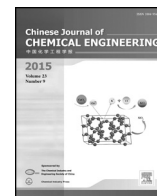




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Catalysis, Kinetics and Reaction Engineering

Production of glycerol carbonate *via* reactive distillation and extractive distillation: An experimental study☆HuaJun Wang^{1,2,*}, Lei Pang¹, Chao Yang¹, Yihua Liu¹¹ Hubei Key Laboratory of Material Chemistry & Service Failure, School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan 430074, China² Key Laboratory for Large-Format Battery Materials and System, Ministry of Education, School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan 430074, China

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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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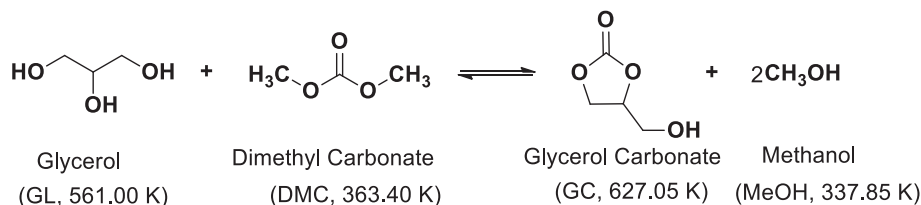


Fig. 1. Synthesis of glycerol carbonate from glycerol and dimethyl carbonate.

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 (%)

and GC concentration (%) in the residual reaction mixture, respectively, and M_{GL} and M_{GC} are the molecular weights of GL and GC, respectively.

3. Results and Discussion

3.1. The process for production of GC

The proposed process to produce GC from GL and DMC is shown in Fig. 2, with RD and ED in different columns (RD-ED process). GL and DMC as raw materials are introduced to the reactive section of RD column. The bottom product of RD column, which contains GC and some unreacted DMC (it may have a little MeOH), is sent to a recovery column, where DMC is separated from the mixture for producing high purity GC. Recovered DMC is sent back to the RD column. The distillate of RD column, which is MeOH-DMC azeotrope, is fed into an ED column with the solvent. Then, MeOH is withdrawn as the distillate of the ED column, while the DMC and solvent are obtained from the bottom. DMC and the solvent are separated in a recovery column. The solvent and DMC return to the ED and RD columns, respectively. The proposed RD-ED process has some advantages for industrial production of GC: the process can be easily developed because the operations such as distillation and ED for separation of MeOH-DMC azeotrope have been investigated [21] and satisfactory results are obtained; high GC yield and GL conversion above 99.0% can be obtained with a suitable DMC/GL molar ratio and appropriate conditions in RD column.

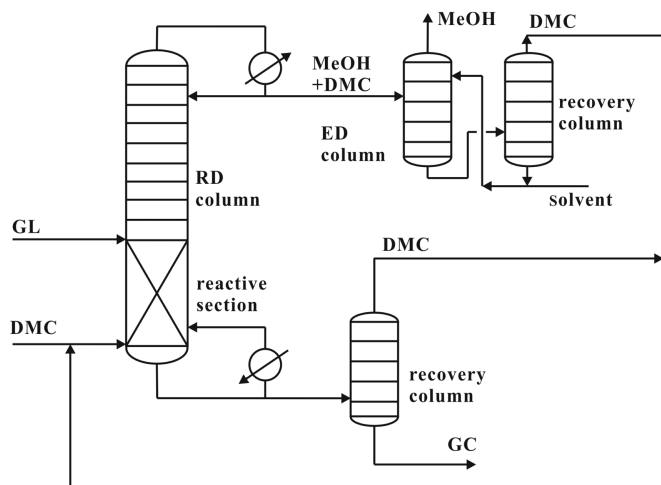


Fig. 2. Flowsheet of the proposed RD-ED process for production of GC.

3.2. Selection of solvent

A suitable solvent is extremely important for an ED process. Fig. 3 shows the effect of solvents on MeOH/DMC mass ratio in distillate in the ED process. Toluene, ethyl benzene, and *o*-xylene present better separation performance than cumene, 1-octane, and furfural. Among these solvents, the performance of toluene is the best and the MeOH/DMC mass ratio in distillate in the ED process reaches 12.86, which is significantly higher than the initial ratio 2.33. It is found that GL can be used to separate MeOH-DMC azeotrope as solvent and the MeOH/DMC mass ratio in the distillate decreases from 2.33 to 1.41, with DMC concentrating in the distillate and MeOH being the bottom product. As GL is one of the raw materials, new solvent is not needed in the reaction system. Compared with toluene, ethyl benzene, and *o*-xylene, GL is a more suitable alternative solvent for separation of MeOH-DMC azeotrope.

