Synthesis of Solketal from Glycerol and Its Reaction with Benzyl Alcohol

Narintorn Suriyaprapadiloka and Boonyarach Kitiyanan

Abstract

Due to the high growth of biodiesel production, glycerol, a major by-product from transesterification, is also produced at the same growing rate, resulting in its oversupply. This situation brings the price of glycerol to drop dramatically. Solketal, a derivative from glycerol, can be utilized by blending with gasoline or biodiesel as an additive. This work studies the synthesis of solketal from glycerol and acetone using homogeneous acid catalyst. The reaction progresses successfully when using the acetone in excess. Subsequently, the prepared solketal is used for synthesizing benzyl solketal ether by performing reaction with benzyl alcohol. However, several other products such as benzyl glycerol ether, dibenzyl ether and glycerol are formed. It was found that the high ratio of solketal to benzyl alcohol is required to increase selectivity toward benzyl solketal ether.

Keywords: Glycerol; Solketal; Benzyl alcohol; Benzyl solketal ether

1. Introduction

In the first generation biodiesel production, triglyceride from vegetable oil and methanol are reacted by transesterification reaction to produce fatty acid methyl ester or biodiesel and also obtain glycerol as an unavoidable by-product. Since the production of biodiesel has been increasing rapidly, this causes the glycerol obtained as a by-product to be oversupplied, leading to the price drop of glycerol. Therefore, finding the way to utilize glycerol is suggested to help the overall economic of biodiesel production.

Solketal is a derivative which the two adjacent hydroxyl groups of glycerol are reacted via condensation acetone [1]. Solketal can be blended for fuel additives in gasoline [2] or biodiesel [3]. Nowadays solketal can be produced by condensation reaction of glycerol and acetone with acid catalyst [2]. The interesting derivative from solketal is benzyl solketal ether. Benzyl solketal ether is the
oxygenated compound and also can be used for fuel additives. Currently, benzyl solketal ether was produced by organic synthesis. In this organic synthesis, solketal is reacted with benzyl chloride with solvents [4]. The problem is using a lot of solvents in the synthesis of benzyl solketal ether. The purpose of this work is divided into two parts. First is the solketal production from glycerol and acetone. Subsequently, the synthesis of benzyl solketal ether from solketal and benzyl alcohol is investigated in the system without solvent. The effect of molar ratio is studied in this part and the optimum condition to produce benzyl solketal ether is investigated.

2. Experimental procedure

2.1. Preparation of solketal

A mixture of glycerol, acetone, and \( p \)-toluenesulfonic acid as a catalyst is reacted in glass reactor with total reflux for 12 hours. After 12 hours of the reaction, the reaction flask was put in an ice bath to stop the reaction. Then sodium carbonate is added to neutralize the product. The samples are taken at 2, 4, 6, 8, 10, 12 hour for analyzing the glycerol conversion and products by GC. To characterize the solketal production, GC×GC time of flight mass spectroscopy (GC×GC TOF MS) and FTIR spectroscopy are used. Vacuum distillation was also applied to purify the product if needed.

2.2. Etherification of solketal and benzyl alcohol

Solketal and benzyl alcohol with desired molar ratio are reacted in the batch system with total reflux condition. When the temperature is heated up to 110°C, the 2.2%wt \( p \)-toluenesulfonic acid is added to start the reaction for 12 hours. At the end of reaction, the products mixture is cooled down in an ice-bath and sodium carbonate is also added to stop the reaction. The samples are taken every 2 hours to analyze the benzyl alcohol conversion and selectivity of benzyl solketal ether, benzyl glycerol ether and dibenzyl ether by GC, GC×GC TOF MS and FTIR spectroscopy.

3. Results and Discussion

3.1. Synthesis of solketal from glycerol

Glycerol and acetone are the raw materials used for producing solketal by condensation reaction. Solketal or isopropylidene glycerol contains the center of glycerol backbone which an isopropylidene group bound to two neighboring hydroxyl group as shown in Fig. 1.

![Condensation reaction of glycerol and acetone to obtain solketal.](image)

Fig. 1. Condensation reaction of glycerol and acetone to obtain solketal.

First, 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 relationships between conversion of glycerol and time of the reaction is shown in Fig. 2. For the acid...
catalyst (Fig. 2), 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%. To increase the conversion of this reaction, the acetone concentration should be increased to drive the reaction to the right hand side. The effects of glycerol:acetone molar ratio (1:2, 1:4 and 1:6) with 1%wt p-toluenesulfonic acid as acid catalyst are selected. As shown in Fig. 2, the increasing of molar ratio increases the conversion of glycerol to solketal. 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, however, we cannot achieved 100% conversion due to the equilibrium limitation.

3.2. Synthesis of benzyl solketal ether by etherification between solketal and benzyl alcohol

Benzyl solketal ether is derived from etherification between solketal and benzyl alcohol (Fig. 3). Benzyl solketal ether can be used as fuel additive. Moreover benzyl solketal ether can be deprotected to obtained benzyl glycerol ether with the ether group at α position of glycerol. In general, benzyl solketal ether is synthesized by reacting benzyl chloride or benzyl bromide and solketal with solvent [5]. 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. However, there were several by-products, which are glycerol, acetone, benzyl solketal ether, benzyl glycerol ether and dibenzyl ether. Fig. 3 is shown the possible reactions and products from reaction of solketal and benzyl alcohol. The main reaction is the reaction between solketal and benzyl alcohol to produce benzyl solketal ether and water (Fig. 3 (1)). From the acid catalyst, solketal could be able to be decomposed to produce acetone and glycerol (Fig. 3 (2)). Benzyl alcohol is also reacted with each other to produce dibenzyl ether and water (Fig. 3 (3)). Glycerol from the deprotection is able to react with benzyl alcohol to produce benzyl glycerol ether (Fig. 3 (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 (Fig. 3 (5)).

