

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Synthesis of Protected Glycerol (Solketal) from Glycerol

Glycerol and acetone are the raw materials used for producing protected glycerol (solketal) by condensation reaction. Solketal or isopropylidene glycerol contains the center of glycerol backbone which an isopropylidene group bound to two neighboring hydroxyl group shown in Figure 4.1.

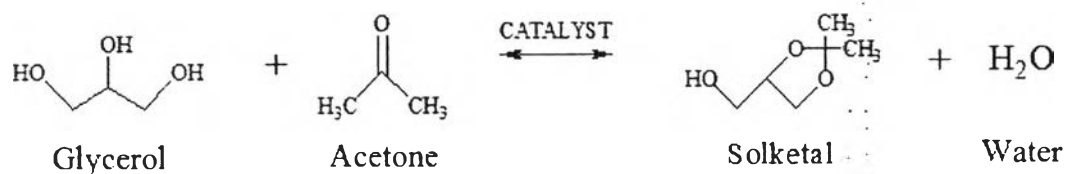


Figure 4.1 Condensation reaction to produce solketal.

Solketal has been used in many industries for example: drug and pharmaceutical, fuel additives in gasoline (Claudio *et al.*, 2010) and biodiesel (García *et al.*, 2008) and synthesis mono-, di- and triglyceride (Makkam., 2010).

4.1.1 The Effect of Catalyst Systems on Conversion of Glycerol to Solketal

The reaction occurs under atmospheric pressure and refluxing temperature with acid catalyst. Initially, the glycerol to acetone molar ratio is 1:2 with 1%wt *p*-toluenesulfonic acid as an acid catalyst in batch reaction system with total reflux. Gas chromatography is used for the quantitative analysis. The analysis procedure and detail are reported in section 3.3.5. The sample is diluted by isopropanol for internal standard. The relationships between conversion of glycerol and time in the system that contain catalyst and molecular sieve 3A, only catalyst and only molecular sieves 3A are shown in Figure 4.2.

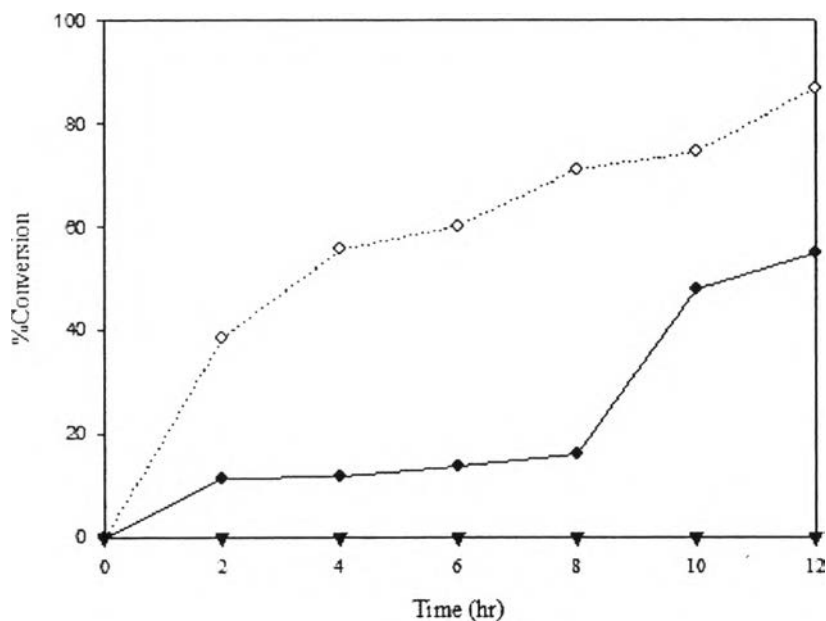


Figure 4.2 Conversion of glycerol to solketal at different time: (◆) with acid catalyst, (○) with acid catalyst and Mol3A and (▼) with Mol3A.

After the reaction, the product mixture is clear and colorless (Figure 4.3). The conversion is slightly increased up to 8 hours. After 8 hours, the conversion increased moderately. At the end of 12 hours, the conversion is only 54.9%. The final conversion is very low because of equilibrium limitation.



Figure 4.3 The product mixture obtained from the reaction using acid catalyst.

To increase the conversion, the use of molecular sieve 3A (Mol3A) is proposed. The molecular sieve 3A can adsorb water. This can shift the reaction forward (Figure 4.1) and increase the conversion. The dash line is shown for using

acid catalyst and molecular sieve 3A (Figure 4.2). The product mixture is translucent yellow color (Figure 4.4A). But after sedimentation, the mixture is clear and colorless (Figure 4.4B). There are some yellow color solid settlings because the magnetic stirrer crushed the molecular sieve 3A into small pieces during the reaction. As observed in Figure 4.2, conversion increases significantly to 86.8% at 12 hours which is much higher than the conversion when using only acid catalyst. In this case, removing of water from reaction by using molecular sieve 3A can shift the reaction to the right hand side.

As shown in Figure 4.2, the long-dashed line is referred to the reaction with molecular sieve 3A only. It can be observed that, when only molecular sieve 3A is used, the reaction does not take place. This concluded that molecular sieve 3A acts as adsorbent for water only.

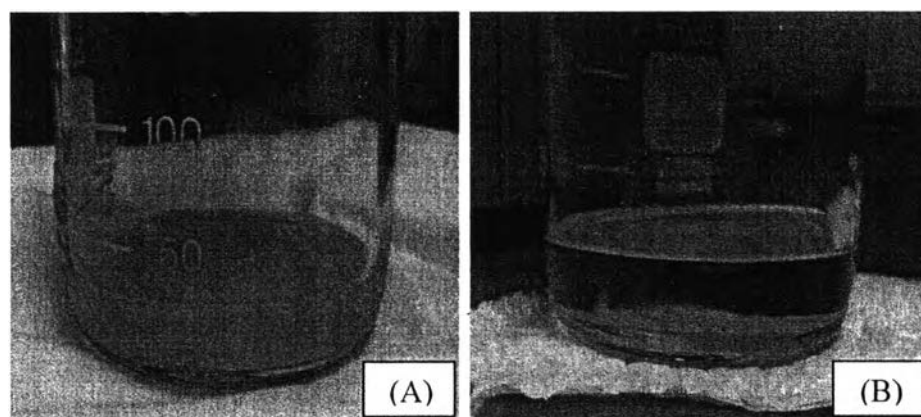


Figure 4.4 (A) The product mixture with acid catalyst and molecular sieve 3A. and (B) The product mixture after sedimentation.

4.1.1.1 The Effect of Glycerol to Acetone Molar Ratio

To increase the conversion of this reaction, the increasing acetone concentration should drive the reaction to the right hand side of the reaction from Le Châtellier's Principle. The effects of 1:2, 1:4 and 1:6 glycerol:acetone molar ratio with 1%wt *p*-toluenesulfonic acid as acid catalyst are selected for the role models in this work. As shown in Figure 4.5, the increasing of molar ratio increases the conversion of glycerol to solketal. For 1:2 molar ratio, the conversion is slightly increased up to 8 hours (16%). After 8 hours, the conversion increases moderately

(54.9%). For 1:4 molar ratio, the conversion is slightly increased up to 10 hours (56.7%). After 10 hours, the conversion increases moderately (70.9%). But for 1:6 molar ratio, the conversion is only slightly increased for 12 hours (82.7%). The cause of slightly increasing conversion is from the water which is by-product. The effect of water is the equilibrium conversion which drove solketal back to glycerol. Moreover water slows down the reaction. At the end of 12 hours, 1:6 molar ratio gave the highest conversion (82.7%) following by 1:4 molar ratio (70.9%) and 1:2 molar ratio (54.9%) respectively. In conclusion, the increasing of molar ratio increases the conversion of glycerol and the optimum condition for this effect is 1:6 glycerol:acetone molar ratio.

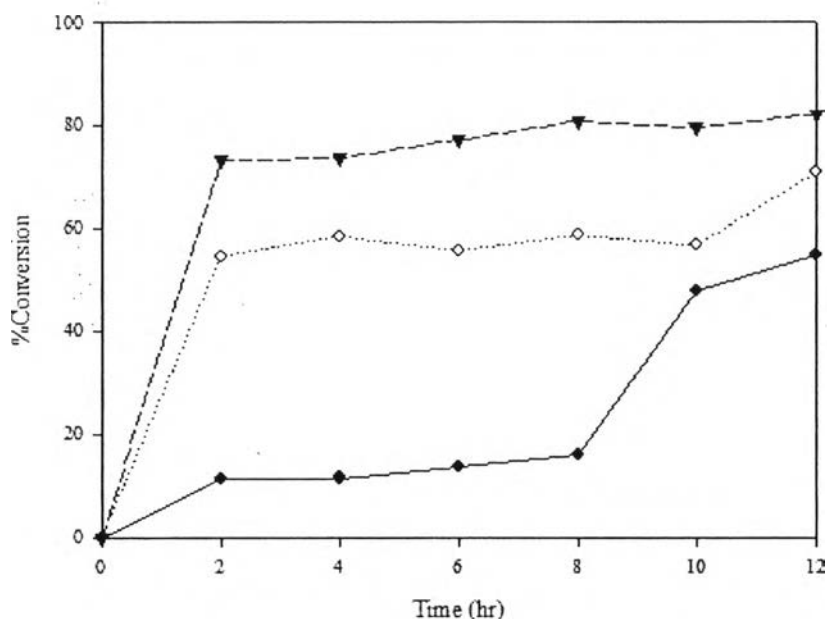


Figure 4.5 The effect of increasing glycerol to acetone molar ratio with 1%wt acid catalyst: (◆) 1:2 molar ratio, (○) 1:4 molar ratio and (▼) 1:6 molar ratio.

