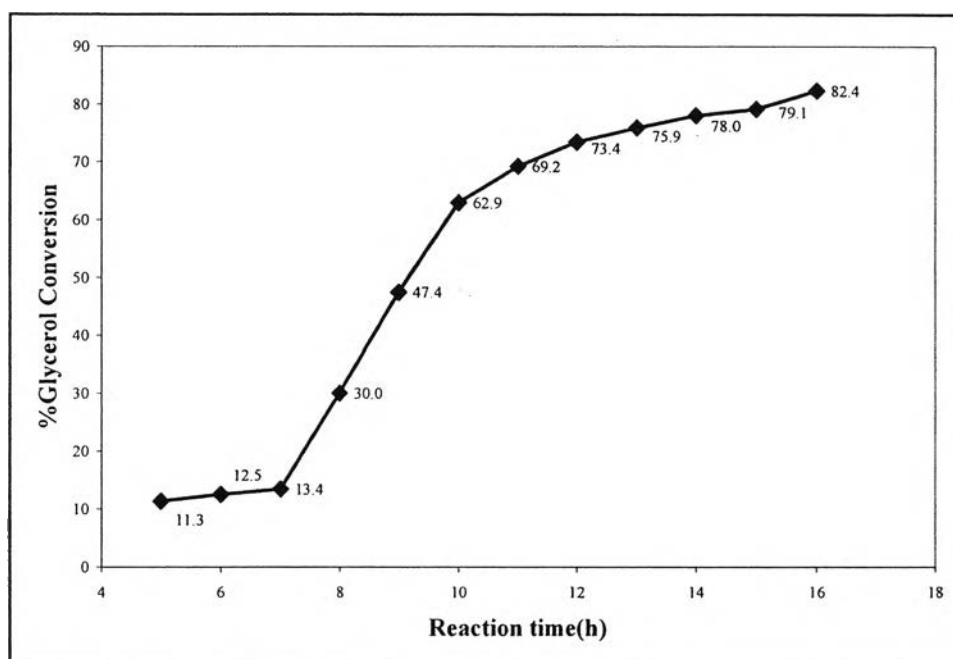


Figure 4.2 Profile of the glycerol conversion in the protection of glycerol as a function of time. The reaction mixture was refluxed at 80 °C, using glycerol to acetone mass ratio of 5:6 and *p*-toluenesulfonic acid as a catalyst under 300 rpm magnetic agitation.

The reaction scheme for protected glycerol formation was shown in Figure 4.3. It can be observed that glycerol is not completely converted to 1,2-O-isopropylidene glycerol due to the equilibrium limitation. It is known that the equilibrium can be shifted by removing one of products or adding the one of

reactants. In this case, water is a byproduct (Figure 4.3), therefore, the rate of reaction and conversion should be improved by removing of water during the reaction.

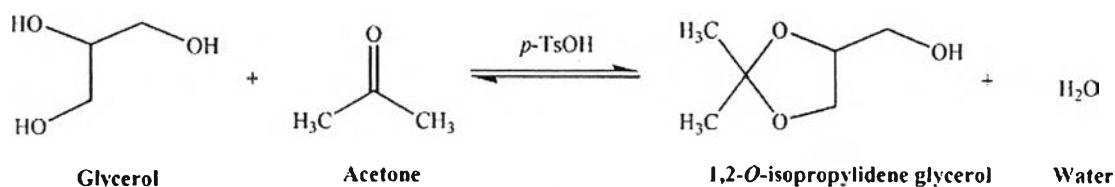


Figure 4.3 Schematic of reaction between glycerol and acetone to obtain 1,2-O-isopropylidene glycerol.

4.1.2 Purification of 1,2-O-Isopropylidene Glycerol

The product was purified by 2 steps-distillation: the first distillation had been done under atmospheric condition to remove the excess acetone and then another distillation had been done under vacuum (10 mmHg) condition. After distillation, the purity of the product was analyzed by GC. The glycerol's peak was disappeared and only the peak of 1,2-O-isopropylidene glycerol was present. The FTIR spectra of purified 1,2-O-isopropylidene glycerol is illustrated in Figure 4.4 and summarized in Table 4.1.

