



Coupling reaction and azeotropic distillation for the synthesis of glycerol carbonate from glycerol and dimethyl carbonate

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ARTICLE INFO

Article history:

Received 7 January 2010

Received in revised form 9 April 2010

Accepted 9 April 2010

Available online 24 April 2010

Keywords:

Glycerol carbonate

Glycerol

Dimethyl carbonate

Azeotropic distillation

ABSTRACT

A new process, coupling reaction and azeotropic distillation was proposed for the synthesis of glycerol carbonate (GC) from glycerol (G) and dimethyl carbonate (DMC). The bench scale experimental investigation was systematically conducted for this new process. With calcium oxide (CaO) as the solid catalyst, the high yield of glycerol carbonate can be obtained at a low molar ratio of dimethyl carbonate to glycerol with the method of coupling reaction and azeotropic distillation. The effect of azeotropic agents on glycerol carbonate yield was explored, and indicated that benzene was the most effective azeotropic agent. The effects of the process parameters, tower height, amount of added benzene, final temperature of tower bottom and reflux ratio were investigated. Glycerol carbonate yield can be as high as 98% under the conditions at molar ratio of dimethyl carbonate to glycerol 1:1, final temperature of tower bottom 85 °C, 1.5 mass ratio of added benzene to that in the azeotrope with methanol theoretically produced and reflux ratio 4. By continuously removing methanol from reaction system with the method of coupling reaction and azeotropic distillation, the yield of glycerol carbonate can be retained at high level using the recycled catalyst.

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1. Introduction

Under the threat of petroleum depletion and global warming, renewable biodiesel derived from transesterification of various renewable vegetable oils or animal fats and methanol, has attracted much more attention [1–3]. In the biodiesel preparation, glycerol (G) is produced as a byproduct with the amount as one-tenth of biodiesel. So much attention has been focused on the utilization of glycerol. Now, many fine chemicals such as acrolein [4], 1,3-propanediol [5], docosahexaenoic acid [6], polyglycerols [7], glycerol carbonate (GC) have been derived from glycerol.

Glycerol carbonate, as a new high value-added product, can be widely used for many applications. It can be used as the emulsifier for cosmetics [8], the additives in lithium battery [9], and liquid membrane for the separation of carbon dioxide and nitrogen [10]. In addition, the high reaction activity of glycerol carbonate allows it to participate in many reactions, and can be used as the intermediate for many chemicals, such as, glycerol glycoside [11], glycerol carbonate (meth)acrylate [12], glycerol carbonate esters [13], and N-(2,3-dihydroxy)propyl anilines [14]. Glycerol carbonate can be reacted with carboxylic acid to form high purity monoglyc-

erides [15]. Avoiding the non-environmental friendly method using epichlorohydrin, glycidol can be prepared from glycerol carbonate [16]. The application in polymer science such as the synthesis of hyperbranched aliphatic polyethers from glycerol carbonate has also been exploited [17].

Glycerol carbonate can be prepared from glycerol by different methods. Direct carbonation of glycerol with phosgene [18] or carbon monoxide and oxygen [19] has been reported to produce glycerol carbonate, but phosgene and carbon monoxide were toxic and unsafe. Sn-catalysts ($n\text{-Bu}_2\text{Sn}(\text{OMe})_2$) catalyzed carbonation of glycerol with carbon dioxide could also produce glycerol carbonate [20,21], while the yield of glycerol carbonate directly from glycerol and carbon dioxide is below 35% due to the thermodynamic limitation. Glycerol carbonate could be prepared by the reaction of glycerol and urea catalyzed by ZnO [16], zinc sulfate [22] or c-zirconium phosphate [23]. However, the reaction of glycerol with urea must be conducted at the pressure below 20–30 mbar in order to remove formed ammonia, and the purification process is also complicated. The synthesis of glycerol carbonate can also be achieved by reaction of glycerol with cyclic carbonate, such as ethylene carbonate, in the presence of the zeolite having basic sites or ion exchange resins, such as Ambersep A26 HCO_3 [24,25] and basic oxides (MgO, and CaO) or mixed oxides (Al/Mg, Al/Li) derived from hydrotalcites [26]. However, the carbonylation agent is expensive, and the purification of glycerol carbonate is difficult due to the high boiling point of the byproduct diol.

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Another way of preparing glycerol carbonate is from glycerol and dimethyl carbonate (DMC) [17] or diethyl carbonate [27]. As an environmentally benign chemical which can be prepared from methanol and urea [28], DMC is widely used as a carbonylation agent. Utilizing environmentally benign dimethyl carbonate and biodiesel's byproduct glycerol to prepare value-added glycerol carbonate becomes an attractive process. Potassium carbonate was reported to catalyze the reaction of dimethyl carbonate and glycerol [17]. In this homogeneous reaction system, the catalyst was difficult to be separated from the product. Recently, the heterogeneous catalysts such as calcium oxide have been used for the synthesis of glycerol and dimethyl carbonate in a batch reactor [29]. However, the high molar ratio of dimethyl carbonate to glycerol about 3.5 was needed to shift the reaction equilibrium in order to obtain high yield of glycerol carbonate. Excess dimethyl carbonate and produced methanol must be removed by distillation to get high purity product. The excess dimethyl carbonate must be recovered for recycle by special distillation such as azeotropic distillation or extractive distillation. Additionally, the presence of excess DMC could cause the side reactions during both reaction and separation stage, and reduce the yield of glycerol carbonate. Another problem is that deactivated calcium oxide leads to the significant reduction of the yield of glycerol carbonate in the catalyst recycle experiments. Immobilized lipase Novozym 435 was also reported as the heterogeneous catalyst with the molecular sieves 5 Å as the scavenger for methanol [30]. Removal of the byproduct methanol led to a high yield of glycerol carbonate with low molar ratio of dimethyl carbonate to glycerol. However, the activity of the lipase catalyst was low and the reaction time needed more than 25 h. On the other hand, the lipase catalyst was also expensive. The large amount of the molecular sieve was used due to its low absorption capacity for methanol.