4.1.1.2 The Effect of Adding Molecular Sieve 3A (Mol3A)

In order to increase the conversion, the use of molecular sieve 3A (Mol3A) is proposed. Mol3A could adsorb water into its pores for 20%wt of Mol3A. This can rapidly shift the reaction to the right hand side to increase the conversion. In this case, the combination of Mol3A and high concentration of

acetone could be able to shift the reaction to complete the conversion. The excess of Mol3A and 1%wt of catalyst are fixed for the role model in this effect. The results are shown in Figure 4.6. As expected, the 1:2 molar ratio with surplus Mol3A increases the conversion to 86.8% at 12 hours which is much higher than the conversion when using only acid catalyst (Figure 4.5). The 1:4 molar ratio with surplus Mol3A completes 100% conversion in 8 hours. Moreover the 1:6 molar ratio with surplus Mol3A completes 100% conversion in 6 hours. Thus the combination of acid catalyst, increasing molar ratio and Mol3A gives the high efficiency to convert glycerol to solketal. The 1:6 glycerol:acetone molar ratio with surplus Mol3A is suggested for the optimum condition.

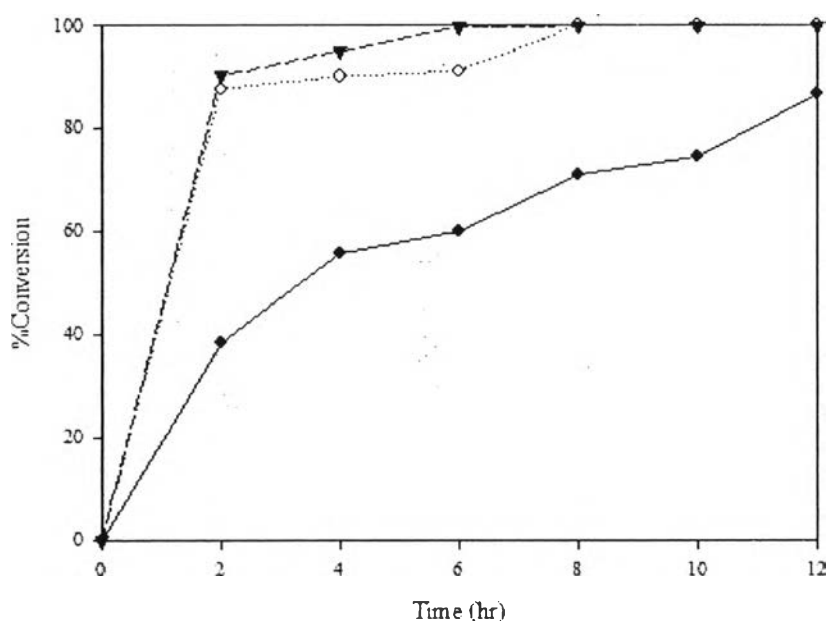


Figure 4.6 The effect of increasing glycerol to acetone molar ratio with 1%wt acid catalyst and surplus Mol3A: (◆) 1:2 molar ratio, (○) 1:4 molar ratio and (▼) 1:6 molar ratio.

4.1.1.3 The Effect of Amount of Mol3A with Acid Catalyst

From Figure 4.7, the combination between acid catalyst and Mol3A is able to increase the conversion. For the optimum condition for using Mol3A, the effect of amount of Mol3A is investigated (shown in Figure 4.7). 1:4 glycerol to acetone molar ratio and 1%wt of *p*-toluenesulfonic acid as acid catalyst

are fixed in this case. The amount of water in the reaction and the amount of Mol3A in the batch are calculated by mass balance. Without Mol3A, the conversion is just slightly increased to 70% from the beginning to 12 hours because of the equilibrium with water. From Figure 4.7, the adding Mol3A = 0.5 water equivalent refers to the 50%wt of the amount of water which occurs in the complete reaction equivalent to the amount of Mol3A for adsorbed the 50% of water in the reaction. If 0.5 water equivalent of water is removed, the conversion does not increase much from the beginning time to 2 hours (55.5%). Then the conversion is moderately increased to 74.1% at the end of 12 hours which is better than without Mol3A. For 0.75 water equivalent removed water, the conversion is increased to 63.9% at 2 hours. And then it increased moderately to 81.2% at 12 hours. The 0.5 water equivalent and 0.75 water equivalent do not increase the conversion as much as expected because the magnetic stirrer crushed the molecular sieve 3A into small pieces during the reaction. In order to avoid this situation, the surplus or excess amounts of Mol3A is investigated. The conversion is increased to complete 100% conversion at the end of 8 hours. Therefore the condition for amount of Mol3A is the excess Mol3A.

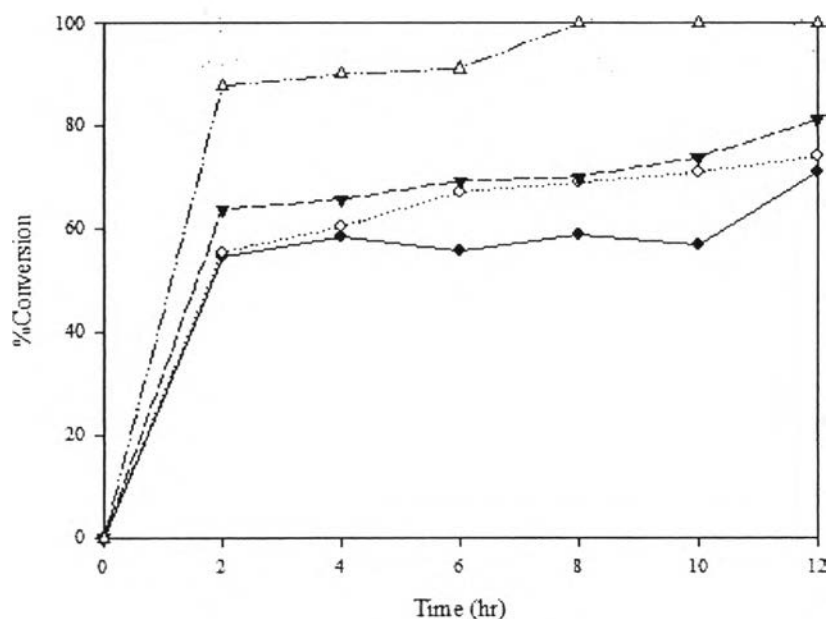


Figure 4.7 The effect of increasing amount of Mol3A with 1%wt acid catalyst: (◆) without Mol3A, (○) adding Mol3A=0.5 water equivalent, (▼) adding Mol3A=0.75 water equivalent, and (Δ) adding Mol3A=1.25 water equivalent (excess Mol3A).

4.1.1.4 Use of Ion-Exchange Resin as Heterogeneous Catalyst

The homogeneous acid catalyst can produce solketal from glycerol and acetone. But the drawback is the waste salt from neutralization by sodium carbonate and the catalyst could not be regenerated or reused. In this case, the heterogeneous catalyst is suggested and investigated. The advantages of the heterogeneous catalyst are ability to be recycled, easy separation and less waste. The heterogeneous catalyst which is suitable for this reaction should contain strong acid cation. The one of the commercially available heterogeneous catalyst for this reaction is Dowex monosphere M-31 ion exchange (Dowex M-31) from Dow chemical company. The specification for Dowex M-31 is shown in Table 4.1.

Table 4.1 Specification for Dowex monosphere M-31 commercial catalyst

Type	Matrix	Function group
Strong acid cation	Styrene-DVB, Macroporous	Sulfonic acid
Typical physical and chemical properties	Units	
Physical form		Hard opaque beads
Typical surface area	m ² /g	30
Average pore diameter	Angstroms	220
Pore Volume	%	33
Water retention capacity	%	50-54 by wt.
Particle size distribution	Microns	575±50
400-650 microns	%	> 95
Wet volume acid capacity	meq/mL, min.	1.85
Dry weight acid capacity	meq/mL, min.	5

The reaction condition is the same as the condition when using homogeneous catalyst. The molar ratio is 1:4 glycerol to acetone molar ratio with 75 °C for the model of this effect. The comparison of conversion between 1%wt *p*-toluenesulfonic acid as homogeneous catalyst and 1%wt Dowex M-31 as

heterogeneous catalyst is shown in Figure 4.8. Dowex M-31 is able to convert glycerol and acetone to solketal. The conversion of using Dowex M-31 is 45.2% at 2 hours. This conversion is less than the *p*-toluenesulfonic acid at the same time (54.6%). But after 4 hours to 10 hours the conversion of using Dowex M-31 is closed to the conversion of using *p*-toluenesulfonic acid because the reaction of solketal is reached the equilibrium conversion with water. For 12 hours, the Dowex M-31 is completed the conversion at 60.3% which less than the use of *p*-toluenesulfonic acid. However the Dowex M-31 can not break the equilibrium because of the water. In conclusion, Dowex M-31 can be used to produce solketal. Moreover there are several advantages of using Dowex M-31. First, the pH of the product mixture is 7 which is more suitable than *p*-toluenesulfonic acid (pH=5). And, it is easy to separate the Dowex M-31 catalyst. But the rate of reaction is slower than using the *p*-toluenesulfonic acid at the beginning of reaction.