Table 4.1 IR spectra of 1,2-O-isopropylidene glycerol from protection step

Band	Frequency range (cm ⁻¹)
• OH stretching	3400-3200
• CH stretching	3000-2800
• CH bending	1470-1350
• COC stretching	1250-1070

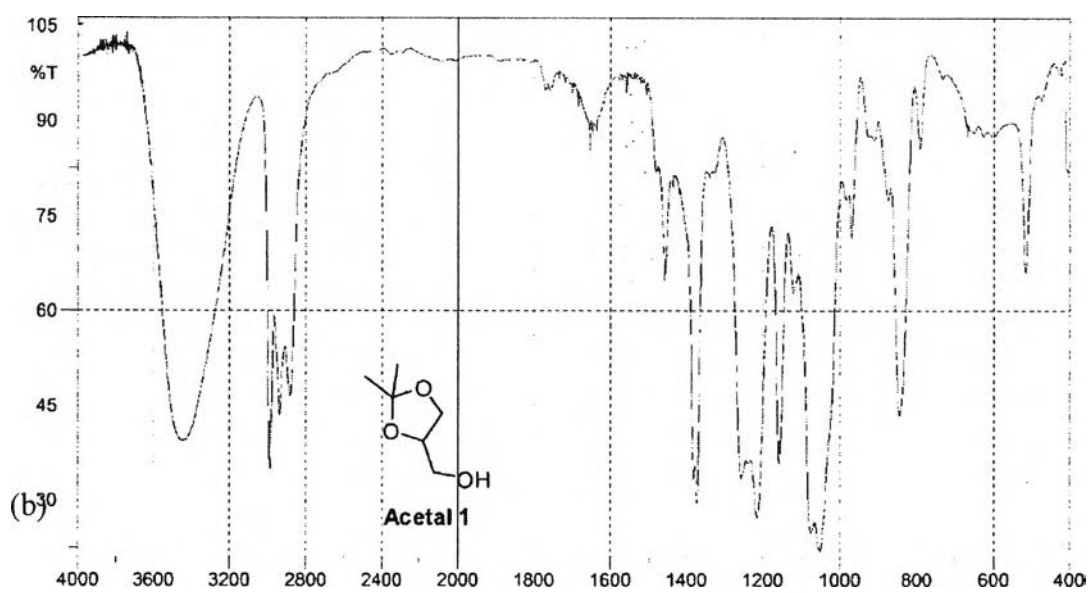
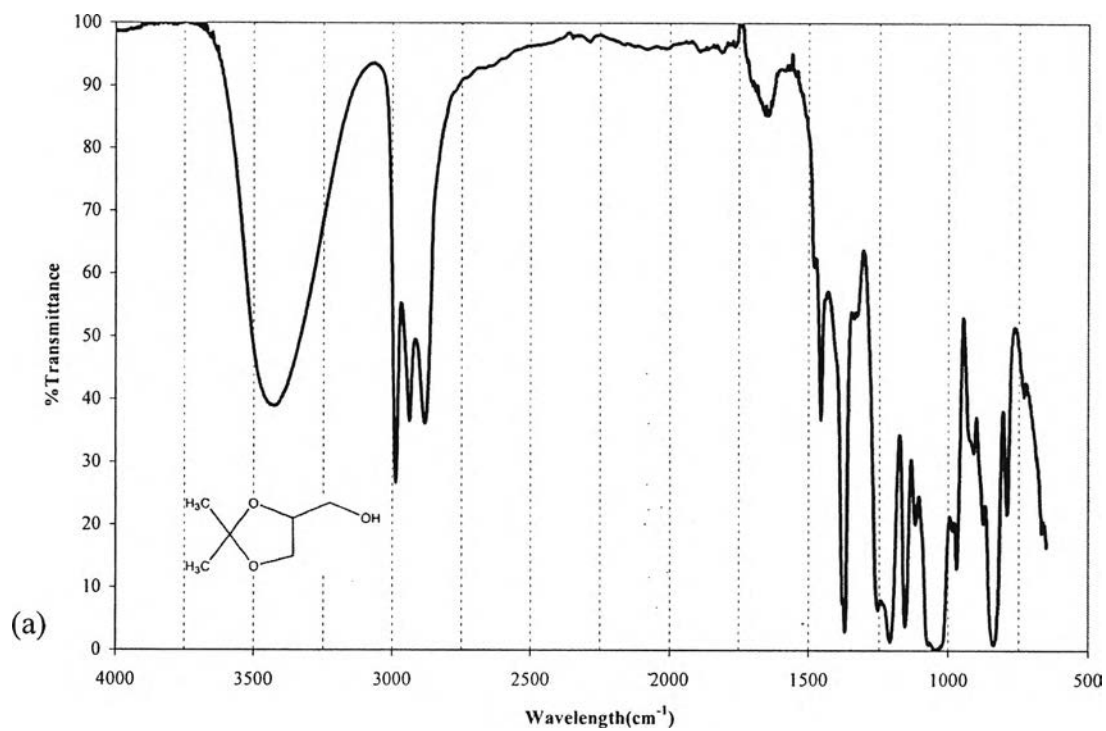


Figure 4.4 IR spectra of 1,2-isopropylidene glycerol: (a) from this work and (b) from García and coworker (2008).

