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# Utilization of glycerol for the production of glycerol carbonate through greener route

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ABSTRACT

Availability of glycerol is increased in recent years due to production of biodiesel. Glycerol carbonate, an important compound, can be manufactured using glycerol as a raw material. This work describes the synthesis of glycerol carbonate from glycerol via an enzymatic transesterification reaction using dimethyl carbonate as co-substrate and in presence as well as in absence of solvent. It has been observed that the glycerol and methanol (generated during transesterification) showed an inhibitory effect on the enzyme activity. In presence of solvent i.e. tertiary butanol, the rate of reaction is increased due to higher solubility of glycerol in it. Methanol was removed using molecular sieves. After the optimization of various parameters affecting the reaction, 94.85% conversion of glycerol was achieved with 1.5:1 molar ratio of dimethyl carbonate to glycerol and catalyst amount of 22.02% Novozym 435 at 60 °C in 14 h.


## Introduction

Glycerol is a key co-product produced during the biodiesel manufacture. An increased use of biodiesel will lead to much greater glycerol availability at lower cost. Therefore, researchers have attracted to work on the utilization of glycerol to useful materials [1]. Glycerol carbonate (4-hydroxymethyl-1,3-dioxolan-2-one, CAS no. 931-40-8) is a new and interesting material in chemical industry and is one of the most attractive derivatives of glycerol. It has excellent properties such as low toxicity, biodegradability, low flammability and a high boiling point which makes it a very attractive chemical for a variety of applications such as a high boiling polar solvent, as an emulsifier for cosmetics, the additives in lithium battery, as a source of new polymeric materials for the production of polycarbonates and polyurethanes, as a novel component of gas separation membranes, and as a surfactant component. Furthermore, glycerol carbonate is a valuable intermediate for the production of glycidol, used in resins, plastics, and throughout the pharmaceutical and cosmetics industries.

This glycerol carbonate is produced based on the reaction of glycerol with carbonyl sources like phosgene, carbon monoxide, carbon dioxide, urea, and dialkyl carbonates or alkylene carbonates. Direct carbonation of glycerol with phosgene [2] or carbon monoxide [3–5] has been reported to produce glycerol carbonate, but phosgene and carbon monoxide are toxic and unsafe. Sn-catalysts (n-$Bu_2Sn(OMe)_2$) catalyzed carbonation of glycerol with carbon dioxide could also produce glycerol carbonate, however the yield is below 35% due to the thermodynamic limitation [6,7]. The use of supercritical $CO_2$ as a reaction medium and as a source for carbonation of glycerol using zeolite as catalyst has been investigated. But, there is no evidence that a direct $CO_2$ insertion occurred as glycerol carbonate was only produced when another organic carbonate was added as a reactant [8]. Glycerolysis of urea is another method for preparing glycerol carbonate [9,10]. Several catalysts have been used, mainly based on metal oxides of variable basicity. Nevertheless, the vacuum is needed to remove evolved ammonia to accelerate the reaction and to reduce the formation of undesirable side products such as isocyanic acid and biuret. The reaction of glycerol with cyclic carbonate, such as ethylene carbonate could yield glycerol carbonate [11–13]. However, the carbonylation agent is expensive, and the purification of glycerol carbonate is difficult due to the high boiling point of the byproduct diol.

Another way of preparing glycerol carbonate is from glycerol and dimethyl carbonate. Since dimethyl carbonate (DMC) is lower toxic, it can be used as a green substitute for phosgene in the production of polycarbonates and polyurethanes. It has also been employed as a carboxylating agent as a green alternative to urea and $CO_2$ because carboxylation with DMC can be operated at much milder conditions without the production of problematic side products. For the transesterification of glycerol and dimethyl

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carbonate, various homogeneous and heterogeneous catalysts have been studied [14–18]. The catalytic activity is extremely low for acidic catalysts. On the contrary, high conversions and yields were obtained using basic catalysts. However, the high molar ratio of dimethyl carbonate to glycerol is needed to shift the reaction equilibrium in order to obtain high yield of glycerol carbonate [14] and another problem is that deactivated calcium oxide leads to the significant reduction of the yield of glycerol carbonate in the catalyst recycle experiments [18].

Enzyme catalyzed transesterifiation of glycerol and DMC is one of the best alternatives to overcome these drawbacks. The synthesis of glycerol carbonate from glycerol and dimethyl carbonate has been successfully carried out using immobilized lipase from *Candida antarctica* (CALB, Novozym 435) in presence of THF [19]. Similarly, the solvent free synthesis of glycerol carbonate in which excess dimethyl carbonate played as the reaction medium has also been explored using silica-coated glycerol [20]. Although, glycerol carbonate has been successfully prepared by Novozym 435-catalyzed in THF under mild reaction conditions, it suffers from the major drawbacks such as longer reaction time of 30 h and use of environmentally unfriendly solvent THF. Therefore, in present work, enzymatic transesterification for the production of glycerol carbonate was studied in detail and this paper describes the optimization of the production of glycerol carbonate from glycerol and DMC in presence of non toxic solvent to obtain higher yield at lesser time.