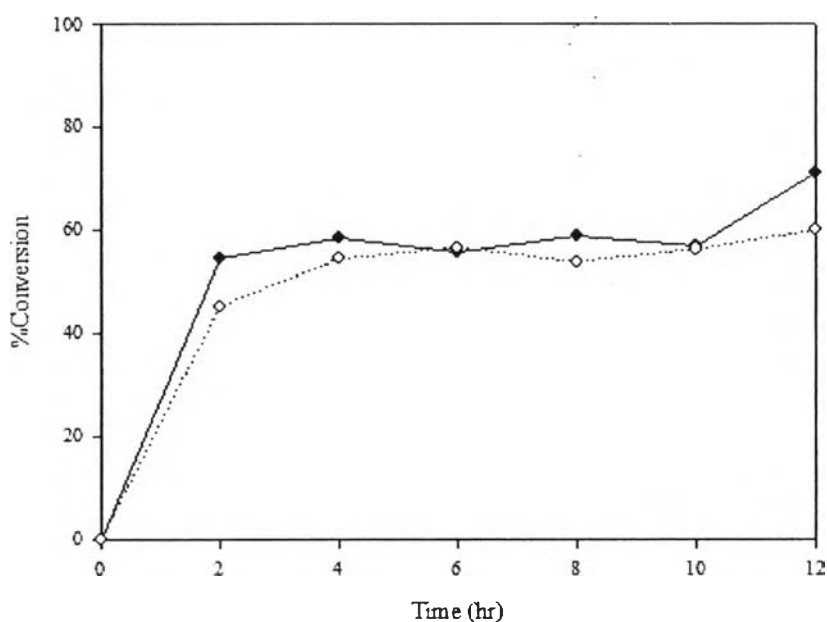


Figure 4.8 The comparison of conversion between *p*-toluenesulfonic acid and Dowex M-31 ion exchange resin : (♦) 1%wt *p*-toluenesulfonic acid and (○) 1%wt Dowex M-31 ion exchange resin.

4.1.1.5 The Effect of Amount of Dowex Ion Exchange Resin

From the previous section, the Dowex ion exchange shows a potential to be used as a catalyst to produce solketal. Then the optimum of amounts of Dowex ion exchange resin is studied. The 1:4 molar ratio of glycerol to acetone at 75 °C is the role model in this effect. The effect of the amount of Dowex ion exchange resin is shown in Figure 4.9. For 0.1% wt of Dowex ion exchange resin, The conversion is only 41% at 2 hour. And then the conversion is moderately increased to 50% at 6 hour. The conversion is reached the equilibrium around 56% conversion at the end of the reaction. For 0.5%wt, The reaction is rapidly increased the conversion to 55% at 2 hour. But the reaction is slightly increased because of the equilibrium. However, the conversion is reached 60% conversion at 12 hour. For 1%wt, the conversion is increased to 45% at 2 hour. And then the conversion is slightly increased to 60 % at 12 hour because of the equilibrium. The last condition is increasing the amounts of Dowex ion exchange resin to 3%wt Dowex ion exchange resin. Unfortunately, 3%wt Dowex ion exchange does not increase the conversion because of its equilibrium reaction. Moreover this conversion are lower than 0.5% wt Dowex ion exchange resin. Thus, this effect concluded that the surplus Dowex ion exchange resin did not help to increase the conversion passed through the equilibrium. The optimum condition for amount of Dowex ion exchange resin is 0.5%wt Dowex ion exchange resin.

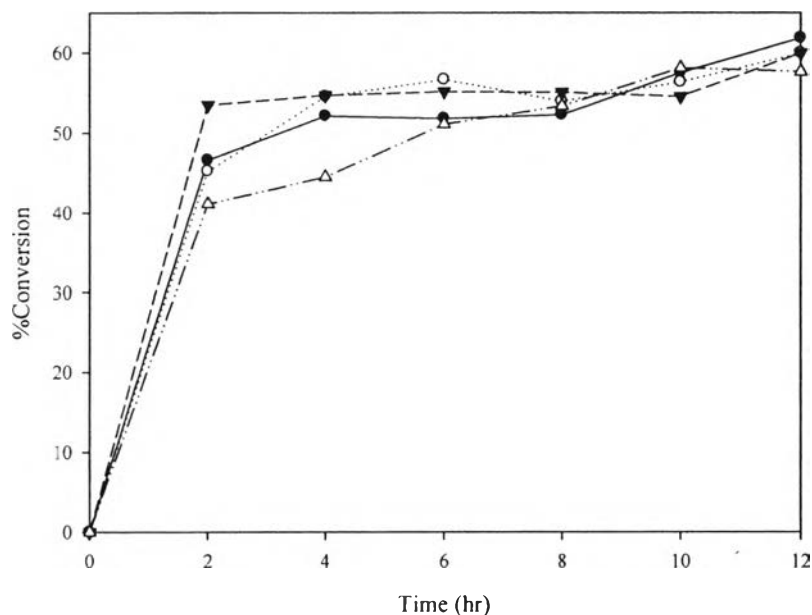


Figure 4.9 The effect of increasing amount of Dowex ion exchange resin: (◆) 3%wt Dowex ion exchange resin, (○) 1%wt Dowex ion exchange resin, (▼) 0.5%wt Dowex ion exchange resin, and (△) 0.1%wt Dowex ion exchange resin.

4.1.1.6 The Effect of Dowex Ion Exchange Resin with Mol3A

The Dowex ion exchange resin has a potential to produce solketal. From Figure 4.10 (◆), the equilibrium limitation is also the main problem of this heterogeneous catalyst. In this case, the use of molecular sieve 3A can be combined with Dowex ion exchange resin. From the previous effect, the Mol3A has the potential for adsorbed water and broken through the equilibrium limitation. The 1:4 glycerol to acetone molar ratio with 1%wt of Dowex ion exchange and surplus Mol3A is used for the model of this effect. As shown in Figure 4.10 (○), The combination of Dowex ion exchange resin and Mol3A result is looked promising. The conversion is lifted to 78% at 2 hours. And it continuously increases to 99% at 8 hour. Then, the conversion can be completed after 8 hours. In conclusion, this combination is more efficiency than use only Dowex ion exchange resin. Moreover, the use of Dowex ion exchange resin and Mol3A has a potential to complete the reaction as same as the use of homogeneous catalyst and Mol3A from the previous part and it has more advantage than the use of homogeneous catalyst.

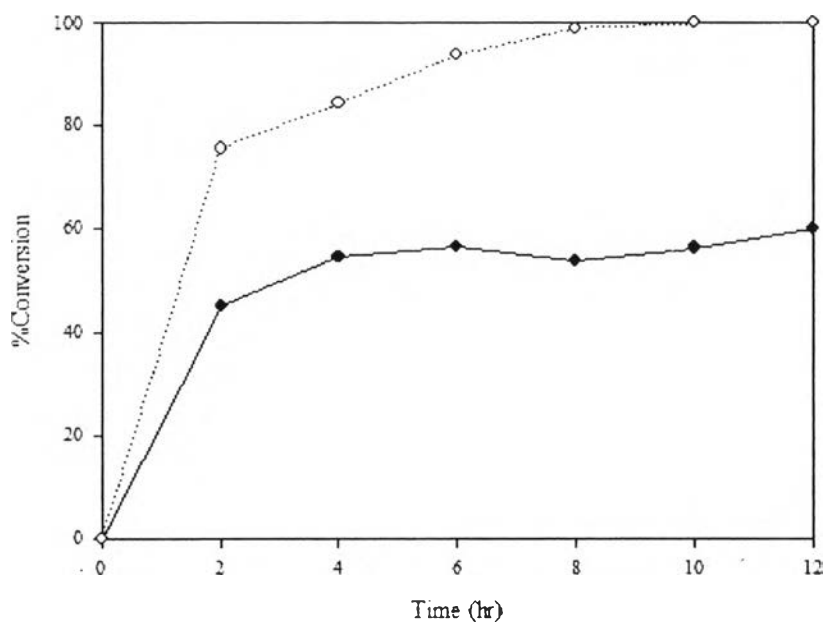


Figure 4.10 The effect of Dowex ion exchange resin with Mol3A: (♦) 1%wt Dowex ion exchange resin, and (○) 1%wt Dowex ion exchange resin with Mol3A.

4.1.2 Characterization of Products Mixture by Fourier Transform Infrared Spectroscopy (FT-IR Spectroscopy) and Mass Spectroscopy

For qualitative analysis, FT-IR spectroscopy is used for characterizing the products. Moreover this instrument also analyzes the functional groups of the sample by compared with the reference. The spectra as shown in Figure 4.10 confirmed that solketal is occurred as a product in this reaction.