IR spectra pattern of 1,2-O-isopropylidene glycerol from protection step as Figure 4.4(a), comparing to Figure 4.4(b), which is the IR spectrum of 1,2-O-isopropylidene glycerol from García and coworkers (2008). It can be observed that both spectra are identical.

Besides IR characterization, the purified product from protection step was also identified by Nuclear Magnetic Resonance Spectroscopy (NMR). The chemical shift of purified 1,2-O-isopropylidene glycerol; $^1\text{H-NMR}$: $\delta = 1.346$ (3H), 1.415 (3H), 3.549 (1H), 3.680 (1H), 3.779 (1H), 4.026 (1H), 4.213 (1H) and 4.223 (1H); $^{13}\text{C-NMR}$: $\delta = 25.230$, 26.660, 62.075, 76.106 and 109.391. From IR and NMR results, it can be concluded that the 1,2-O-isopropylidene glycerol synthesis was successful. Indeed, the reaction of glycerol with acetone in the presence of acid catalyst should give the two possible cyclic ketals, 1,2-O-isopropylidene glycerol and 1,3-dioxane (as illustrated in Figure 4.5).

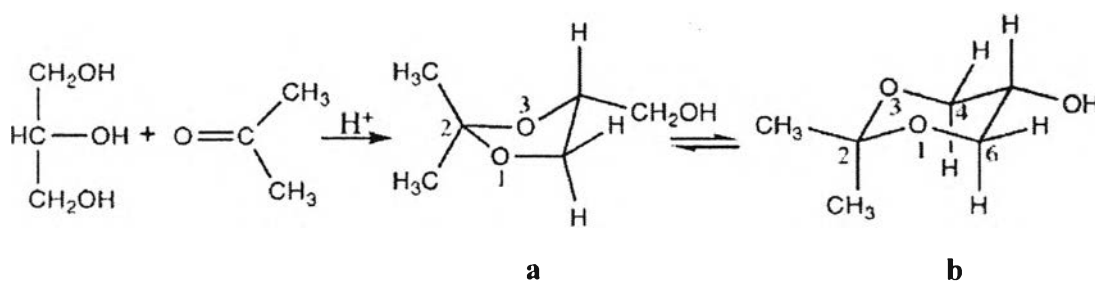


Figure 4.5 Reaction of glycerol with acetone in the presence of acid catalyst (Miljkovic *et.al.*, 2009).

However, from NMR result reveals that 1,3-dioxane formation is insignificant. The reason why the formation of 1,3-dioxane is neglected is six-membered O-isopropylidene ketal is disfavorable because one methyl group must take the axial orientation in the chair conformation of 1,3-dioxane ring **b** and this conformation is even less favorable since the C-O bonds are shorter (1.43 Å) than the C-C bonds (1.54 Å).

4.2.1 Effect of Molar Ratio of Protected Glycerol to Refined Palm Oil on Transesterification

The protected glycerol is then transesterified with refined palm oil. The schematic diagram of this reaction is shown in Figure 4.6. The transesterification was performed by using sodium hydroxide as homogeneous catalyst at 1% by wt. (based on the protected glycerol). The reaction was carried out at 140 °C for 5 h under nitrogen atmosphere and 300 rpm magnetic agitation. To investigate the effect of protected glycerol to refined palm oil molar ratio on protected monoglyceride formation, the molar ratio was varied at 5:1, 7:1, 10:1, 13:1 and 17:1.

