# Transesterification of glycerol and dimethyl carbonate for the synthesis of glycerol carbonate/glycidol using ionic liquids as catalyst

**Swapna Gade,[a] Ashutosh A. Kelkar[b], Ganpati D. Yadav[a,*]**

[a]*SERB-National Post-Doctoral Fellow, Institute of Chemical Technology, Mumbai, 400019, India*

[b]*Ashutosh A. Kelkar, Senior Scientist, National Chemical Laboratory, Pune, 411008, India*

**Prof. Dr.Ganpati D. Yadav, Vice Chancellor of Institute of Chemical Technology, Mumbai, 400019, India, Fax number: 022-33611002/336111020, E-mail address: gdyadav@gmail.com*

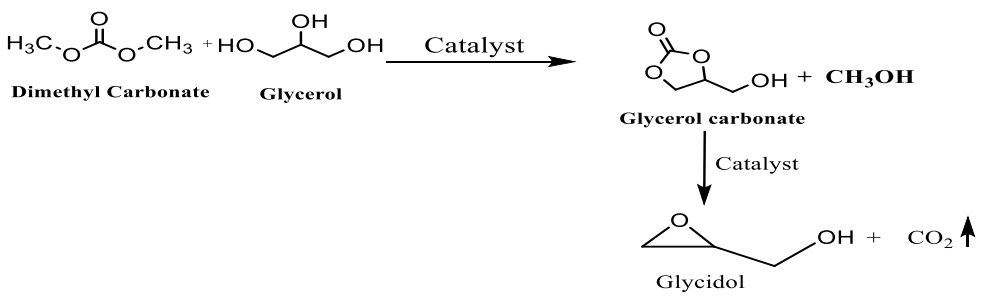
**Abstract:**

Transesterification of dimethyl carbonate (DMC) with glycerol was investigated using various ionic liquids as catalysts. Synthesis of glycerol carbonate (GC) with high selectivity (97%) has been achieved using choline hydroxide ([Cho][OH]) as a catalyst at 90$^{o}$C. Effect of various reaction conditions on the activity and selectivity was investigated among which catalyst concentration had a significant influence on conversion as well as selectivity to GC as well as glycidol (GD). Use of recycled catalyst indicated a slight drop in conversion and selectivity to GC due to dilution of reactants as well as presence of products from the previous experiment.However, the catalyst was active for the reaction. Also heterogenisation of catalyst was done to study its effect on activity, selectivity and reusability. A kinetic model is being developed.

**Keywords:** Glycerol, Glycerol carbonate, Glycidol

## 1. Introduction

Glycerol is one of the renewable feedstocks that is being produced in large amount during biodiesel production. The effective utilization and valorization of glycerol is a key factor to promote biodiesel commercialization and future developments. This has led to the development of catalysts for the synthesis of value added products from glycerol as evidenced by a number of review articles published so far [1-3]. Among various products, glycerol carbonate (GC) and glycidol (GD) are important with many applications in the fields of pharmaceuticals and fine chemical industries. Transestrification of glycerol with dimethyl carbonate (DMC) is one of the routes for the synthesis of glycerol carbonate and glycidol. Various basic ionic liquids were prepared and characterized by IR and NMR spectroscopy. There are several reports on the synthesis of glycerol carbonate from glycerol and dialkyl carbonate as reactants using acidic/basic catalysts [2]. However, only few reports are available on the synthesis of glycidol using homogeneous catalyst [3]. So there is a need to develop new catalyst or process in transestrification reaction of glycerol with dialkyl carbonate selectively for glycidol synthesis (Scheme 1). In this work we report the synthesis of glycerol carbonate and glycidol using a variety of ionic liquids as efficient catalysts.




**Scheme1**: Conversion of glycerol to glycerol carbonate and glycidol

## 2. Experimental

The transesterification of glycerol was carried out in a 50 ml round bottom flask equipped with a reflux condenser under vigorous stirring. In a typical run, 0.02 wt% of choline hydroxide (Cho-OH) as catalyst with respect to glycerol was charged to 50 ml round bottom flask containing glycerol 2 g, and DMC 5.87 g. The reaction was carried out at refluxing temperature for the selected reaction time. Standard reaction was carried out for 3 h. Periodically the reaction mixture was cooled, a sample withdrawn and diluted with N,N-dimethylformamide to analyse by gas chromatography. Identification of products was done using gas chromatography–mass spectrometry (GC–MS). Activity of catalyst was based on conversion of limiting reagent measured under standard conditions of reaction.

## 3. Results and discussion

Various basic ionic liquids were prepared and screened. From the preliminary screening all the ionic liquids prepared were found to be active for the reaction. Selectivity pattern varied with the type of ionic liquid used and glycidol formation in significant quantity was observed by decarboxylation of glycerol carbonate formed as primary product. Detailed investigations were carried out using choline hydroxide as a catalyst. Best results were obtained with ((94%) glycerol conversion, and (97%) selectivity to GC and (3%) selectivity to GD at 0.02% Cho-OH catalyst loading, whereas with cho-bicarbonate gave 97% glycerol conversion to 59% glycidol and 34% glycerol carbonate under optimized reaction conditions (Figure 1). Activity as well as selectivity of the catalyst decreased significantly with increase in moisture content. Use of recycled catalyst indicated a slight drop in conversion and selectivity to GC due to dilution of reactants as well as presence of products from the previous experiment.

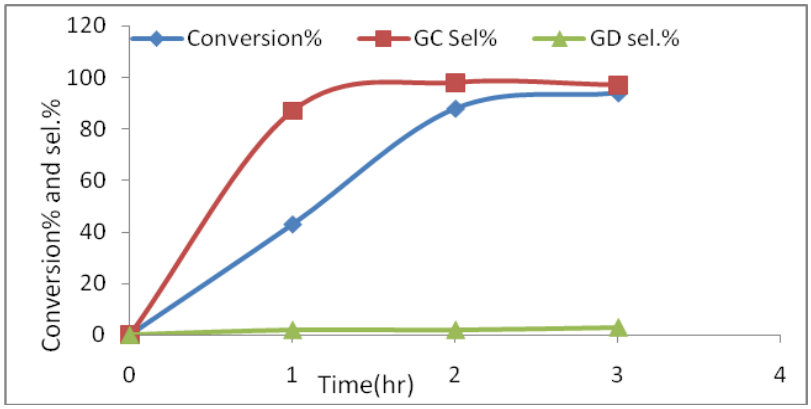



**Figure1:** Typical concentration–time profile for transesterification of DMC with glycerol using Cho-OH as catalyst. Reaction Condition: Catalyst 0.02% Choline-OH w.r.t. glycerol, 90°C,1:3(Glycerol:DMC), 3h

## 4. Conclusions

Various ionic liquids were prepared and characterized in detail. Cho-OH were active for the reaction and gave best conversion (97%) with high selectivity to GC (97%) and GD (3%). Effect of various reaction conditions on the activity and selectivity has been investigated using Cho-OH as a catalyst. Heterogenisation of ionic liquids is being done.

## 5. References

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