



## Production of glycerol carbonate from glycerol with aid of ionic liquid as catalyst



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### HIGHLIGHTS

- Green production of glycerol 1,2-carbonate with an environmentally friendly catalyst was proposed.
- Screening and optimisation of the catalysts were comprehensively performed.
- The basic ionic liquid (emim[Ac]) showed best catalytic activity and recyclability.
- Detail understanding on the glycerol-catalysts and glycerol 1,2-carbonate-catalysts interactions has been well explored.

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### ABSTRACT

The rapid growth of biodiesel industry has led to a large surplus of its major unintentional byproduct particularly glycerol. Thus, finding a new application is necessary to convert glycerol to value added products. In this study, glycerol has been subjected to a transesterification reaction to synthesis glycerol carbonate (GC) over several selected ammonium and imidazolium-based ionic liquids (ILs) as catalysts. It is believed that the variation of catalytic performance between ILs was due to the anion strength of ILs. The glycerol conversion, yield and selectivity of GC were followed the anion order of [Ac] > [Dca] > [Fmt] > [DMP] > [NO<sub>3</sub>] > [Cl] > [BF<sub>4</sub>]. Effects of reaction temperature, time, diethyl carbonate (DEC)/glycerol molar ratio and catalyst loading on glycerol conversion and GC yield have been analysed. The IL, 1-ethyl-3-methylimidazolium acetate (emim[Ac]) shows best performance under solvent-free with conversion of glycerol and GC yield reached highest at 93.50% and 88.70%, respectively under reaction temperature of 120 °C reaction time of 2 h, DEC/glycerol molar ratio of 2 and catalyst loading of 0.5 mol%. Also, this emim[Ac] can be reused as catalyst at least three times without any significant reduction in conversion, yield and selectivity. Reaction mechanism of the transesterification reaction catalysed by emim[Ac] has been proposed in this study.

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### 1. Introduction

Formation of glycerol (glycerine or 1,2,3-propanetriol) as a by-product during biodiesel production has led to a major concern. The surplus of glycerol has dropped its price [1] and exerts a great impact on the refined glycerol market. Thus, it becomes a research focus to find an innovative way to revalorize glycerol and transform to value-added chemicals [2]. One of the most celebrated

products reported in the last 5 years is glycerol carbonate (GC). GC has many applications in various industrial sectors. GC is useful not only as a polar high boiling solvent or intermediate in organic synthesis such as glycidol [3], it also can be used as green substitution for petro-derivatives compounds (ethylene carbonate or propylene carbonate) [4]. In polymer and plastics industry, GC is use as an intermediate for the synthesis of polycarbonates, polyesters, polyamides and hyper branched polyethers [5,6]. In addition, GC also can be used as electrolytes and solvents in lithium-ion batteries, by planting activating agent in agricultural industry and as components for gas separation membranes [7].

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GC having low toxicity and good biodegradability that can be synthesized from glycerol as alcohol OH-source with various carboxylation sources, including carbon dioxide (CO<sub>2</sub>), urea, and dialkyl carbonates [8,9]. The simple and effective of direct carbonylation of glycerol with CO<sub>2</sub> with tin complexes as catalyst however facing major limitations particularly due to unfavourable thermodynamic equilibrium and low yields (less than 8% of product). The use of phosgene as the carbonylation sources somehow has imparted a negative drawback in which highly toxic and corrosive nature of phosgene has turn the process become hazardous. Alternatively, direct routes such as transesterification reaction with alkylene or dialkyl carbonate to synthesis GC have been explored. Transesterification reaction using alkylene carbonate requires applying reduced pressure in order to separate by-product from reaction medium [10]. Transesterification of glycerol with dialkyl carbonate is the most attractive process for GC synthesis since the process starts with non-toxic materials under mild operation conditions and obtains a good GC yield [11–13]. Moreover, the non-toxicity, biodegradability and cleaner production process of dialkyl carbonate make it as a green reagent to be used as carbonylating agent [14]. This reaction is favoured using an alkaline base catalyst compare to acidic catalysts as their catalytic activity are extremely low [8].

Recently, researchers have shown an increased interest in employing homogeneous [15–17] (inorganic metal salts, quaternary ammonium salts and ionic liquids (ILs)) as well as heterogeneous [18–21] (metal oxides, mixed metal oxides, hydrotalcites, supported hydroxyapatite and Sn-complexes) catalysts for the transesterification reaction. In attempt to find an alternative energy source, Teng et al. [22] has successfully performed microwave-assisted transesterification using CaO as catalyst. It is noted that, 93.4% GC yield was obtained in five minutes reaction time. However, despite its high activity and easily separate, heterogeneous catalyst suffers from several major drawbacks including deactivation of catalyst in presence of water, leaching of catalyst active sites and energy intensive process due to calcination step needed. On the other hand, homogeneous catalysts possess highly catalytic activity and enhanced reaction rate which is preferable to be used as catalysts in view of the demerit of heterogeneous catalysts.