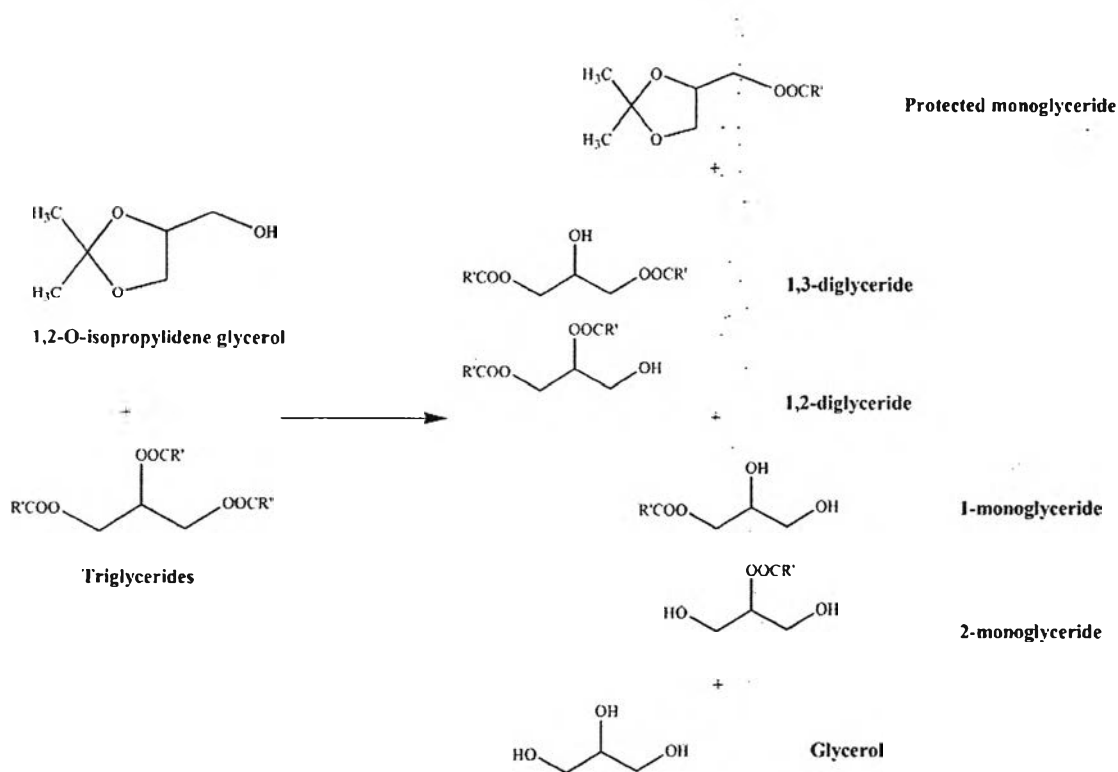


Figure 4.6 Schematic of transesterification of refined palm oil with protected glycerol.

After transesterification was terminated, the liquid was separated into two phases. The upper phase is oil-soluble phase consisting of unreacted triglycerides, diglycerides and protected monoglycerides; and the lower phase is

excess unreact protected glycerol phase. The transesterified products in oil-soluble phase were analyzed both qualitatively and quantitatively by HPLC.

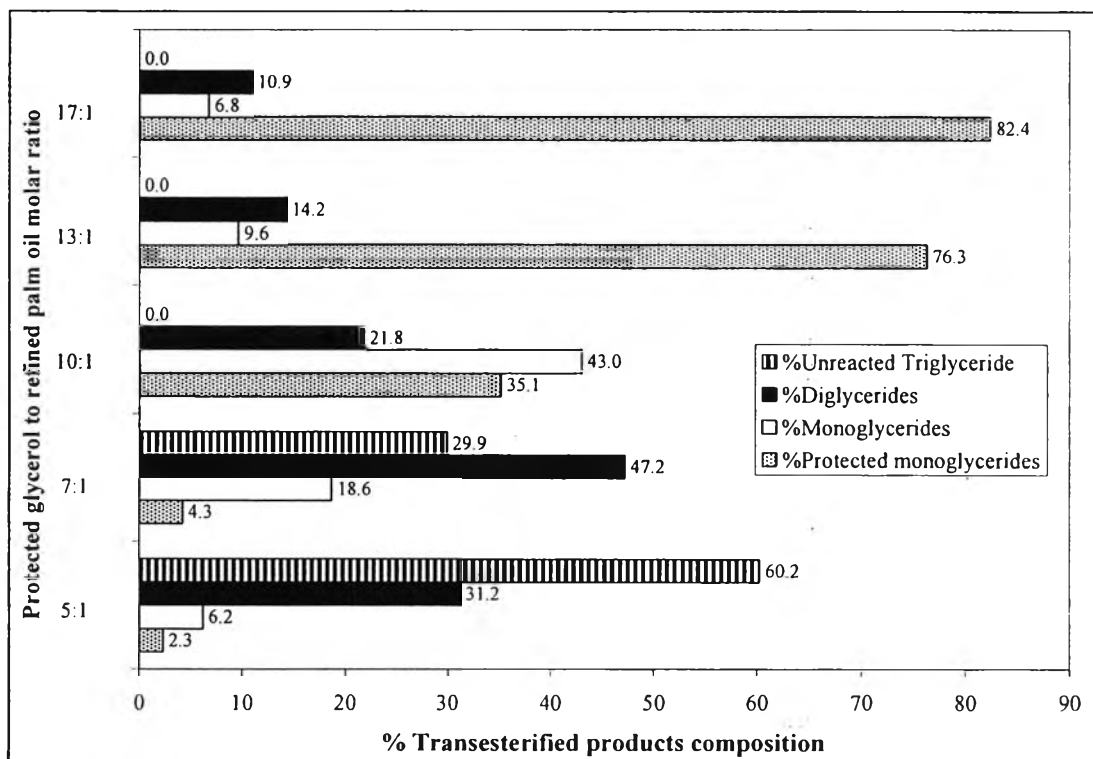


Figure 4.7 Effect of protected glycerol to refined palm oil mass ratio on protected monoglyceride formation. The reaction was carried out at 140 °C for 5 h under nitrogen atmosphere and 300 rpm magnetic agitation.