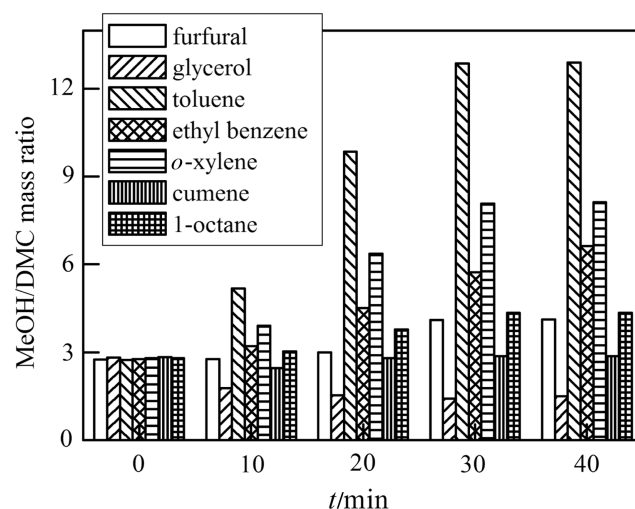


Fig. 3. Effect of solvents on MeOH/DMC mass ratio in the distillate of ED column. Initial MeOH/DMC mass ratio: 2.33:1; reflux ratio: 5; feed rate of solvent: $2.0 \text{ g} \cdot \text{min}^{-1}$; stirring rate: $600 \text{ r} \cdot \text{min}^{-1}$; tower height: 800 mm.

The liquid-liquid equilibrium data of ternary system DMC(1) + MeOH(2) + GL(3) at 333.15 K with the selectivity are shown in Table 1 [19]. All concentrations are expressed in mole fractions. The effectiveness of MeOH extraction by GL is given by its selectivity

$$S = \frac{(x_2/x_1)_{\text{GL-rich phase}}}{(x_2/x_1)_{\text{DMC-rich phase}}} \quad (3)$$

where subscripts 1 and 2 represent DMC and MeOH, respectively. As shown in Table 1, the selectivity values are greater than 1, so that separation of MeOH-DMC azeotrope by GL is possible.

3.3. Effect of DMC/GL molar ratio on RD process

The RD process is important for the RD-ED process, so the RD process is further studied. The reactive kinetics of transesterification of GL with DMC over CaO catalyst is also important for the design of RD process [22]. The effect of DMC/GL molar ratio on the RD process is shown in Fig. 4. GL conversion increases significantly from 69.72% to 97.05% and GC yield is from 44.31% to 57.66% as DMC/GL molar ratio increases from 1.0 to 2.0. As the DMC/GL molar ratio increases from 2.0 to 4.0, the GL conversion increases slightly from 97.05% to 99.93% and the GC yield increases significantly from 57.66 to 99.0%. Both the GL conversion and GC selectivity increase with the DMC/GL molar ratio.

In the RD process to produce GC, DMC is used not only as one of the reactants, but also as the azeotropic agent to remove MeOH from the reactive zone. Thus the proposed RD is virtually a coupling process of RD and azeotropic distillation. In addition, DMC can prevent the leaching of CaO [23,24]. Table 2 lists the calcium concentration and

Table 1

Experimental liquid-liquid equilibrium data on mole fractions (x) and selectivities (S) of ternary system DMC (1) + MeOH (2) + GL (3) at 101.3 kPa [19]

T/K	DMC-rich phase			GL-rich phase			Selectivity (S)
	x_1	x_2	x_3	x_1	x_2	x_3	
333.15	0.9263	0.0570	0.0167	0.0627	0.1404	0.7970	36.39
	0.8405	0.1365	0.0229	0.0709	0.2021	0.7270	17.55
	0.7869	0.1765	0.0366	0.0847	0.2955	0.6198	15.55
	0.7336	0.2254	0.0410	0.1039	0.3353	0.5608	10.50
	0.6306	0.2915	0.0779	0.1249	0.3669	0.5082	6.35
	0.5737	0.3377	0.0886	0.1675	0.4055	0.4270	4.11
	0.5443	0.3490	0.1067	0.2002	0.4240	0.3758	3.30