As shown in Figure 4.11, the solid line and the dash line present the FT-IR of the product mixture at 12 hour with acid catalyst and standard solketal, respectively. The product mixture has %transmittance at wavenumber around 3400 cm^{-1} to 3600 cm^{-1} higher than the standard solketal. This wavenumber refers to the O-H stretching. Thus the mixture has hydroxyl group from glycerol more than solketal standard. This evident shows that the product still has the unreacted glycerol in the mixture product. Moreover the wavenumber at 1700 cm^{-1} represents to C=O stretching in ketone which is excess acetone. This FT-IR result also corresponds with GC result.

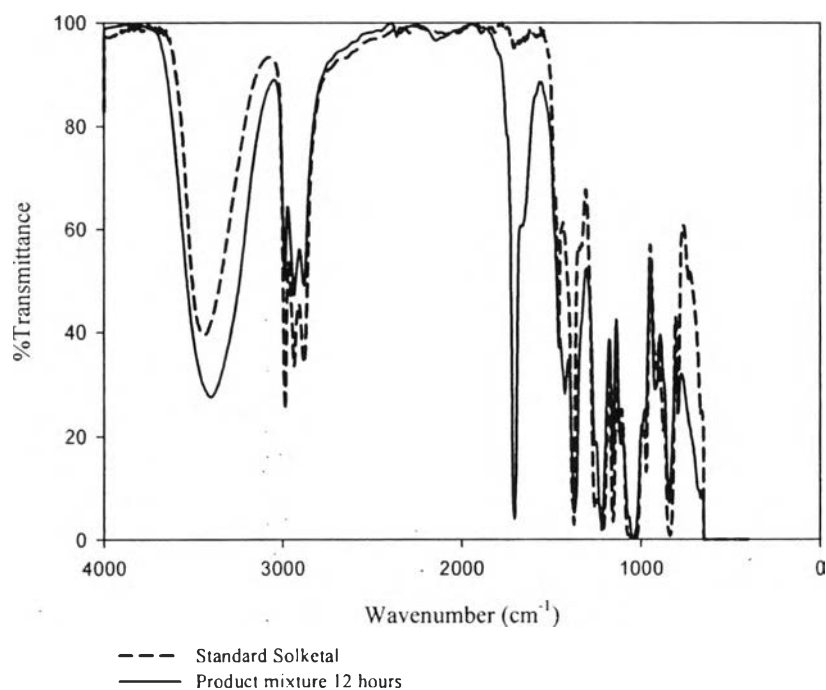


Figure 4.11 FT-IR spectra of solketal product mixture with acid catalyst.

Figure 4.12 represents the FT-IR spectra of product mixture with acid catalyst and molecular sieve 3A. The solid line and the dash line presents the FT-IR of the product mixture 12 hour with acid catalyst and molecular sieve 3A and standard solketal. The product mixture looks similar to the standard solketal. But at wavenumber around 3000 cm^{-1} to 2800 cm^{-1} refers to C-H stretching in CH_3 and CH_2 . The standard has much %transmittance than the product mixture. And wavenumber at 1700 cm^{-1} of the product mixture represents to C=O stretching in ketone. These evidents suggest to excess acetone in the product. Moreover the O-H stretching at wavenumber around 3400 cm^{-1} to 3600 cm^{-1} seems to almost glycerol convert to solketal. This result also corresponds with GC result which is higher conversion than acid catalyst.

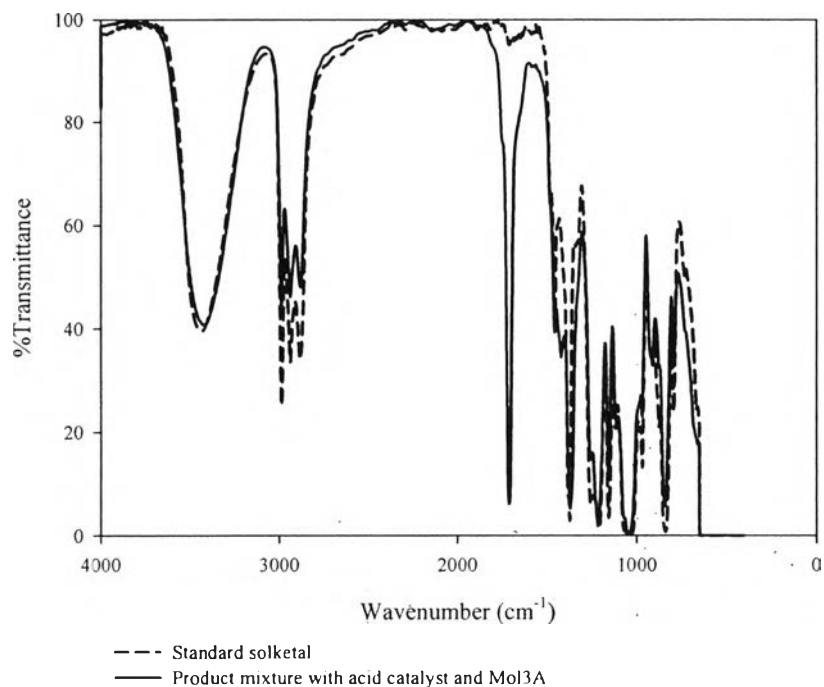


Figure 4.12 FT-IR spectra for acid catalyst and molecular sieve 3A.

Solketal products is then further analyzed by GC×GC time of flight Mass spectroscopy (GC-TOF). The MS result confirms the structure of solketal. The advantage of this instrument is that it combines the analysis of both GC technique and Mass spectroscopy (MS) technique. Moreover this instrument can separate the peak which appears at the same time by 2D analysis. The MS of solketal is shown in Figure 4.13. Solketal's molecular weight is 132. In the MS result, the first number is 117. This number is due to the ionization by losing one methyl group from the protecting group. The last number is 43. This number is due to the lost of dioxolane group or opening protecting group of solketal.

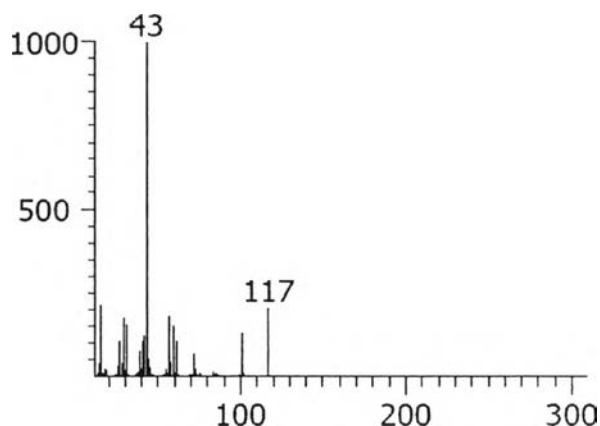


Figure 4.13 Mass spectroscopy result of solketal.

4.2 Synthesis of Benzyl Solketal Ether by Etherification between Solketal and Benzyl Alcohol

Solketal is very useful component. The advantages of this chemical are fuel additives, pharmaceutical and fine chemicals. The famous use of solketal is to synthesize mono-, di-, triglyceride by esterification with fatty acid. Benzyl alcohol is a natural, colorless and pleasant aromatic odor. This useful alcohol derivative has been found in fruits and essential oils such as jasmine and hyacinth. Benzyl alcohol has been used in many applications such as textiles, pharmaceutical, perfumes and flavor industries and coating process. Benzyl solketal ether is the protected function group by etherification between solketal and benzyl alcohol. Benzyl solketal ether is also used in fuel additives. Moreover benzyl solketal ether is able to be deprotected the protected group to produce linear benzyl glycerol ether. In general, benzyl solketal ether is synthesized by reacting benzyl chloride or benzyl bromide and solketal with solvent (Merino *et al.*, 2003). But there are many disadvantages from this organics synthesis for example: a lot of waste from used solvent. In this work, the etherification reaction between solketal and benzyl alcohol without solvent is investigated (Figure 4.14).



Figure 4.14 Etherification between solketal and benzyl alcohol.

4.2.1 Synthesis of Benzyl Solketal Ether and the Method to analyze Product Mixture

According to da Silva's synthesis (da Silva *et al.*, 2009), the reaction occurred under atmospheric pressure and 110 °C for temperature with acid catalyst. Initially, the glycerol per benzyl alcohol molar ratio is 1:1 with 2.2%wt *p*-toluenesulfonic acid as an acid catalyst in batch reaction system with total reflux for 12 hours. Unfortunately, a typical GC cannot identify the component in this product mixture because the result has many peaks without comparing standard. This problem could be solved by using GC×GC time of flight Mass spectroscopy (GC-TOF). The advantage of this instrument is that it combines the analysis of both GC technique and mass spectroscopy (MS) technique. Moreover this instrument can separate the peaks which appear at the same time by 2D analysis. The chromatograph of this sample is shown in Figure 4.15. The peaks at 200, 760, 855, 1296, 1302, 1364 and 1820 seconds are acetone, solketal, benzyl alcohol, benzyl solketal, benzyl glycerol, dibenzyl ether and glycerol respectively. The mass spectroscopy results are shown in characterization section.