Subsequently, the transesterified products, were analyzed by HPLC. As illustrated in Figure 4.7, the protected monoglycerides (1,2-O-isopropylidene monoglycerides) increased with the increasing molar ratio of protected glycerol to refined palm oil. At the molar ratio of 5:1 and 7:1, the triglycerides contents in oil-soluble phase were still high (60.2 % and 29.9% respectively). Moreover, the conversion of triglycerides at ratio of 5:1 and 7:1, as shown in Figure 4.7, were not completely transesterified (39.8% and 70.1%, respectively). On the other hand, if the protected glycerol to refined palm oil molar ratio was increased to 10:1, 13:1 and 17:1, triglycerides were completely converted to other esters, as summerized in

Figure 4.8. Besides, the higher protected glycerol to refined palm oil molar ratio, particularly 10:1, 13:1 and 17:1, resulted in other ester formation, the protected monoglycerides content increased (35.1%, 76.3% and 82.4%, respectively) while the monoglycerides decreased (43.0%, 9.6% and 6.8%, respectively) as well as diglycerides content decreased (21.8%, 14.2% and 10.9%, respectively). The explanation for this phenomena is that at low ratio of protected glycerol to refined palm oil, the transesterified products, consisting of protected monoglyceride, monoglycerides and diglycerides, were produced from only reaction between protected glycerol and triglyceride so transesterified products formations increased with protected glycerol to refined palm oil molar ratio. Nevertheless, at high molar ratio of protected glycerol to refined palm oil, not only the transesterification between protected glycerol and triglyceride was in the system but the transesterification between protected glycerol and monoglycerides or diglycerides were in the system also. Hence, at high ratio of protected glycerol to refined palm oil, the monoglycerides and diglycerides formation decreased since these formed esters were further transesterified to protected monoglyceride.