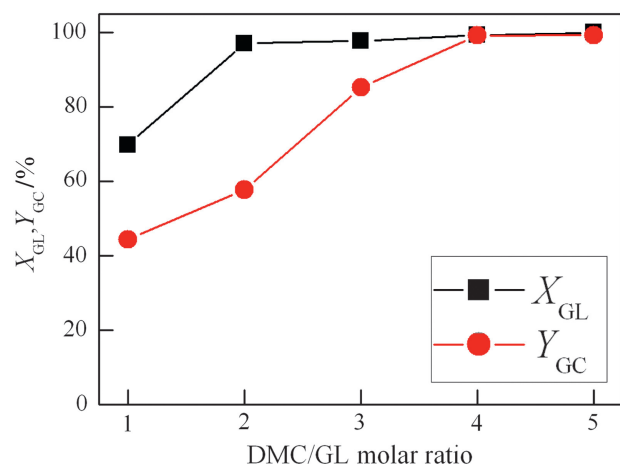


Fig. 4. Effect of DMC/GL molar ratio on GL conversion and GC yield. CaO amount: 1.2 g; total amount of GL and DMC: 75 g; final temperature of tower bottom: 363 K; reflux ratio: 5; stirring rate: 600 r·min⁻¹; tower height: 400 mm.

the phase state of residual reaction mixture at given DMC/GL molar ratio. When the ratio is less than 3.0, the calcium mass concentration in the residual reaction mixture is larger than 0.3%. At high calcium concentration, the residual reaction mixture transforms from a white emulsus solution to a gel-like state after 24 h. As the ratio increases to above 4.0, the calcium mass concentration in the residual reaction mixture decreases to below 0.08%, and the residual reaction mixture is a clear solution. Therefore, a DMC/GL molar ratio of about 4.0 is suitable for the RD process.

3.4. Effect of final temperature at the tower bottom on RD process

In this work, the RD is a batch process, so the temperature at the tower bottom will increase continuously as the distillate is withdrawn from the tower. High temperature at the tower bottom is beneficial for the production of GC because it can promote the removal of MeOH from the reactive zone, but the energy consumption will increase. Therefore, there is an optimum final temperature at tower bottom to obtain a high yield of GC. The effect of the final temperature at tower bottom on GL conversion and GC yield is illustrated in Fig. 5. The GL conversion increases from 98.21% to 99.27% and the GC yield is from 86.64% to 99.13% as the final temperature at the tower bottom increases from 353 K to 358 K, while they almost keep constant as the temperature further increases to above 358 K. Therefore, appropriate final temperature at the tower bottom is 358 K in the RD process. According to the report of Ochoa-Gomez *et al.* [4], the reaction temperature is one of the most important factors and has positive contribution to GL conversion and GC yield in the conventional batch reactor. For reaction temperature of 368 K, the pressure in the conventional batch reactor would reach 0.6 MPa due to the evaporation of DMC and MeOH, which is much higher than 0.1 MPa in the RD column. In this RD column, the same reaction temperature 368 K is reached at atmospheric pressure due to the reflux of condensate.

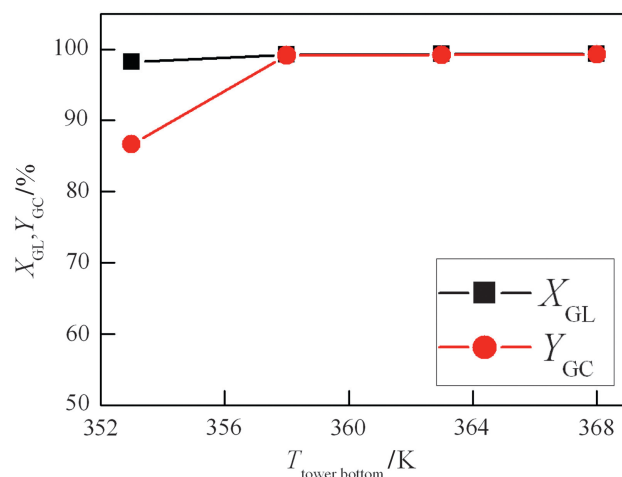


Fig. 5. Effect of the final temperature at tower bottom on GL conversion and GC yield. DMC/GL molar ratio: 4:1; CaO/GL molar ratio: 0.13:1; GL starting amount: 0.166 mol; reflux ratio: 5; stirring rate: 600 r·min⁻¹; tower height: 400 mm.

