



Catalysis, Kinetics and Reaction Engineering

Production of glycerol carbonate *via* reactive distillation and extractive distillation: An experimental study[☆]

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ABSTRACT

A process for the production of glycerol carbonate (GC) is proposed with the transesterification of glycerol (GL) and dimethyl carbonate (DMC) with CaO as catalyst by reactive distillation and extractive distillation. The performance of solvents in separating DMC-methanol azeotrope and the effects of operation parameters on the reactive distillation process are investigated experimentally. The results indicate that both the GL conversion and GC yield increase with the DMC/GL molar ratio, reflux ratio, final temperature of tower bottom, and CaO/GL molar ratio and decrease as the recycle number of CaO increases. The calcium concentration in the residual reaction mixture also decreases remarkably as the DMC/GL molar ratio increases. At DMC/GL molar ratio 4.0, reflux ratio 1.0, final temperature of tower bottom 358 K, and CaO/GL molar ratio 0.05, both the GL conversion and GC yield can reach above 99.0%, and the mass concentration of calcium in the product is less than 0.08%.

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1. Introduction

Glycerol (GL) is largely produced as a by-product of plant oil methanolysis for biodiesel production [1–3]. GL production in the United States has been already more than 350000 tons per year, while in Europe it has tripled within the last ten years [4,5]. Therefore, converting GL into high value-added chemical is highly necessary in biodiesel industry.

Glycerol carbonate (GC) is one of the promising value-added derivatives of GL due to its potential uses. GC is a stable and colorless liquid with low toxicity, good biodegradability, and high boiling point and is useful in various fields. For example, GC can be used as a polar solvent with high boiling point, a surfactant component, and an intermediate for many polymers such as polyesters, polycarbonates, and polyamides [6–8].

Several processes for the synthesis of GC have been reported. GC can be obtained from direct carboxylation of GL with carbon dioxide under supercritical condition [9–12], carbamoylation–carbonation reaction between GL and urea [13–15], or transesterification of GL with ethylene carbonate [10,16], the disadvantage of which is low GC yield, vacuum

operation condition to separate ammonia continuously, or difficulty in separation of products [10]. An alternative process is the transesterification of GL with dimethyl carbonate (DMC) because DMC can be produced by environmental benign method and the reaction condition is milder [1]. Ochoa-Gomez *et al.* [4] examined different basic and acid homogeneous and heterogeneous catalysts for synthesis of GC by transesterification of GL with DMC and found that the best heterogeneous catalyst was CaO, with which the GC yield can reach 95% at 368.15 K and DMC/GL molar ratio of 3.5. Lee *et al.* [5] studied the mechanistic pathway for transesterification of GL with DMC to produce GC in the presence of CaO and found that an active species, $\text{Ca}(\text{C}_3\text{H}_7\text{O}_3)(\text{OCO}_2\text{CH}_3)$, was generated from the interaction of CaO with GL and DMC at the DMC/GL molar ratios less than 2.0.

The transesterification of GL with DMC is shown in Fig. 1 (the number in parentheses is the boiling point). This reaction is reversible and the relative volatility of product, consisting of GC and methanol (MeOH), is very large, so a suitable method for the production of GC is the reactive distillation (RD) [17,18]. As the reaction and distillation are integrated in one apparatus in a RD process, one of the products, MeOH, can be removed continuously from reactive section by distillation. A high GL conversion can be obtained by shifting chemical equilibrium. Unfortunately, when MeOH is removed by distillation, DMC will be removed together because MeOH and DMC form an azeotrope at mass ratio of 70:30 [19]. Therefore, separation of MeOH-DMC azeotrope is important in the RD process to produce GC. Wang and Li [20] reported a process coupling reaction and azeotropic distillation for the synthesis of GC from GL and

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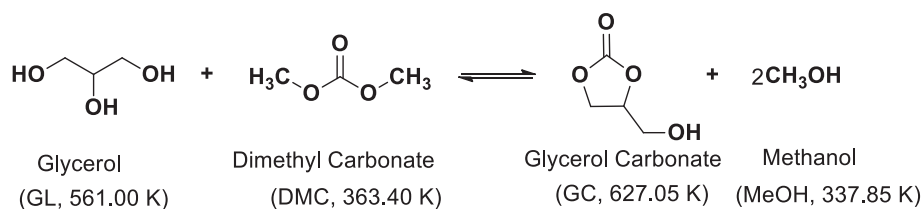


Fig. 1. Synthesis of glycerol carbonate from glycerol and dimethyl carbonate.

DMC by using CaO as the catalyst and benzene as the azeotropic agent. Azeotropic distillation was used to separate MeOH-DMC azeotrope and a high GC yield was obtained at DMC/GL molar ratio of 1.0, however, energy consumption is high due to the evaporation of azeotropic agent and regeneration of azeotropic agent is difficult due to the formation of a MeOH-benzene azeotrope. In a method to produce GC [1], molecular sieve 5 Å is used as the scavenger for MeOH with immobilized lipase as the catalyst and a high GC yield can be obtained, but a large amount of molecular sieves are needed due to their low adsorption capacity and the regeneration of molecular sieves needs high energy consumption. Compared with azeotropic distillation and adsorption, extractive distillation (ED) has more advantages to separate DMC-MeOH azeotrope: the variety of solvent is more than that of azeotropic agent, while the dosage of solvent is more flexible than that of azeotropic agent; the energy consumption of ED process is lower than that of azeotropic distillation because the solvent is almost not vaporized in an ED process [21].