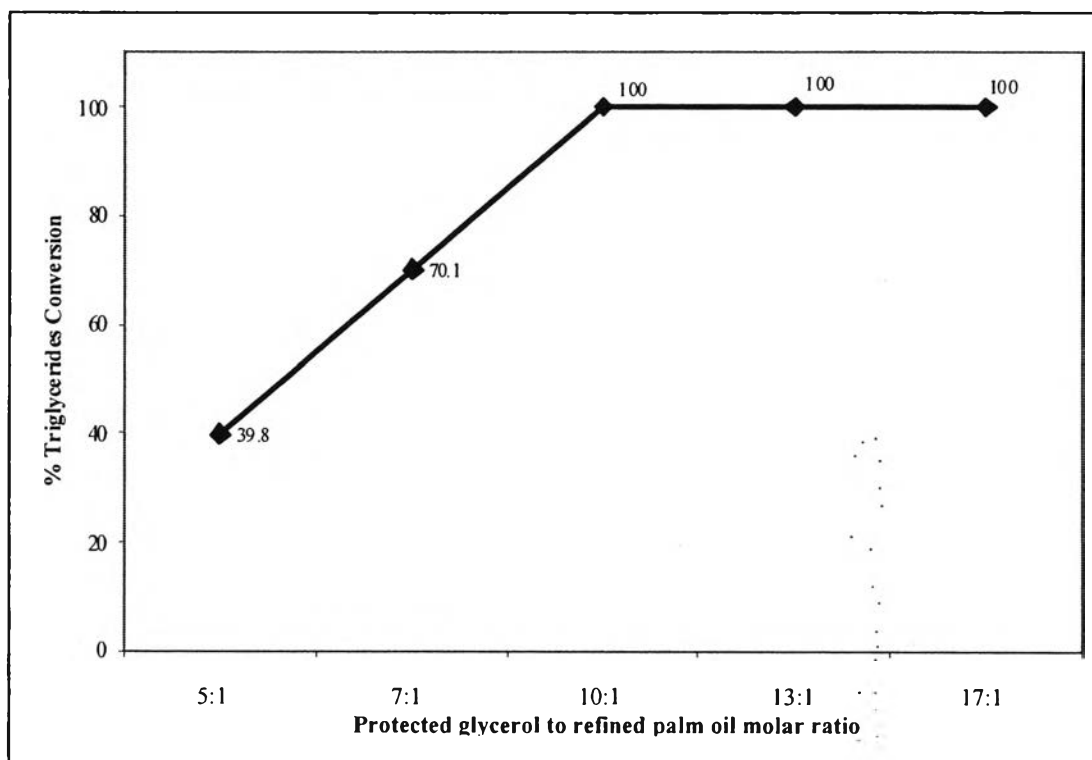


Figure 4.8 Effect of protected glycerol to refined palm oil mass ratio on triglycerides conversion. The reaction was carried out at 140 °C for 5 h under nitrogen atmosphere and 300 rpm magnetic agitation.

As a result, the protected monoglycerides content increased with protected glycerol to refined palm oil molar ratio increased because the excess amount of protected glycerol leading to avoid the other byproduct formation such as mono-, diglycerides and glycerol and provide high conversion of triglycerides and yield of protected monoglycerides. Stoichiometrically, as shown in Figure 4.9, for every one mole of triglycerides, it requires three moles of protected glycerol to yield three moles of protected glycerol and one mole of glycerol.



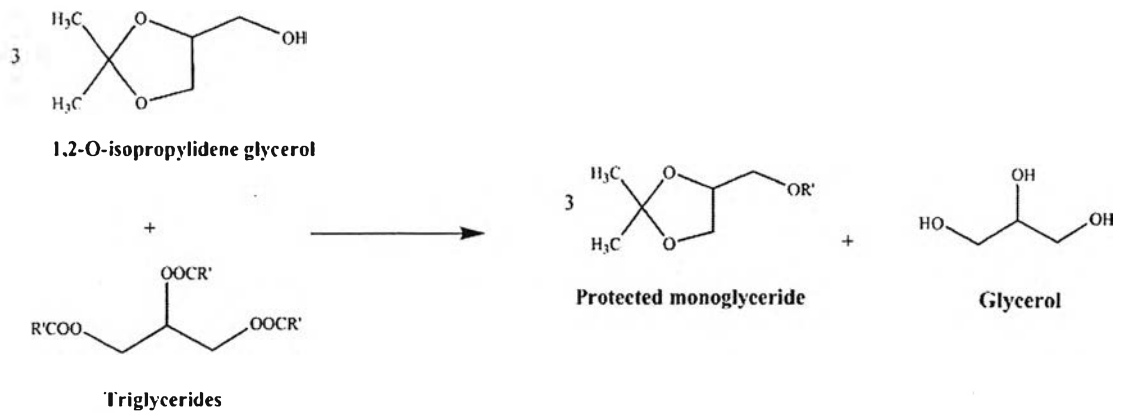


Figure 4.9 Schematic of reaction of theoretical transesterification of triglycerides with protected glycerol.

Nevertheless, the triglycerides may not totally transesterified with protected glycerol or the formed glycerol can also react resulting in others glycerides such as monoglycerides and diglycerides. This should be taken into account that the chemical reaction for transesterification represented as Figure 4.9 is a simplification, since it considers the formation of the predominant protected monoglycerides only. Thus, the high yield of protected monoglycerides can be reached by using the excess amount of protected glycerol in order to provide high conversion of triglycerides and yield of protected monoglycerides.

4.2.2 The Effect of Reaction Temperature on Transesterification of Refined Palm Oil with Protected Glycerol

To study the effect of reaction temperature, the transesterification with protected glycerol to refined palm oil molar ratio of 17:1; 5 h reaction time and catalyst concentration 1% wt. was performed at various reaction temperatures ranging from 120 °C to 180 °C. The results were shown in Figure 4.10.