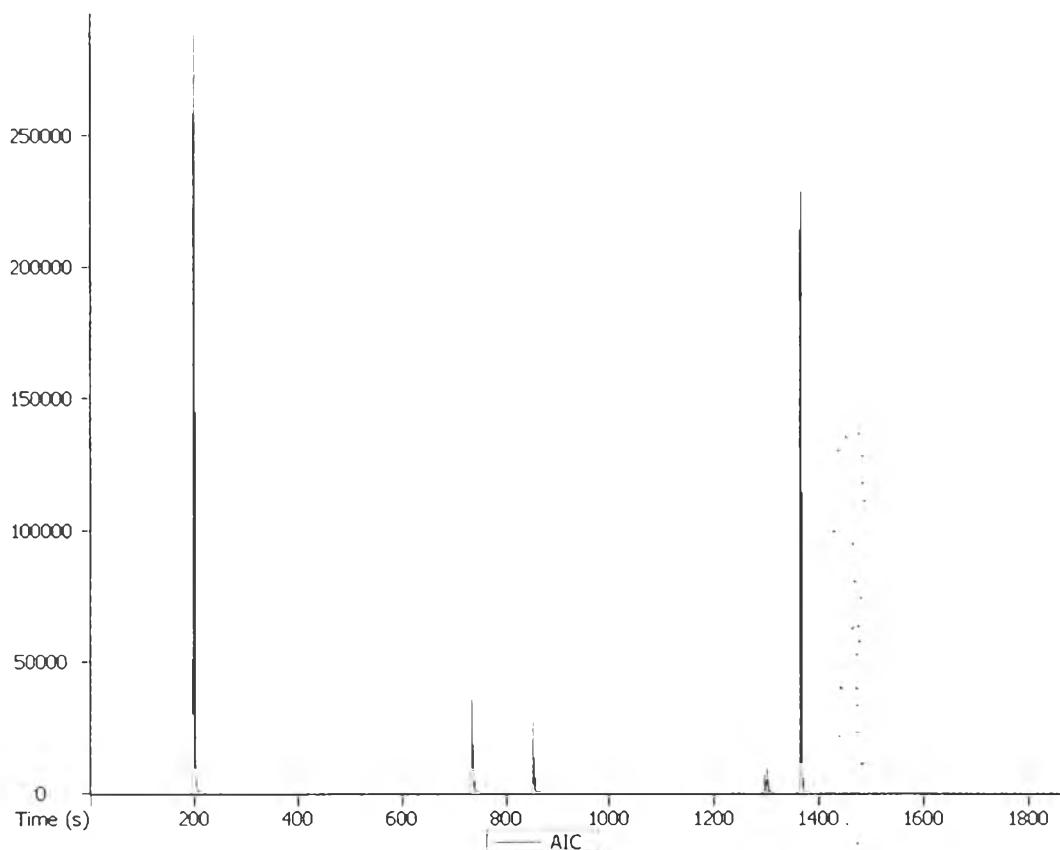


Figure 4.15 The chromatograph for product mixture.

From these by-products, the reactions are suggested in Figure 4.16. The main reaction is the reaction between solketal and benzyl alcohol to produce benzyl solketal ether and water (1). From the acid catalyst, solketal could be able to deprotect to produce acetone and glycerol (2). Benzyl alcohol is also reacted with each other to produce dibenzyl ether and water (3). Glycerol from the deprotection is able to react with benzyl alcohol to produce benzyl glycerol ether (4). Fortunately, the di and tri benzyl glycerol ether are not observed from the GC×GC time of flight mass spectroscopy. In this case, glycerol reacted with acetone back to produce solketal to protected glycerol before reacted with other benzyl alcohol. The last suggested reaction is benzyl solketal ether is deprotected by the water in the system to produce benzyl glycerol ether (5). The main problem in analyzing is the lack of standards chemicals for benzyl solketal ether, benzyl glycerol ether and dibenzyl ether. Luckily, the calibration curve of dibenzyl ether is able to make from the reaction of benzyl alcohol with acid catalyst. The assumption for the calculation of

selectivity is area ratio of benzyl glycerol ether to benzyl solketal ether equaled to mass ratio of benzyl glycerol ether to benzyl solketal ether. Moreover the calculated conversion is based on benzyl alcohol conversion. For this reason, this thesis concerns about the selectivity of benzyl solketal ether, benzyl glycerol ether and dibenzyl ether.

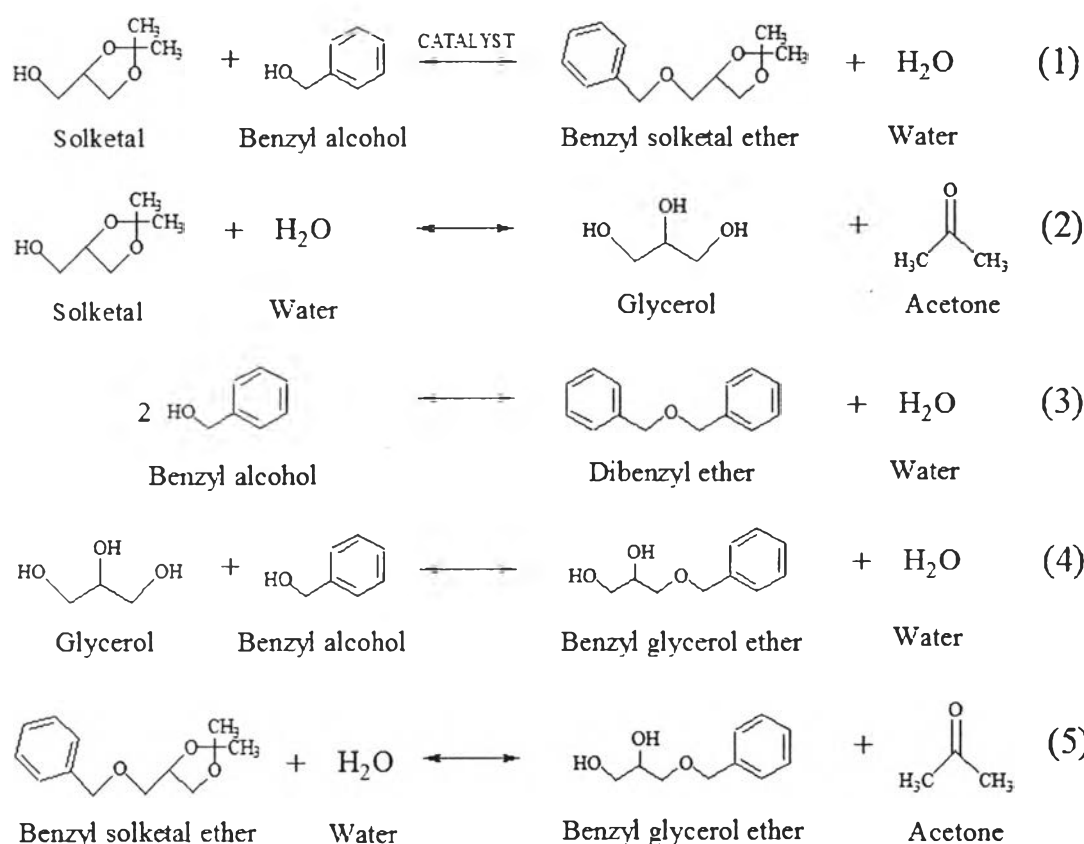


Figure 4.16 The overall reaction for produced benzyl solketal ether.

4.2.1.1 The Effect of Solketal to Benzyl Alcohol Molar Ratio

The solketal to benzyl alcohol molar ratio is first set at 1:1 solketal to benzyl alcohol molar ratio. Figure 4.17 shows the relationships between benzyl alcohol conversion, selectivity and time. The benzyl alcohol conversion looks promising. The benzyl alcohol conversion rapidly converts at 2 hour (57.5%) and then continuously converts to 92.9% at 12 hours. The selectivity of dibenzyl ether is very high at 2 hour (59.4%). And then its selectivity is decreased until the end of reaction time. This can be explained by the dibenzyl alcohol reaction (Figure 4.16

(3)). The dibenzyl ether reaction is faster than benzyl solketal ether and benzyl glycerol ether. But after 2 hours, the selectivity drops dramatically because dibenzyl ether reacts with water and converts back to benzyl alcohol. And then the benzyl alcohol reacts with glycerol and solketal to produce more benzyl glycerol ether and benzyl solketal ether. The selectivity of benzyl glycerol ether is 21% at 2 hour. The selectivity of benzyl glycerol ether is continuously increased due to the reaction time. This behavior explained that solketal is deprotected from the water in system to convert back to glycerol and acetone. The remaining glycerol is also reacted with benzyl alcohol to produce more benzyl glycerol ether. For this 1:1 molar ratio, solketal has converted back to solketal more than converted to produce benzyl solketal ether. The selectivity of benzyl solketal ether is 19.6% at 2 hour. And then it slightly decreases to 11.6% selectivity at 10 hour. After that the conversion slightly increases up to 15.9% selectivity at 12 hours. In this case, the selectivity of benzyl solketal ether is very low. The reaction could be explained by Figure 4.16 (5). The conversion is decreased from 2 hour to 10 hour because benzyl solketal ether is deprotected by water to produce benzyl glycerol ether. In conclusion, the 1:1 solketal to benzyl alcohol is suitable to produce benzyl glycerol ether (48.6% at 12 hour) compared to other products. On the other hand, this molar ratio did not increase the selectivity of benzyl solketal ether (15.9%).