![Fig. 3. Possible reactions during synthesis of benzyl solketal ether from solketal and benzyle alcohol without using solvent.](image)

The solketal to benzyl alcohol molar ratio is first set at 1:1 solketal to benzyl alcohol molar ratio. Fig. 4 shows the relationships between benzyl alcohol conversion, selectivity and time. As observed, after 2 hours, the benzyl alcohol quickly converts to 57.5% conversion and then continuously converts to 92.9% after 12 hours. The selectivity of dibenzyl ether is very high at 2 hour (59.4%), then decreased until the end of 12 hours. The reaction for dibenzyl ether is faster than that for 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, which would react with glycerol and solketal to produce more benzyl glycerol ether and benzyl solketal ether. The selectivity of benzyl glycerol ether is 21.0% 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 resulting glycerol can also reacted with benzyl alcohol to produce more benzyl glycerol ether. For this 1:1 molar ratio, solketal has converted back to glycerol more than benzyl solketal ether. The selectivity of benzyl solketal ether is 19.6% at 2 hour, and then it slightly decreases to 11.6% at 10 hours. 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 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 at the studying condition produce benzyl glycerol ether (48.6% at 12 hour). On the other hand, at this molar ratio, the selectivity towards benzyl solketal ether is not significant (15.9%).

To increase the selectivity of benzyl solketal ether, the 4:1 solketal to benzyl alcohol molar ratio is investigated. At this molar ratio, the reaction should be shifted to the right hand side. The result is shown in Fig. 5. As expected, the benzyl alcohol conversion is lifted to 96.6% at 2 hours. After that the benzyl
alcohol conversion leveled off around 98.0-99.0% due to the limiting reactant. 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. The rate of dibenzyl ether is slower than the rated of benzyl solketal ether and benzyl glycerol ether because concentration of benzyl alcohol molar is much less than concentration of solketal, resulting in solketal has higher chemical potential to perform the reaction than benzyl alcohol. Therefore, the benzyl alcohol etherification with itself would be much less than the reacting with solketal in the system. The selectivity of benzyl glycerol ether is increased moderately to 51.0% after 6 hours. And then the selectivity is decreased to 39.9% at 12 hours. This behavior is caused by the remaining acetone from the deprotected solketal reacted 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. After 12 hours, the selectivity is slightly decreased (50.1%) because of the slightly increasing of benzyl glycerol ether.

Fig. 4. Benzyl alcohol conversion and selectivity of products 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 (▲) Benzyl alcohol conversion.

Fig. 5. Benzyl alcohol conversion and selectivity of products 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 (▲) Benzyl alcohol conversion.
3.3. Characterization of products

The GC×GC TOF MS and FT-IR spectroscopy are the two main techniques for qualitative analysis. The advantage of GC×GC TOF is that it combines the analysis of both GC technique and MS technique. Moreover, this instrument can separate the peak which appears at the same time by 2D analysis. The MS result of solketal is shown in Fig. 6. Molecular weight of solketal 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 loss of dioxolane group or opening the protecting group of solketal. Furthermore, FT-IR spectroscopy was also used to analyze the functional group of products. The FT-IR spectra confirmed that solketal is occurred as a product in this reaction. As shown in Fig. 6 the solid line presents the FT-IR of spectra of obtained solketal at 12 hour with acid catalyst. Comparing to solketal standard, the FT-IR of the solketal product shows stronger peak at wavenumber around 3400 cm\(^{-1}\) to 3600 cm\(^{-1}\) which is assigned to the O-H stretching. Thus the mixture has hydroxyl group possibly from unreacted glycerol more than solketal standard. Moreover, the wavenumber at 1700 cm\(^{-1}\) represents C=O stretching that is due to the unremoved excess acetone. For benzyl solketal ether, its MS result is shown in Fig. 7. The molecular weight of benzyl solketal ether is 222. From 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 which is due to the loss of the remaining solketal. And the last number is 43. This number is due to the loss of the benzene ring. Subsequently, the FT-IR spectroscopy of benzyl solketal ether product mixture is shown in Fig. 7. The solid line presented the product mixture with p-toluenesulfonic acid after 12 hours. This FT-IR result is compared to the standard benzyl solketal ether. 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 which represents the remaining benzyl glycerol ether and glycerol from deprotected solketal. Moreover, the wavenumber around 1700 cm\(^{-1}\) represents to C=O vibration which is the remaining acetone.

![Fig. 6. (a) FT-IR Spectra of synthesis solketal and (b) mass spectra of solketal product.](image-url)
4. Conclusion

For synthesis of solketal, with increasing acetone to glycerol molar ratio, the conversion toward solketal is increased. However, the conversion of glycerol cannot achieve 100% due to the equilibrium limitation. Water as a byproduct from this reaction should be removed in order to obtain higher conversion toward solketal. For the benzyl solketal ether, the higher solketal to benzyl alcohol ratio drives the reaction to yield higher benzyl solketal ether. However, water formed during the reaction can cause other unwanted reaction, such as conversion solketal back to glycerol, therefore removing water during the reaction is suggested to make the reaction in high conversion and yield.

Acknowledgements

This work is financially supported by Thailand Research Fund-Master Research Grants (TRF-MAG), and Verasuwan Co., Ltd.

References