3.5. Effect of CaO/GL molar ratio on RD process

Fig. 6 shows the effect of CaO/GL molar ratio on the GL conversion and GC yield in the RD process. The GL conversion increases from 93.44% to 99.25% and the GC yield is from 91.58% to 99.14% as CaO/GL molar ratio increases from 0.02 to 0.05, but they increase slightly as the ratio increases further. The increase of ratio enhances the number of catalytic sites, so the GL conversion and GC yield also increase. However, at the CaO/GL molar ratio of 0.05, the reaction is near the chemical

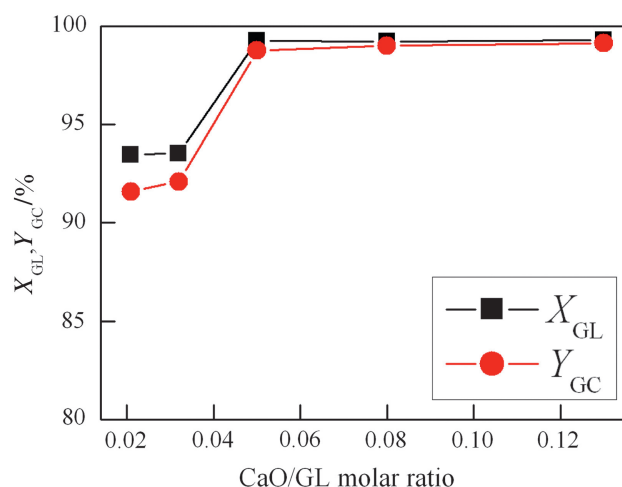


Fig. 6. Effect of CaO/GL molar ratio on GL conversion and GC yield. DMC/GL molar ratio: 4:1; GL starting amount: 0.166 mol; reflux ratio: 5; final temperature of tower bottom: 358 K; stirring rate: 600 r·min⁻¹; tower height: 400 mm.

Table 2

Calcium concentration and phase state of residual reaction mixture at different DMC/GL molar ratios. (CaO amount: 1.2 g; total amount of GL and DMC: 75 g; final temperature of tower bottom: 363 K; reflux ratio: 5; stirring rate: 600 r·min⁻¹; tower height: 400 mm)

n_{DMC}/n_{GL}	$C_{\text{calcium}}/\%$	Phase state of residual reaction mixture	
		At the end of reaction	24 h after the end of reaction (in open-end bottle)
1.0	1.049	White emulsus solution	Gel-like
2.0	0.685	White emulsus solution	Gel-like
3.0	0.323	White emulsus solution	Gel-like
4.0	0.072	White emulsus solution	Clear solution
5.0	0.004	White emulsus solution	Clear solution

equilibrium state, so the GL conversion and GC yield increase slightly with the ratio. Hence, appropriate CaO/GL molar ratio is 0.05 in the process.

3.6. Effect of reflux ratio on RD process

The effect of reflux ratio on GL conversion and GC yield is also important. As shown in Fig. 7, the GL conversion increases significantly from 95.05% to 99.13% and the GC yield is from 94.81% to 99.08% as the reflux ratio increases from 0.2 to 1.0. Then they increase minimally as the reflux ratio increases further. Higher reflux ratio improves the separation performance of RD column, which is beneficial for removing MeOH from the reactive zone of the column, so that the GL conversion and GC yield increase with the reflux ratio, while the operation cost will increase. Hence, a reflux ratio of 1.0 is suitable to the process. Both the GL conversion and GC yield can reach above 99.0% at DMC/GL molar ratio 4.0, final temperature of tower bottom 358 K, CaO/GL molar ratio 0.05, and reflux ratio 1.0. These conditions are mild for an industrial production.