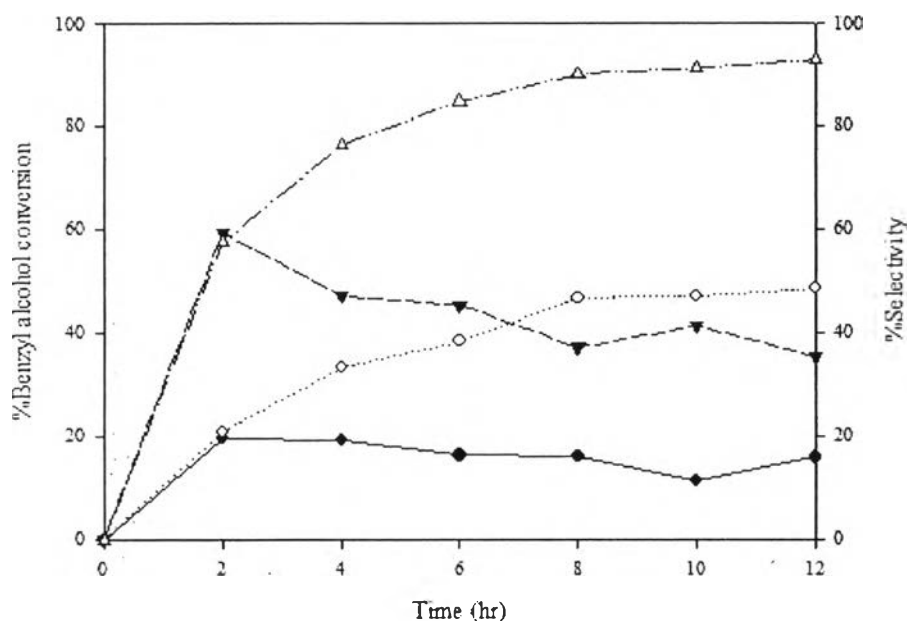


Figure 4.17 Benzyl alcohol conversion and selectivity of product mixture at different time for 1:1 glycerol to benzyl alcohol molar ratio: (▼) Selectivity of dibenzyl ether, (○) Selectivity of benzyl glycerol ether, (◆) Selectivity of benzyl solketal ether, and (Δ) Benzyl alcohol conversion.

According to increasing the benzyl alcohol conversion, the 1:2 solketal to benzyl alcohol molar ratio is investigated in this part. The increasing of molar ratio shifts the reaction to the right hand side of the reaction from Le Châtelier's Principle. The result is shown in Figure 4.18. As expected, the benzyl alcohol conversion is increased significantly to 72% from the beginning to 2 hours and continuous increased to 92.3% at the end of reaction. Although, the increased of benzyl alcohol molar is increasing the rate of benzyl alcohol conversion at the beginning time. The selectivity of dibenzyl ether is increasing from the beginning time to 4 hours (60.5%). From 4 hour to 12 hour, the selectivity of dibenzyl ether is decreasing to 52.5% which is still higher than the selectivity of benzyl glycerol ether and benzyl solketal ether. The selectivity of benzyl glycerol is increased moderately from the beginning to 10 hours (39.8%). After that, the selectivity is slightly dropped to 35.8% at the end of reaction. This behavior is the same as 1:1 solketal to benzyl alcohol molar ratio because solketal is deprotected to glycerol and then glycerol is

also reacted with the excess benzyl alcohol to produce benzyl glycerol ether (Figure 4.16 (2)). The selectivity of benzyl solketal is increased from the beginning to 2 hour. Then, the selectivity is slightly decreases to 9.8% at 10 hours. After that the conversion is slightly increased to 11.8% at 12 hours. This behavior explains by Figure 4.16 (5). Benzyl glycerol is protected by acetone to produce benzyl solketal ether. In conclusion, the 1:2 solketal to benzyl alcohol molar ratio is suitable for produced dibenzyl ether (52.5% selectivity). This molar ratio does not help to increase the selectivity of benzyl solketal ether (11.8%).

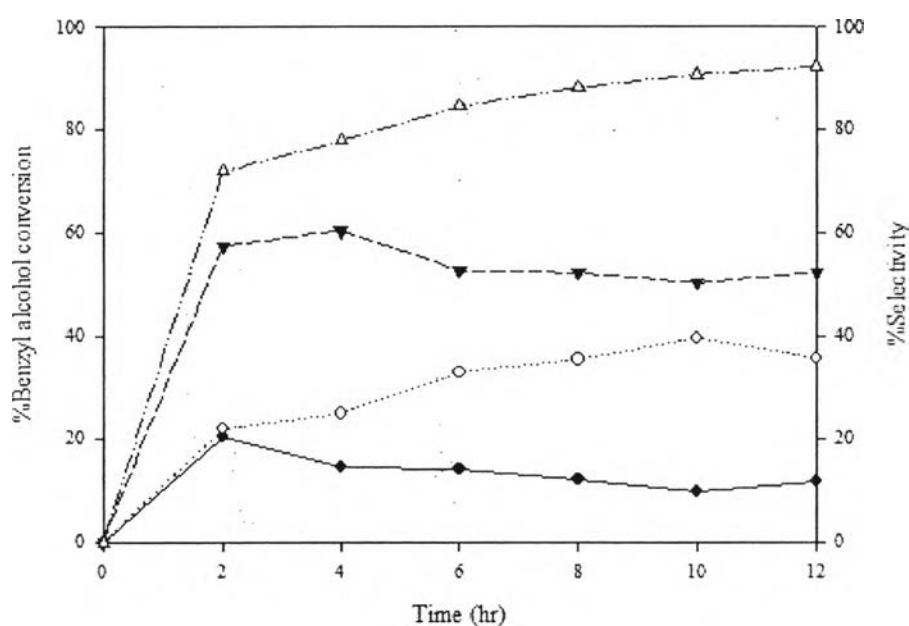


Figure 4.18 Benzyl alcohol conversion and selectivity of product mixture at different time for 1:2 glycerol to benzyl alcohol molar ratio: (▼) Selectivity of dibenzyl ether, (○) Selectivity of benzyl glycerol ether, (◆) Selectivity of benzyl solketal ether, and (Δ) Benzyl alcohol conversion.

The increasing of benzyl alcohol molar ratio does not enhance the selectivity of benzyl solketal ether. The increasing solketal molar ratio also shifts the reaction to the right hand side of the reaction as same as the increasing benzyl alcohol molar ratio. Thus the 2:1 solketal to benzyl alcohol molar ratio is studied in this part. The result is shown in Figure 4.19. The benzyl alcohol conversion is increased significantly to 98.5% after 12 hours of reaction. The selectivity of

dibenzyl ether is 60% at 1 hour. After that the selectivity of dibenzyl ether is continuously decreased to 20.4% at 12 hours. The behavior also confirmed the selectivity of dibenzyl ether from the 1:1 solketal to benzyl alcohol molar ratio which explained by equation (3) in Figure 4.16. Benzyl alcohol is initially converted to dibenzyl ether. After the equilibrium, the dibenzyl ether is converted back to benzyl alcohol by reacted with water in the system. The selectivity of benzyl glycerol ether is also done with the same behavior compared to the 1:1 solketal to benzyl alcohol molar ratio. The selectivity has been increased for 4 hours (48.7%). After that, the selectivity is leveled off until 12 hours (49.7%). The selectivity of benzyl solketal ether is increased from the beginning to 2 hours (20.3%). Then the selectivity is decreased to 14.3% at 4 hour because of the increasing of benzyl glycerol ether. After that, the selectivity of benzyl solketal ether is moderately increased to 26.9% at 12 hours. In this case, the selectivity of benzyl solketal ether increased due to the decreasing selectivity of dibenzyl ether. In conclusion, the 2:1 solketal to benzyl alcohol molar ratio enhances the selectivity of benzyl solketal ether (26.9%) which is higher than the previous parts. In the other hand, the molar ratio also produces too much of benzyl glycerol ether.

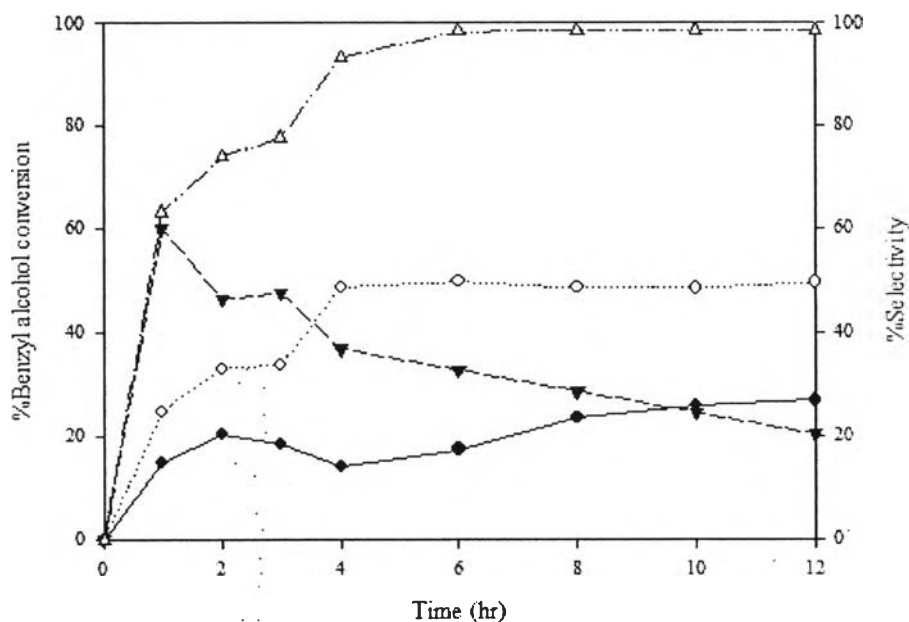


Figure 4.19 Benzyl alcohol conversion and selectivity of product mixture at different time for 2:1 glycerol to benzyl alcohol molar ratio: (▼) Selectivity of dibenzyl ether, (○) Selectivity of benzyl glycerol ether, (◆) Selectivity of benzyl solketal ether, and (Δ) Benzyl alcohol conversion.