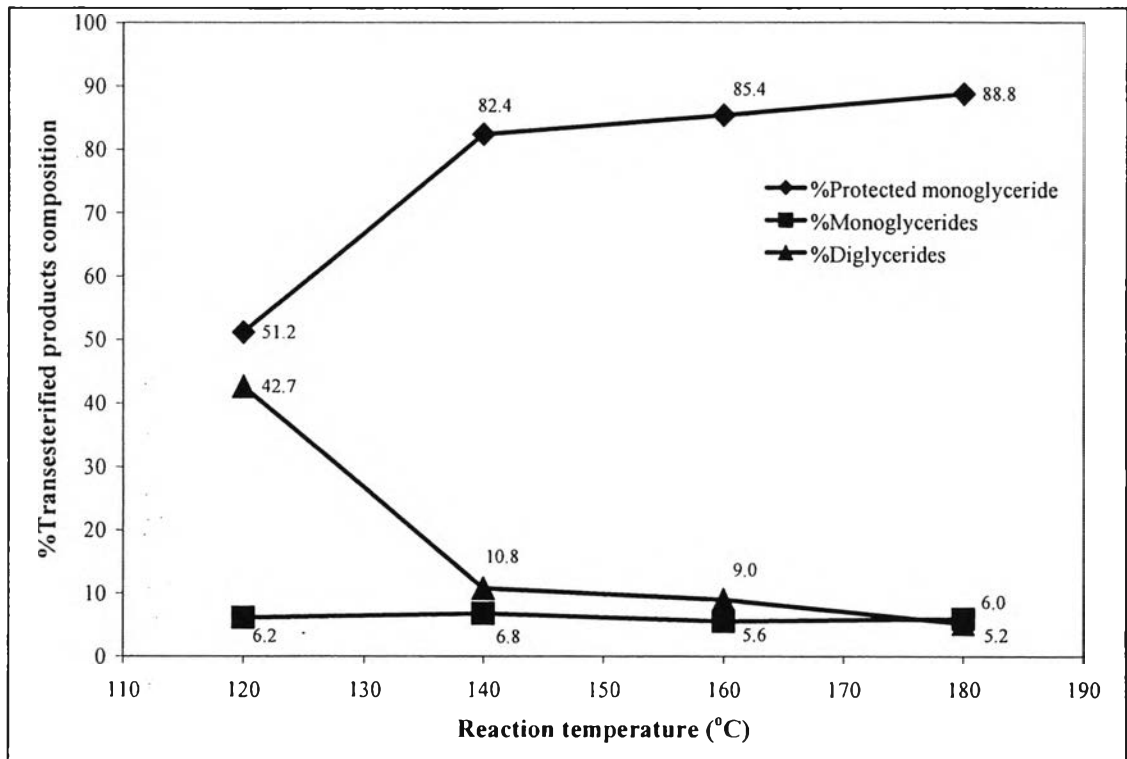


Figure 4.10. Effect of reaction temperature on protected monoglyceride formation. The reaction was carried out using fixed protected glycerol to refined palm oil molar ratio of 17:1 with various temperatures for 5 h under nitrogen atmosphere and 300 rpm magnetic agitation.

For the 5h–reaction time, the transesterification temperature at 120 °C provided lowest selectivity of protected monoglycerides. On the other hand, the protected monoglycerides selectivity increases with transesterification temperature (140, 160 and 180 °C). It can be explained that, reaction takes place in the oil soluble phase, and at lower temperature, the solubility of protected glycerol into oil-soluble phase is low, therefore, the high yield of protected monoglycerides cannot be obtained. The reaction will proceed faster as protected glycerol solubility in the oil-soluble phase increases (Ferretti et. al., 2009) and also the rate of reaction increases with temperature (Corma et. al., 1998). Moreover, the darker color of the reaction mixture at 180 °C suggests that at higher temperature, the more degraded products are formed. As a result, the high reaction temperature (above 180 °C) is not suggested because it is near its boiling point and leading protected glycerol to deteriorate.

4.2.3 1,2-O-isopropylidene Monoglycerides Identification by Fourier Transform Infrared Spectroscopy (FTIR)