In this work, a RD process is used to produce GC from the transesterification of GL with DMC and an ED is used to separate the DMC-MeOH azeotrope. CaO is used as the heterogeneous catalyst due to its high activity and low price. The effects of operation parameters on RD process are investigated experimentally. A new solvent, GL, for separation of MeOH-DMC azeotrope is found. It is also found that DMC is not only as one of the reactants, but also as the azeotropic agent to remove MeOH from the reactive section of RD column. Furthermore, DMC can prevent the leaching of CaO. Thus the proposed RD is a coupling process of RD and azeotropic distillation.

2. Experimental

2.1. Chemicals

DMC (Tianjin Guangfu Fine Chemical Research Institute, Tianjin, China) used was of 99% purity. The purities of GL and MeOH (Sinopharm Chemical Reagent Co., Ltd., China) were 99%. *n*-Butanol (Shanghai Zhanyun Chemical Co., Ltd., Shanghai, China) was of 99% purity. Tetraethylene glycol (Acros Organics) was 99.5%. GC (Tokyo Kasei Kogyo Co., Ltd., Tokyo, Japan) had a purity over 90%. All these chemicals were used without further purification. The CaO catalyst was obtained from a commercial CaO (Sinopharm Chemical Reagent Co., Ltd., China), grinded and sieved using the standard sieve with 0.18 mm (80 mesh).

2.2. Experimental setup and procedure

RD was carried out in a batch distillation column. Its bottom was a 150 ml three-neck flask, heated by an electric heating jacket. The column was a glass tube with 30 mm I.D. and 400 mm or 800 mm height. There three or four openings were along the column shell for measurement of temperature or feeding. The stainless steel θ -mesh rings of $\phi 3$ mm \times 3 mm were packed in the distillation column. A total condenser was at the top with cold ethanol as a cooling medium. The reflux ratio was regulated by a time relay.

In the RD, DMC, GL, and CaO or recovered CaO were mixed in specified amounts at the tower bottom. The mixture was quickly heated with

a slow magnetic stirring. When the temperature of the mixture reached 343.15 K, the magnetic stirring was set at 600 r·min⁻¹. The distillate was withdrawn at a specific reflux ratio after keeping the total reflux for 30 min and the sample was taken from the distillate at specified time. When the temperature at the tower bottom reached a specified value, the heating was stopped, and the cooling ethanol in the condenser was closed when the reaction system was cooled to room temperature. The reaction mixture was all taken out from the tower bottom. After the catalyst was separated by centrifugation, the reaction mixture was sampled to be analyzed. Collected catalyst was washed with MeOH three times and dried at 353.15 K for 120 min, and then reused in the recycle experiment.

The ED was also carried out using the distillation tower. In the experiment, DMC and MeOH were mixed at mass ratio of 70:30 in the tower bottom and quickly heated to boiling state by an electric heating jacket with magnetic stirring at the rate of 600 r·min⁻¹. After keeping the total reflux for 30 min, the solvent was fed into the column at the feed inlet of its upper section using peristaltic pump with a specific flow rate. Meanwhile, the sample was taken from the distillate every 10 min. When the composition of the distillate did not change, one experiment finished.

2.3. Product analysis

All the components were analyzed by a gas chromatograph (Agilent GC1790) equipped with a flame ionization detector and a capillary column DM-FFAP (30 m long, 0.25 mm i.d.). The internal standard method was used. Nitrogen (99.999% pure, Sichuan Tianyi Science & Technology Co., Ltd., Sichuan, China) was used as the carrier gas with a flow rate of 30 ml·min⁻¹ at 0.3 MPa. The temperatures of injector and detector were 250 °C and 270 °C, respectively. The temperature of column was programmed to have a 2-min initial hold at 70 °C, a 15 °C·min⁻¹ ramp from 70 °C to 250 °C, and a 15 min hold at 250 °C. A good separation for components was achieved under these conditions. *n*-Butanol was used as the internal standard to determine DMC and MeOH, while tetraethylene glycol was used as that internal standard to determine GL and GC.

The concentration of calcium in the products was determined at 422.7 nm with Atom Absorption Spectrophotometer (Perkin Elmer, AA300) with air-ethine flame. The volumetric velocity of both ethine (99.999% pure, Sichuan Tianyi Science & Technology Co., Ltd., Sichuan, China) and air was 5500 ml·min⁻¹ and the lamp current was 10 mA.

The conversion of GL, X_{GL} , and the yield of GC, Y_{GC} , are calculated as follows.

$$X_{GL} = \frac{m_{GL}^0 - m^t \cdot c_{GL}^t}{m_{GL}^0} \times 100\% \quad (1)$$

$$Y_{GC} = \frac{m^t \cdot c_{GC}^t / M_{GC}}{m_{GL}^0 / M_{GL}} \times 100\% \quad (2)$$

where m_{GL}^0 is the initial mass of GL (g), m^t is the total mass of residual reaction mixture (g), c_{GL}^t and c_{GC}^t are the GL mass concentration (%)

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