It is desired to develop a new process for glycerol carbonate production without using excess dimethyl carbonate. In this paper, a method of coupling the reaction and azeotropic distillation for the synthesis of glycerol carbonate from glycerol and dimethyl carbonate with calcium oxide (CaO) as the catalyst was reported.

2. Experimental

2.1. Chemicals

Dimethyl carbonate (99%) and n-butanol (99.5%) were purchased from A Johnson Matthey Co. Tetraethylene glycol (99.5%) was obtained from Acros Organics. Glycerol carbonate (93.5%) was supplied by Tokyo Kasei Kogyo Co., Ltd. Calcium oxide (99%) and refined glycerol were purchased from Sinopharm Chemical Reagent Co., Ltd. Calcium oxide was grinded and sieved using the standard sieve with 80 mesh. All other chemicals were analytical reagents (AR) and were purchased from Beijing Modern Eastern Fine Chemical Co.

2.2. Reactor setup

Coupling of reaction and azeotropic distillation was carried out using a batch distillation tower. The tower bottom was a 100 ml three-neck flask, which was heated by the electric heating jacket. A condenser was equipped on the top of the tower. The reflux ratio was regulated by a time relay. Several glass tubes ($\varnothing 4 \text{ mm} \times 20 \text{ cm}$) packed with θ ring packing were used to adjust tower height. For comparing, the control experiments without azeotropic distillation were carried out in a 50 ml flask with a condenser for totally refluxing.

2.3. Reaction procedures

The procedure of coupling of reaction and azeotropic distillation was as follows: glycerol, dimethyl carbonate, azeotropic agent and calcium oxide or recovered catalyst were added to the flask. Then, the flask was quickly heated by an electric heating jacket with magnetic stirring at the rate of 300 rpm. The heating rate is $8^\circ\text{C}/\text{min}$. The distillate began to be withdrawn in a specific reflux ratio after keeping the total reflux for 0.5 h. When the temperature in the tower bottom reached the specified value, the heating was stopped, while the cooling water in the condenser was closed until the reaction system was cooled to the room temperature. The catalyst in the reaction mixture was separated by the centrifugation. The collected catalyst was washed with methanol three times and dried at 80°C for 3 h, and then reused in the recycle experiment. The residual azeotropic agent was removed by the vacuum distillation.

The conventional batch reaction procedure for the control experiments was as follows: glycerol and dimethyl carbonate were firstly mixed under magnetic stirring with the rate of 300 rpm. The mixture was heated to a given temperature by an oil bath. Although increasing the reaction temperature would enhance the conversion of glycerol, the selectivity of glycerol carbonate would decrease due to the increased rate of the side reactions (Scheme 2 and possible others) at high temperature. From the primary experiments, 60°C was selected as the reaction temperature for obtaining the high yield of glycerol carbonate. The catalyst was added into the mixture. After the desired reaction time, the catalyst was separated by centrifugation, washed with methanol three times and dried at 80°C for 3 h for reusing in the recycle experiments.

2.4. Analysis

Using nitrogen as the carrier gas, the composition of the reaction mixture was analyzed by a Gas Chromatograph (HP 5890) equipped with a capillary column DM-FFAP ($30 \text{ m} \times 0.25 \text{ mm}$) and a flame ionization detector. n-Butanol was used as the internal standard to determine dimethyl carbonate and methanol, while tetraethylene glycol was used as the internal standard to determine glycerol and glycerol carbonate.

The conversion of glycerol (X_G), and the yield of glycerol carbonate (Y_{GC}) were expressed as:

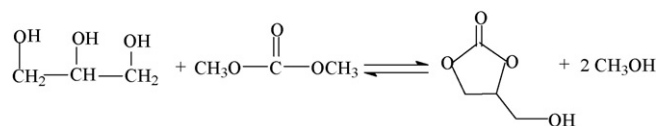
$$X_G = \frac{\text{consumed amount of glycerol (mol)}}{\text{charged amount of glycerol (mol)}}$$

$$Y_{GC} = \frac{\text{amount of glycerol carbonate (mol)}}{\text{charged amount of glycerol (mol)}}$$

3. Results and discussion

Transesterification of glycerol and dimethyl carbonate to glycerol carbonate (Scheme 1) is a reversible reaction.

In order to get high yield of glycerol carbonate for avoiding the separation of high boiling system of glycerol and glycerol carbonate, usually excess dimethyl carbonate is used to positively shift the reaction equilibrium. This was confirmed by the data listed in Table 1. In the case of this reversible reaction, the



Scheme 1. Transesterification of glycerol and dimethyl carbonate to glycerol carbonate.

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