Synthesis of glycerol carbonate by direct carbonatation of glycerol in supercritical CO_2 in the presence of zeolites and ion exchange resins

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Glycerol carbonate is a key bifunctional compound employed as solvent, additive, monomer, and chemical intermediate. We have synthesized it on a pilot scale in the laboratory in cyclic or alicyclic organic carbonate medium. In this study, we examined the use of supercritical CO_2 as a reaction medium and as a source of carbonate for carbonatation of glycerol. Glycerol carbonate could be obtained by direct reaction of carbon dioxide with an organic carbonate in the presence of heterogeneous catalysts. Carbonatation of glycerol into glycerol carbonate went to equilibrium in supercritical CO_2 medium.

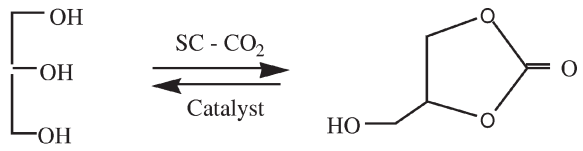
Keywords: glycerol, glycerol carbonate, supercritical fluid, zeolites, ion exchange resins, transesterification

The study was designed to synthesize glycerol carbonate (GC) directly from glycerol (G) according to scheme 1 in supercritical CO_2 medium (SC-CO_2) and to compare the results obtained with those of a previous study in conventional organic carbonate medium [1].

The carbonatation of glycerol under defined operating conditions was carried out in the apparatus illustrated in figure 1. The reactants and catalysts are introduced into the reaction chamber using glass beads to form a fixed bed. The system is then set to the desired temperature and pressure. At the end of the experiment, the supercritical medium is depressurized in acetone. The system is rinsed with acetone using an auxiliary pump, and the reactor is also rinsed with acetone. The catalyst is then desorbed with ethanol and acetone. Acetone makes glycerol carbonate infinitely soluble but partially glycerol. We focus on the recovery of glycerol carbonate. So we used acetone as a solvent to rinse the system after reaction.

The crude reaction products are obtained after evaporation of the solvents and analyzed by gas-phase chromatography on a Carbowax 20 M column using tetraethylene glycol as an internal standard and by high performance liquid chromatography (CarH phase, eluent: water/acetonitrile/sulfuric acid – 60/40/0.01 N) [2]. The results of these two techniques show that only glycerol carbonate and ethylene glycol are formed during reaction.

In the experimental conditions shown in table 1, no glycerol carbonate was formed on contact of glycerol with SC-CO_2 (exp. 1) for 3 h. No reaction took place in the presence of the highly basic resin Amberlyst A26 in the OH^- (exp. 2) or HCO_3^- (exp. 3) forms or with zeolite 13X (exp. 4). SC-CO_2 alone is not a carbonate source for carbonatation of glycerol into glycerol carbonate.



Glycerol (G) Glycerol carbonate (GC)

Scheme 1.

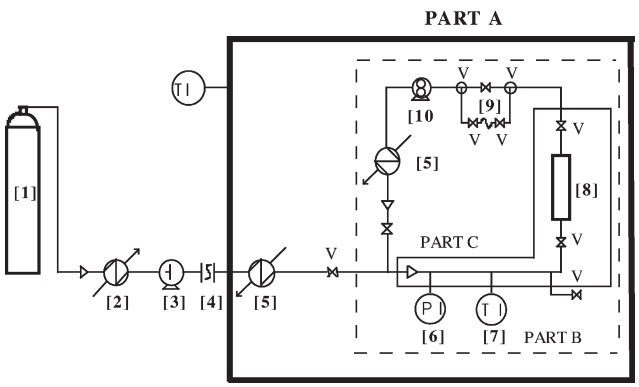


Figure 1. Set-up for synthesis in supercritical CO_2 medium. [1] CO_2 cylinder, [2] cooler (268 K), [3] high pressure pump, [4] safety disk (50 MPa), [5] heater, [6] pressure probe and indicator, [7] temperature probe and indicator, [8] reaction chamber, [9] loop, [10] recirculation pump. V: valve, part A: thermostated chamber, part B: recirculation system (volume 60 ml), part C: closed system (volume 12 ml).