## Materials and methods

### *Materials*

Novozym 435 (lipase B from *Candida antarctica*; immobilized on macro-porous polyacrylic resin beads) was received as a gift sample from Zytex India Pvt. Ltd, Mumbai. Standard glycerol carbonate was received as a gift sample from Huntsman India Pvt. Ltd., Mumbai. Glycerol AR grade, tert-butanol and n-undecane (internal standard) were purchased from S D Fine-Chem. Ltd., Mumbai. All other chemicals such as dimethyl carbonate 99%, THF, Acetone, Toluene were purchased from Himedia Laboratories Pvt. Ltd., Mumbai. Molecular sieves 5 Å were purchased from Rarco chemicals, Mumbai.

### *Experimental method*

The experimental setup consisted of a glass reactor of 50 ml capacity, equipped with six-bladed turbine impeller. The entire reactor assembly was immersed in a thermostatic water bath, which was maintained at the desired temperature (60 °C) with an accuracy of ±5 °C. The reactor was also equipped with a condenser to reduce the losses due to evaporation. The agitation was provided by means of an electric motor having provision for speed control. The mixture of glycerol (10 mmol), dimethyl carbonate (15 mmol) and solvent (final volume 20 ml) was first fed to the reactor and stirred at known RPM. After attainment of the desired temperature, known quantity of the immobilized enzyme (0.50 g) and molecular sieves (3.33 g) as scavenger for the removal of methanol (produced during transesterification) was added to it. Samples from the reaction mixture were drawn at regular intervals of time and analyzed using gas chromatography. The schematic of experimental setup is shown in Fig. 1.

The immobilized enzyme after the reaction was recovered by filtration and was washed with acetone several times. The enzyme was then dried in desiccator and used to determine the esterification activity [21].

### *Instrumental methods*

The composition of reaction mixture was analyzed by gas chromatography (Chemito GC 8610) equipped with flame ionization detector (FID), a packed column OV-17 (1/8″ diameter, 2.00 m length) and nitrogen as carrier gas. Progress of reaction and the % conversion of glycerol were monitored using internal standard method. n-Undecane was added as an internal standard in the reaction mixture. The formation of the product was confirmed using GC–MS (Clarus 500 model, Perkin Elmer) with BPX-5 capillary column (0.25 i.d., 30 m length). Oven temperature was raised from 70 °C to 150 °C at a rate of 10 °C/min. Temperature was maintained at 150 °C for 20 s then again increased to 300 °C at rate of 17 °C/min. Detector and injector temperature were 320 °C.

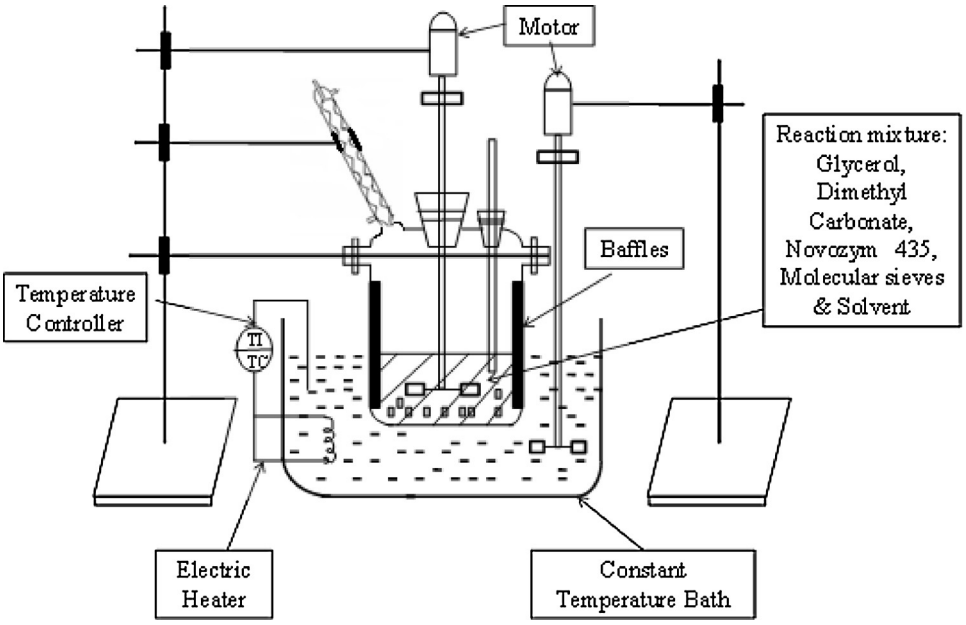


**Fig. 1.** Experimental setup for transesterification reaction.