The 2:1 solketal to benzyl alcohol molar ratio is able to increase the selectivity of benzyl solketal ether. In this part, the solketal molar is doubled the solketal to benzyl alcohol molar ratio to 4:1. Moreover this molar ratio is able to shift the reaction to the right hand side. The result is shown in Figure 4.20. As expected, the benzyl alcohol conversion is lifted to 96.6% at 2 hours because of the limiting reactant. After that the benzyl alcohol conversion leveled off around 98.0% to 99.0% until the end of reaction. The selectivity of dibenzyl ether has been increased to 23.6% for 4 hours. After that, the selectivity of dibenzyl ether is decreased and leveled off around 10% during 4 hours to 12 hours. This selectivity is the lowest selectivity compared to the other effects. This behavior explains by Figure 4.16 (3). The rate of dibenzyl ether is slower than the rated of benzyl solketal ether and benzyl glycerol ether because benzyl alcohol molar is extremely less than solketal molar. Moreover the opportunity of benzyl alcohol reacted with itself would less than the reacted solketal and glycerol in the system. The selectivity of benzyl

glycerol ether is increased moderately to 51.0% from the beginning to 6 hours. And then the selectivity is decreased to 39.9% at 12 hours. The Figure 4.16 (5) explains this decreasing selectivity of benzyl glycerol ether. The remaining acetone from the deprotected solketal reacts benzyl glycerol to produce benzyl solketal ether. The selectivity of benzyl solketal ether is increased to 40.2% at 2 hours. Then the selectivity is dropped at 4 hours (31.8%) because the rate of benzyl glycerol ether is faster than the rate of benzyl solketal ether. Nevertheless the selectivity moderately increased to 52.2% from 4 hours to 10 hours. There are two main reasons for increased selectivity. Firstly, dibenzyl ether conversed back to benzyl alcohol which reacted with solketal to produce benzyl solketal. Lastly, the benzyl glycerol ether is reacted with acetone to produce more benzyl solketal ether. At the end of reaction time the selectivity is slightly decreased (50.1%) because of the slightly increased benzyl glycerol ether. In conclusion, the 4:1 solketal to benzyl alcohol molar ratio gives the highest efficiency to produce the benzyl solketal ether which the selectivity of benzyl solketal ether is higher than the other effects around two times. Moreover this molar ratio is also decreased the selectivity of benzyl glycerol ether and dibenzyl ether.

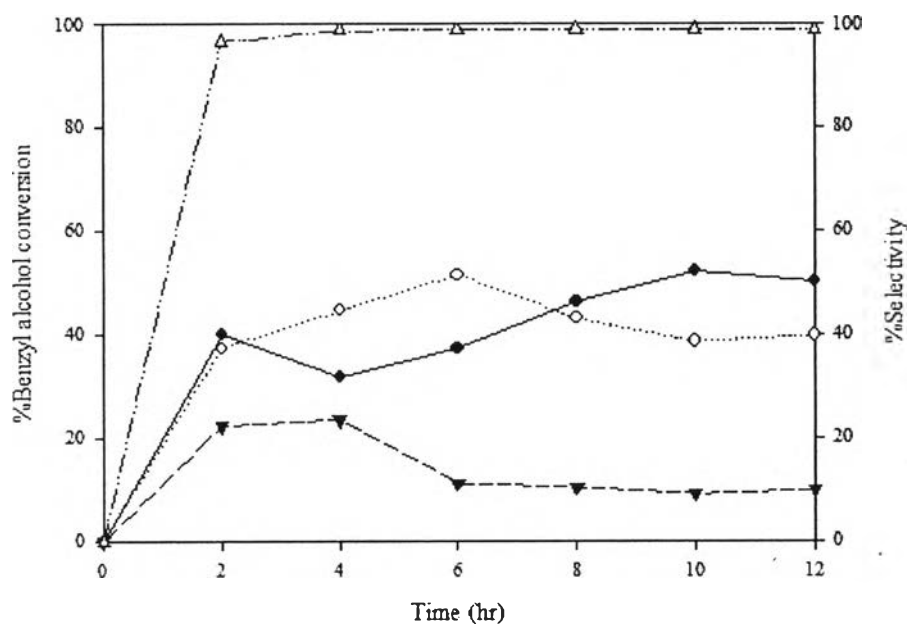


Figure 4.20 Benzyl alcohol conversion and selectivity of product mixture at different time for 4:1 glycerol to benzyl alcohol molar ratio: (▼) Selectivity of dibenzyl ether, (◊) Selectivity of benzyl glycerol ether, (♦) Selectivity of benzyl solketal ether, and (Δ) Benzyl alcohol conversion.

4.2.2 Characterization of Products Mixture by Fourier Transform Infrared Spectroscopy (FT-IR Spectroscopy) and Mass Spectroscopy (MS Spectroscopy)

The FT-IR spectroscopy and GC×GC TOF MS are the two main instruments for qualitative analysis. FT-IR spectroscopy analyzed the functional group of products mixture. The MS spectroscopy from the GC×GC TOF MS is also confirmed the molecular weight of the chemicals.

The FT-IR spectroscopy is shown in Figure 4.21. The solid line presented the products mixture with *p*-toluenesulfonic acid after 12 hours. This FT-IR result is compared to the standard benzyl solketal ether (Figure 4.21). It looks similar to the standard. The wavenumber around 1200 cm^{-1} to 1000 cm^{-1} represents the C-O stretching from the ether product which is also agreed with the standard. But at wavenumber around 3500 cm^{-1} to 3200 cm^{-1} refers to the O-H stretching which represents the remaining benzyl glycerol ether and glycerol from deprotected

solketal. Moreover the wavenumber around 1700 cm^{-1} represents to C=O stretching in ketone which is the remaining acetone.

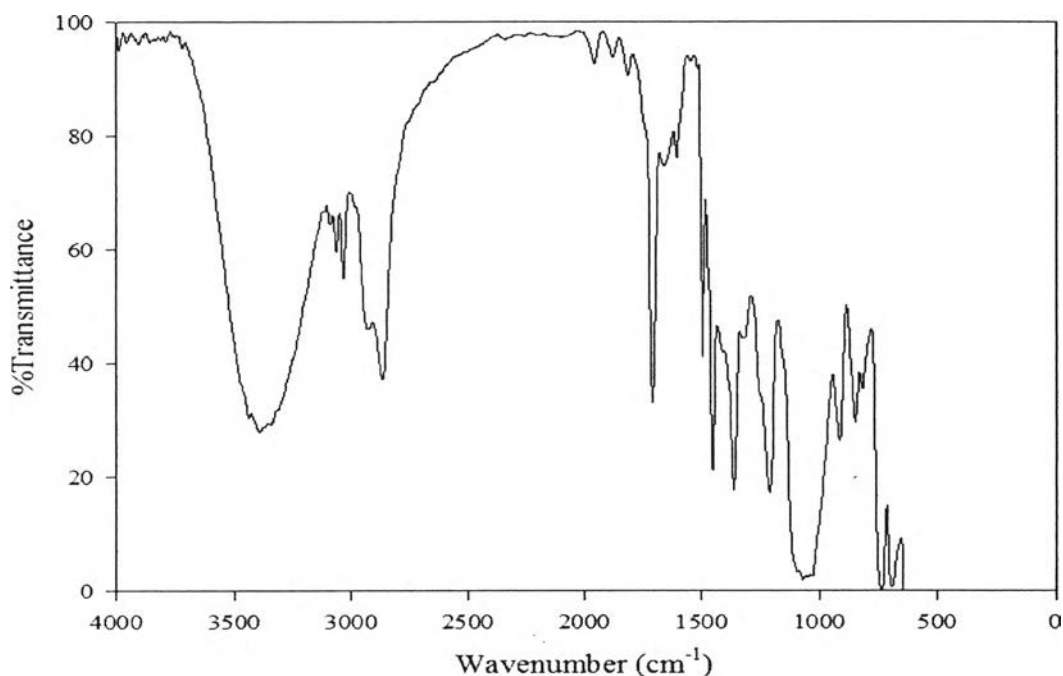


Figure 4.21 FT-IR spectra for benzyl solketal ether production.