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We, therefore, employed an organic carbonate as a coreactant, as described by Mouloungui et al. [1]. Ethylene carbonate was selected for the experiments. The reaction is represented in scheme 2.

Table 1
Experimental conditions on carbonatation of glycerol in supercritical CO_2.

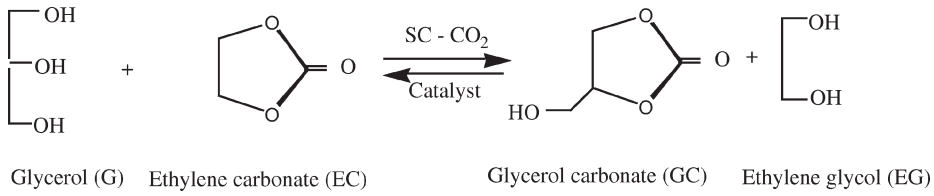
Exp.	Pressure (MPa)	Temperature (K)	Duration (h)	Glycerol (mmol)	Catalyst
1	10	313	3	11	–
2	10	313	3	11	Amberlyst A26.OH^-
3	10	313	3	11	Amberlyst A26.HCO_3^-
4	10	313	3	11	Zeolite 13X (8–12 mesh)

Without catalyst, no glycerol carbonate was formed on contact of the glycerol with ethylene carbonate in SC-CO_2 for 1 h at 313 K and 10 MPa.

We employed a heterogeneous catalyst with a pressure (13 MPa) designed to confer molecular enhancement without producing fluid microcondensation and giving rise to high diffusivity [3,4].

The initial experiments were conducted using Amberlyst A26 resin in the HCO_3^- form (table 2) and zeolites which have been used with success in organic medium [1]. We test these catalysts for use in SC-CO_2.

It can be seen from the results of experiments 5 and 7 that synthesis of glycerol carbonate is thermodynamically possible in supercritical carbon dioxide in the presence of an organic carbonate. However, a low conversion yield was obtained from glycerol. Experiments conducted at



Glycerol (G) Ethylene carbonate (EC) Glycerol carbonate (GC) Ethylene glycol (EG)

Scheme 2.

Table 2
Carbonatation of glycerol in the presence of ethylene carbonate in supercritical CO_2.[a]

Exp.	Conditions			Molar composition				Conversion
	EC (mmol)	T (K)	P (MPa)	GC (mmol)	EG (mmol)	G (mmol)	EC (mmol)	GC/G_0 (%)
5	2.3	313	10	0.147	0.146	2.824	0.855	1.30
6	6.9	313	10	0.103	0.118	2.961	1.241	0.95
7	2.3	347	13	0.511	0.478	2.436	0.449	4.70

[a] Operating conditions: initial quantity of glycerol 1 g ($G_0 = 10.85$ mmol), A26.HCO_3^- 1 g, $t = 1$ h.

Table 3
Carbonatation of glycerol in the presence of ethylene carbonate and various catalysts in supercritical CO_2.[a]

Exp.	Catalyst		Molar composition				Conversion yield
	Type	Mass (g)	GC (mmol)	EG (mmol)	G (mmol)	EC (mmol)	GC/G_0 (%)
8	3A(B)	2	1.243	1.259	7.296	3.800	11.45
9	5A(B)	2	0.474	0.302	6.978	4.944	4.35
10	5A(P)	2	2.015	2.238	2.959	0.375	18.60
11	13X(B)	2	2.684	3.110	2.502	1.077	24.80
12	Purosiv	2	3.487	3.779	3.867	1.249	32.15
13	Baylith	2	0.620	1.231	6.105	3.171	5.70
14	A26.HCO_3^-	1	1.043	2.154	2.287	1.002	9.60
15	A26.OH^-	1	2.315	2.604	5.397	1.441	21.35
16	A26.Cl^-	1	0.408	0.363	6.679	3.816	3.75
17	MP500.Cl^-	1	0.147	0.145	4.762	3.841	1.35
18	K2411	1	0.889	0.458	4.468	2.492	8.20
19	K1481	1	0.427	0.255	1.568	2.820	3.90
20	TBA.Br^-	1	0.507	0.704	6.014	4.045	4.65
21	TBA.$NHSO_4^-$	1	0.056	0.099	7.105	5.675	0.05

[a] Operating conditions: G 1 g ($G_0 = 10.85$ mmol), EC 0.6 g (EC = 6.85 mmol) $P = 13$ MPa, $T = 347$ K, $t = 1$ h.