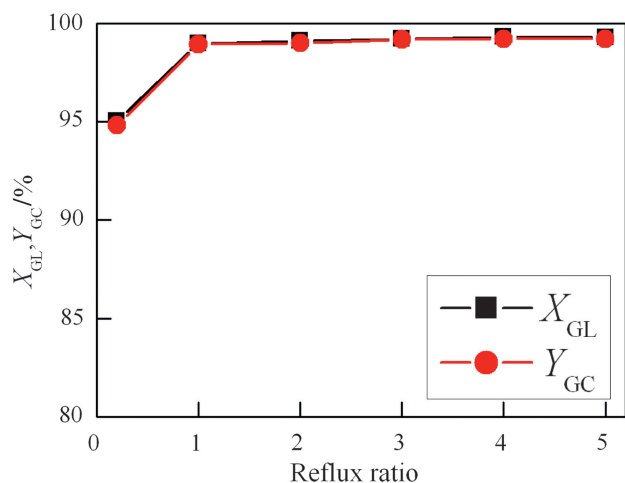


Fig. 7. Effect of reflux ratio on GL conversion and GC yield. DMC/GL molar ratio: 4:1; CaO/GL molar ratio: 0.05:1; GL starting amount: 0.166 mol; stirring rate: 600 r·min⁻¹; final temperature of tower bottom: 358 K; tower height: 400 mm.

3.7. Recycle of CaO

The recycle performance of CaO as catalyst in the RD process is given in Fig. 8. After the first run the catalytic activity of CaO decreases slightly, and the GL conversion and GC yield decrease from 99.50% and 99.10% to 98.68% and 90.62%, respectively. After the third recycle, the catalytic activity of CaO decreases dramatically. It has been reported that the catalytic activity of CaO decreases significantly in the production of biodiesel and the synthesis of GC from GL and DMC by transesterification [4,25–27]. Two factors may result in the catalyst deactivation: carbonation and hydration due to the contact of CaO with air between catalytic runs and decrease in the available catalyst surface area because of particle agglomeration [4,20]. Ochoa-Gomez *et al.* have found that in the conventional batch reactor, the GC yield decreases from initial 95.3% to 17.8% after the third recycle of CaO [4]. In our RD process, although the catalytic activity of CaO decreases when it is reused, the reduction on GL conversion and GC yield is less than that in the conventional batch reactor. Obviously, due to the continuous removal of produced MeOH from the reaction zone to shift positively the reversible transesterification, the GL conversion and GC yield in the RD process are higher than that in the conventional batch reactor even with the decrease of catalytic activity of CaO [20].

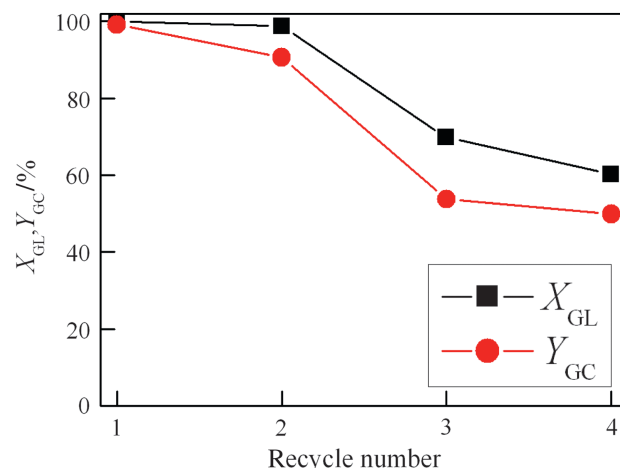


Fig. 8. Effect of recycle of catalyst on GL conversion and GC yield. DMC/GL molar ratio: 4:1; CaO/GL molar ratio in the first run: 0.13:1; initial GL amount: 0.166 mol; stirring rate: 600 r·min⁻¹; final temperature of tower bottom: 358 K; reflux ratio: 1; tower height: 400 mm.

4. Conclusions

A suitable process for the industrial production of GC is proposed. In the process, RD is used to produce GC from the transesterification of GL with DMC with CaO as catalyst while ED is used for the recovery of unreacted DMC. GL is a suitable solvent for the ED process. DMC/GL molar ratio shows an important effect on the RD process. Both the GL conversion and GC yield increase significantly with the DMC/GL molar ratio, while the calcium concentration in the residual reaction mixture decreases remarkably. At DMC/GL molar ratio of 4.0, final temperature of tower bottom of 358 K, CaO/GL molar ratio of 0.05, and reflux ratio of 1.0, 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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