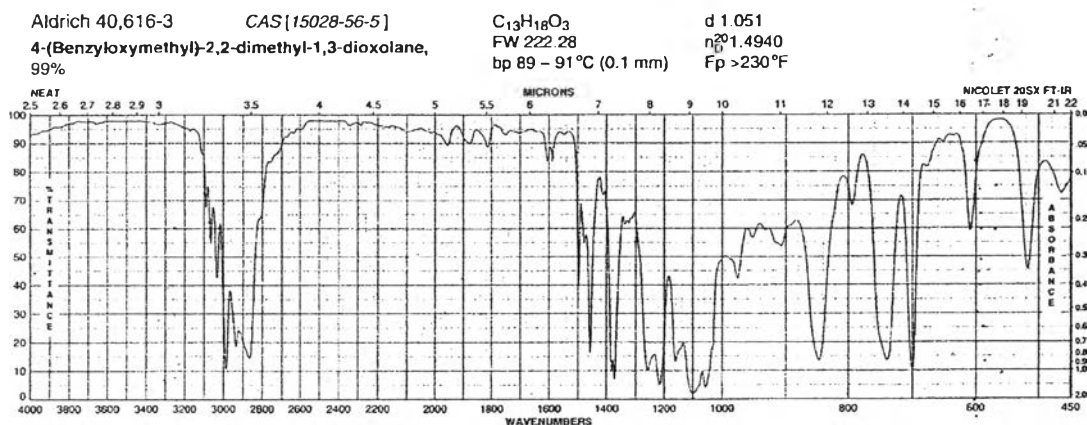


Figure 4.22 FT-IR spectra for standard benzyl solketal ether. (Sigma-Aldrich., 1997).

After the Benzyl alcohol is reacted itself with 2.2% by weight of *p*-toluenesulfonic acid for the standard dibenzyl ether. The FT-IR result is also confirmed the functional group of dibenzyl ether as shown in Figure 4.23 compared to the standard (Figure 4.24). The result looks similar to the standard. But at

wavenumber around 3500 cm^{-1} to 3200 cm^{-1} refers to the O-H stretching which represents the remaining benzyl alcohol. This result confirms the functional group of dibenzyl ether from the synthesis.

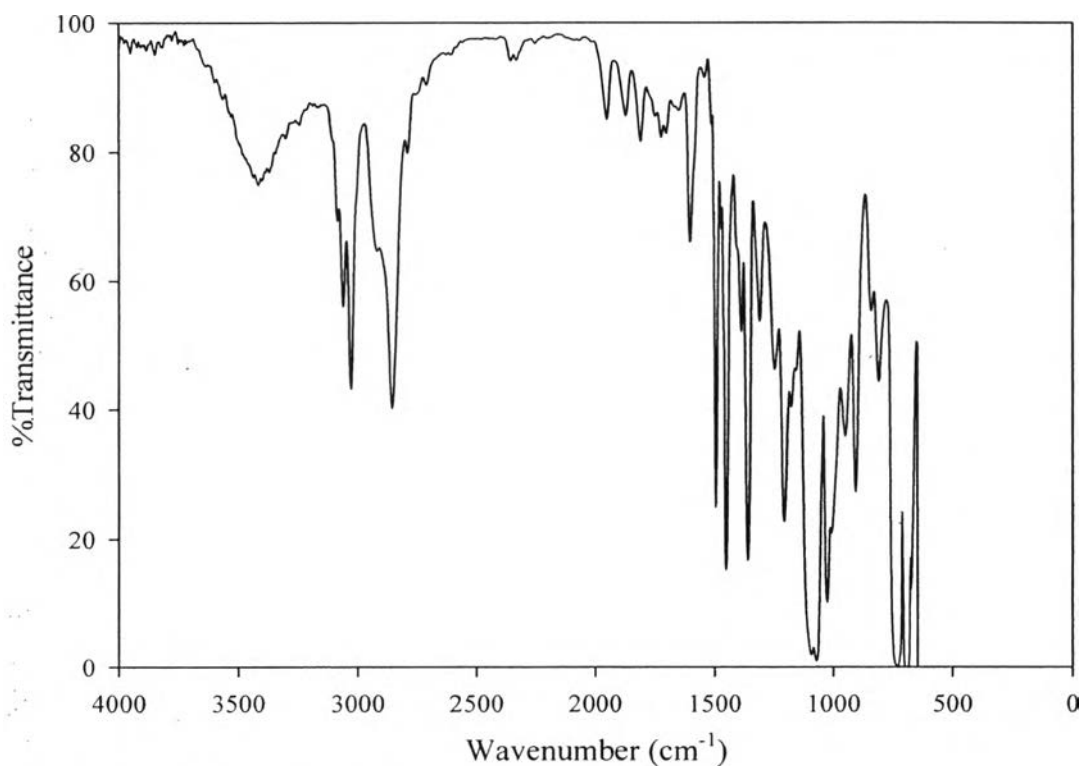


Figure 4.23 FT-IR spectra for dibenzyl ether.

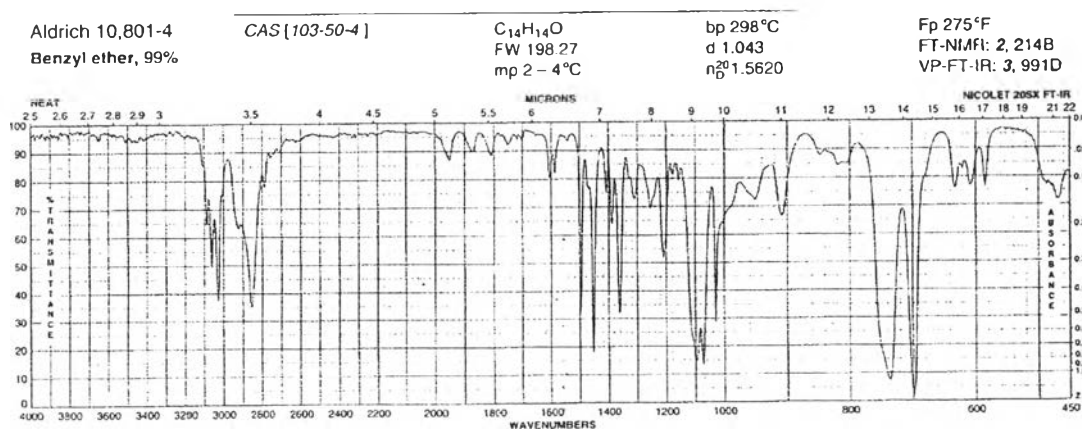
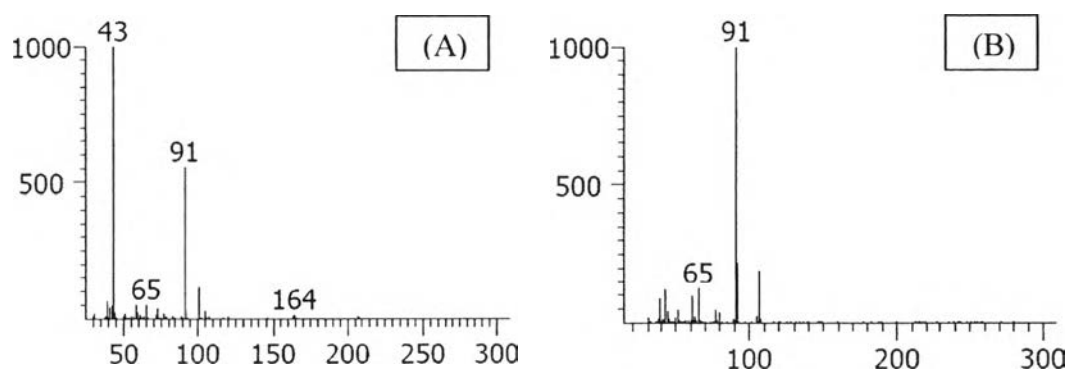


Figure 4.24 FT-IR spectra for standard dibenzyl ether. (Sigma-Aldrich., 1997).

The MS result is also confirmed the molecular weight of chemicals. The results is shown in Figure 4.24. Benzyl solketal ether MS results is Figure 4.25 (A). The molecular weight of benzyl solketal ether is 222. In the MS result, the first number is 164. This number is due to the ionization by losing two alkyl groups and opening the C-O of dioxolane group from the protected side. The next number is 91. This number is due to the lost of the remaining solketal side. And the last number is 43. This number is due to the lost of the benzene ring. Benzyl glycerol ether MS result is represented by Figure 4.25 (B). The molecular weight is 182. The first number is 107, This number is due to the ionization by losing the glycerol side. The next number is 91. This number is also due to the lost of the C-O ether bond. The last number is 65. This number is caused by losing the branch of benzyl alcohol side. The number 65 is also referred to the remaining of benzene ring. Figure 4.25 (C) is shown the MS result for dibenzyl ether. The molecular weight of dibenzyl ether is 198. The First number is 92. This number is also due to the ionization by losing the one side of benzyl group. The last number is 65. This number is also caused by losing the branch of remaining benzyl group.



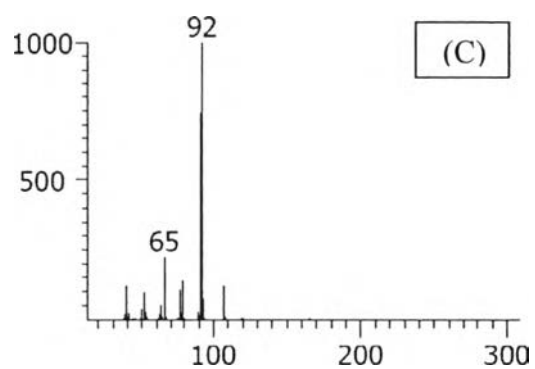


Figure 4.25 The MS results: (A) Benzyl solketal ether, (B) Benzyl glycerol ether and (C) Dibenzyl ether.