313 K in a sapphire reactor showed that glycerol was poorly solubilized in this supercritical medium, although the ethylene carbonate was quite soluble at the amounts used here. The low solubility of glycerol was found to be a major obstacle in this reaction, where mass transfer limits the reactivity of the polyphasic system: G/EC/GC/EG/SC-CO_2.

Raising the temperature from 313 (exp. 5) to 347 K (exp. 7) multiplied the conversion yield by a factor of 3, which is in line with previous results in supercritical medium [5]. The subsequent experiments were, therefore, conducted at 347 K, a temperature comparable to that employed in conventional medium [1].

Decreasing the EC/G ratio from 1/2 to 1/6 did not increase the conversion yield. The subsequent experiments were carried out at an EC/G ratio of 1/2.

We tested the following zeolites for the reaction in SC-CO_2 at 13 MPa and 347 K: 3A, 5A (Aldrich) in the form of rods (8–12 mesh) (3A(B), 5A(B)), 5A (Aldrich) as a powder (5A(P)), 13X (Janssen) in rods (8–12 mesh), Purosiv (UOP) powder, Baylith (Bayer) powder, the strongly acid resins K2411 and K1481, the strongly basic resins Amberlyst A26 in the OH^-, HCO_3^- and Cl^- forms, Amberlyst MP500 in the Cl^- form (these catalysts may be represented in the form P-NR_4^+.X^- with $X^- = OH^-$, HCO_3^- and Cl^-) and phase transfer catalysts TBA.Br^-, TBA.$NHSO_4^-$. The results obtained are listed in table 3.

The conversion yield of glycerol carbonate was found to depend on the nature of the catalyst. Out of the zeolites (exps. 8–13), zeolites 13X in the form of rods (exp. 11) and the Purosiv zeolite in powder form (exp. 12) gave rise to a good yield of glycerol carbonate. The conversion yield appeared to depend on the Si/Al ratio (exps. 8, 9, 11), and also on the diffusion of reactants towards active sites and desorption of products from these sites. Diffusion also depended on the structure of the catalyst. The powder form (exp. 10), which facilitated access to active sites, gave rise to a higher conversion yield than did the macroporous form (exp. 9). This was further indication that the carbonatation reaction took place on the surface of the zeolites.

Satisfactory yields of glycerol carbonate were also obtained in the presence of the basic resins (exps. 14–17). These catalysts appeared to be more stable in the supercritical CO_2 medium at a temperature near the upper end of their operating range. A higher conversion yield was obtained with the hydroxyl form (exp. 15) than with the bicarbonate (exp. 14) and chloride forms (exps. 16, 17).

The sulfonic resins (exps. 18, 19) also led to glycerol carbonate by an acid-catalyzed reaction with a comparable conversion yield to that obtained with the basic resins in the bicarbonate and chloride forms.

A satisfactory conversion yield was also obtained with some phase transfer catalysts (exp. 20), although they could not be recovered at the end of the reaction.

In conclusion, we showed that glycerol carbonate could be synthesized from glycerol in supercritical carbon dioxide medium. We found that an organic carbonate such as ethylene carbonate was required as starting material under the conditions employed here. It is possible that the carbonatation of glycerol in the presence of ethylene carbonate is enhanced with carbon dioxide as co-source of carbonate for synthesis of glycerol carbonate. The zeolite Purosiv or 13X as well as a strongly basic resin catalyst such as Amberlyst A26 in the hydroxyl form effectively enhanced the reactivity of glycerol adsorbed onto the solid catalyst and the ethylene carbonate dissolved in SC-CO_2.

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