As well established today, ILs present many advantages in many reaction using as catalysts or due to the unique properties [23]. The adjustable cation–anion pairing opens up the possibility of tailoring to particular physical and chemical properties. This will also allow the preparation of acidic/basic ILs. Moreover, dual function of ILs often results in increase in rate and/or reactivity, compared to some of the catalyst that need additional of solvent to enhance the transesterification reaction [24,25]. In view of that, many studies using homogenous basic ILs have been reported as they showed a good catalytic activity for GC formation [17,26,27]. Cation and anion of ILs can cooperatively activate electrophiles and nucleophiles to catalyse various reactions which involve carbonyl activation [28]. It has been reported that hydrogen bond basicity is controlled by the anion, while the hydrogen bond donation is dominated by the hydrogen bond basicity of the anions with a smaller contribution from the hydrogen bond acidity of the cation. Changing to more basic anions leads to a dramatic drop in the acidity of cation. Thus, anions have decisive influence on the catalytic performance in the transesterification of glycerol. Apart from catalyst activity, it is also expected that reaction parameters such as reaction temperature, reaction time, molar ratio of reactants and solvent, as well as impurity particularly water content and methanol in the reaction mixture have significantly affected the glycerol conversion and the GC yield [29].

Therefore, the production of GC from glycerol is an attractive reaction that utilises two inexpensive and readily available raw

materials in a chemical cycle. Thus, the present work attempts to explore on an alternative route of transesterification reaction of glycerol with DEC over ammonium and imidazolium-based ILs as catalysts for GC production. Selection of ILs were based on their strength of anion which given by its hydrogen bond basicity reported by parameter  $\beta$ . The effect of the different in  $\beta$  value of anion on the glycerol and GC–IL interaction was examined in this study. The pertinent factors affecting the performance of GC synthesis were studied individually. A time online analysis study with ATR-FTIR and <sup>13</sup>C NMR conducted in this study help to further understand the mechanism and theory of the reaction. Significantly, the synthesis pathways of GC and the possibilities of by-products catalysed by IL were addressed in this study. Scheme 1 shows the schematic reaction of transesterification of glycerol to GC.

## 2. Experimental

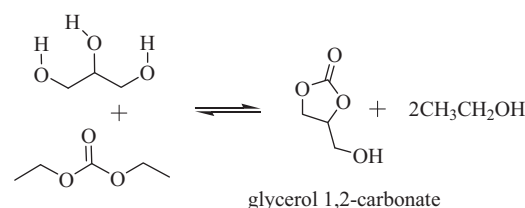
### 2.1. Chemicals

Glycerol (99.5%), glycerol carbonate (GC) (99.5%), diethyl carbonate (DEC) (99.5%) and glycidol (CAS: 556-52-5) were supplied by Aldrich and used without any further purification. Ionic liquids (ILs) namely methylammonium nitrate (MA[NO<sub>3</sub>]), ethylammonium nitrate (EA[NO<sub>3</sub>]), 2-hydroxyethylammonium formate (HEA[Fmt]) were purchased from IoLiTec Inc. (USA). 1-ethyl-3-methylimidazolium dimethyl phosphate (emim[DMP]), 1-butyl-3-methylimidazolium chloride (bmim[Cl]), 1-butyl-3-methylimidazolium tetrafluoroborate (bmim[BF<sub>4</sub>]), 1-butyl-3-methylimidazolium dicyanamide (bmim[Dca]) and 1-ethyl-3-methylimidazolium acetate (emim[Ac]) were obtained from Merck. All ILs were purchased having 99% of purity. Solvents; chloroform (AR grade), ethyl acetate (AR grade), methanol (AR grade) and methanol (GC grade-99.9%) were purchased from Fisher Scientific. Deuterated methanol-*d*<sub>4</sub> (99.8%) (Aldrich) was used as solvent in NMR analysis.

### 2.2. Synthesis of glycerol carbonate

The reaction was carried out using a 150 mL round bottom three-neck glass flask fitted with magnetic stirrer, reflux condenser and sampling device. A constant heating energy was supplied to the glass flask in oil bath with nitrogen gas flow at atmospheric pressure. In a typical experiment, 27.4 mmol of glycerol was heated first, followed with the addition of an excess of DEC into the flask and heated to the desired temperature. Then, the selected IL (0.1–10 mol% with respect to limiting substrate) was then added to the biphasic system as catalyst to start the reaction. The transesterification progress was monitored by analytical thin layer chromatography (TLC) with optimised developing solvent system of ethyl acetate/methanol (4.8:0.2). Alternatively, the formation of a sole phase could be taken as the end point of the reaction.

To recover IL upon completion of the reaction (as determined by TLC and area of glycerol from GC-FID), chloroform (3 × 10 mL) was added to the reaction mixture in order to recover IL. Later, the



**Scheme 1.** Transesterification reaction of glycerol to glycerol 1,2-carbonate.

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