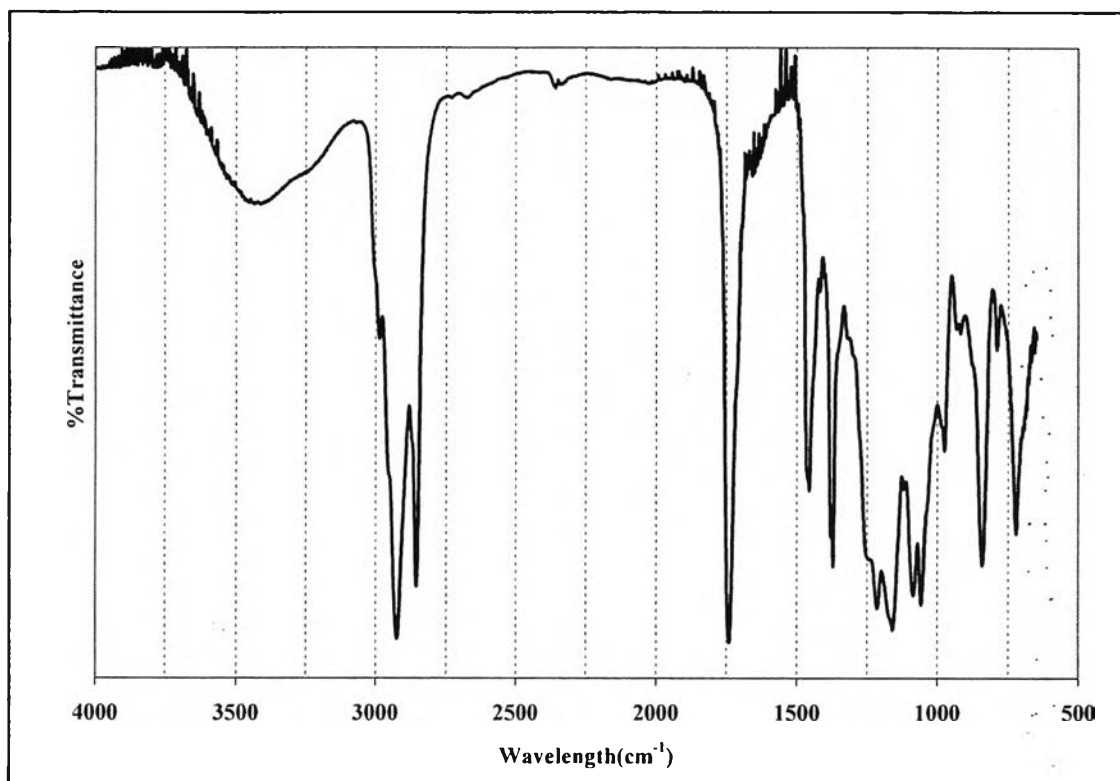


Figure 4.11 IR spectra of 1,2-O-isopropylidene monoglycerides (protected monoglycerides) synthesis.

Figure 4.11 illustrates the FTIR result of transesterified product from transesterification, with protected glycerol to refined palm oil molar ratio of 17:1 at 140 °C for 5 hr under nitrogen atmosphere and 300 rpm stirring agitation. The spectra of transesterified product is illustrated in Table 4.2. The carbonyl stretching band (1750-1700 cm⁻¹) can be observed, which indicates the present of ester group in the sample.

Table 4.2 IR spectra of 1,2-O-isopropylidene monoglyceride from transesterification step

Band	Frequency range (cm ⁻¹)
• CH stretching	3000-2800
• CO stretching	1750-1700
• CH bending	1470-1350
• COC stretching	1250-1070

4.3 Deprotection of Protected Monoglycerides

Selective deprotection or removal of 1,2-O-isopropylidene protecting group is an important step to convert protected monoglycerides (1,2-O-isopropylidene monoglycerides) to glycerol monoglycerides. Firstly, *p*-toluenesulfonic acid was used as acid homogeneous catalyst for ethanolysis but the yield of glycerol monoglycerides was very low due to the hydrolysis of ester group (Yu et. al., 2003). Hence, Dowax®M-31 (wet) ion-exchange resin was then applied to use as acid heterogeneous catalyst instead of *p*-toluenesulfonic acid, the reaction had been done by adding 10 g of transesterified product in ethanol (95%) 40 mL, then refluxed for 3 h in the presence of Dowax®M-31 (1.0 g). The reaction scheme was shown in Figure 4.12. After finish the reaction, the catalysts was easily filtrated out, and then the deprotected product was analyzed by HPLC and FTIR.

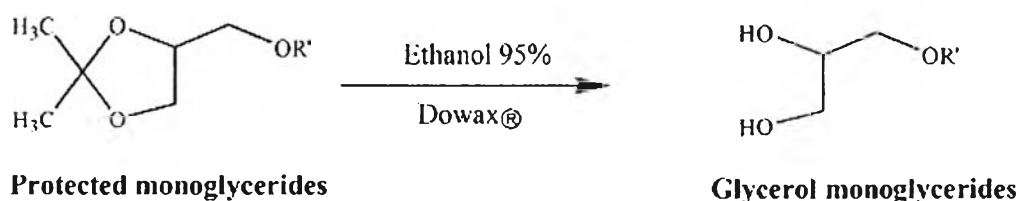


Figure 4.12 Deprotection of protected monoglycerides (isopropylidene group removal).

After filtration, the product was analyzed by HPLC, the result reveals that the yield of glycerol monoglyceride was 65.8% which is higher than the yield of reaction when *p*-toluenesulfonic acid was used as a catalyst. However, the yield of glycerol monoglyceride (65.8%) from ethanolysis with Dowax®M-31 (wet) ion-exchange resin was still low since the water slow down the reaction rate and the hydrolysis product of ester group was increased. Although, the water adding may affect to reaction rate, water is still necessary in this deprotection step in order to decrease catalyst swelling. Due to water content limitation, the extended reaction time should be further investigated.