

PRODUCTION OF GLYCEROL 1,2-CARBONATE FROM GLYCEROL WITH AID OF IONIC LIQUID AS CATALYST

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The surplus formation of glycerol (glycerine or 1,2,3-propanetriol) during biodiesel production has led to a major concern. Glycerol price has dropped and it exerts a great impact on the refined glycerol market. This has triggered an extensive research focus to find an innovative way to revalorize glycerol and transform to value-added chemicals. Yet, it is undeniably a necessary move towards achieving greener and sustainable processes. For instance, glycerol 1,2-carbonate (4-hydroxymethyl-1, 3-dioxolan-2-one) is currently one of the most celebrated glycerol derivatives that captured arising scientific and industrial attentions due to its extensive potential applicability. This cyclic ester of glycerol with carbonic acid is reasonably reactive as it has reactive electrophilic and nucleophilic sites yet having low toxicity and good biodegradability. This important product has attracted numerous applications in chemical industry such as being the novel component of gas-separation membranes, non-volatile solvent for dyes, lacquers, detergents, adhesives and cosmetics, electrolyte ingredient of lithium-based batteries, surfactants and lubricating oils. Likewise, glycerol 1,2-carbonate is beneficial not only as a polar high boiling solvent or intermediate for the synthesis of polycarbonates, polyesters, polyamides and hyper branched polyethers, it also can be used as green substitution for petro-derivatives compounds (ethylene carbonate or propylene carbonate). The reactivity of glycerol 1,2-carbonate having both electrophilic and nucleophilic sites allows for the synthesis of new polymeric materials such as glycidol which is primarily being used in the production of a number of polymers.

Glycerol 1,2-carbonate can be produced either by direct or indirect synthesis route [1-2]. For example, through direct carbonylation, glycerol reacts with carbon dioxide/carbon monoxide with the aid of catalysts; zeolites (under supercritical conditions) or poisonous Sn. This is the most promising way in which two wastes (glycerol and carbon monoxide/carbon dioxide) are converted into a valuable chemical. They are both bio-based reactants and also wastes which were produced by other industries. However, low yield was obtained (less than 8% of product) and the reaction of glycerol with carbon dioxide is unfavourable in thermodynamic equilibrium. Furthermore, direct carbonylation of organic solvents including nitrobenzene, dimethyl sulfoxide or N,N-dimethyl formamide, and methanol will utilize uneasily recoverable catalysts. The use of homogeneous catalysts, high pressure and long heating time at elevated temperatures hampered the negative ecological impacts toward the reactions.

Trans-carbonation of a carbonate source and glycerol was also reported for glycerol 1,2-carbonate syntheses. Glycerol can be reacted with phosgene, thus providing a very simple and effective way to produce glycerol 1,2-carbonate. However, the reaction with phosgene is limited by the hazardous and highly toxic gas originated from it. Looking for a safer method, glycerol 1,2-carbonate can be achieved from the reaction of glycerol with cyclic carbonates such as ethylene carbonate or propylene carbonate in the presence of the zeolite having basic sites or ion exchange resins, such as Amberlyst A26 HCO_3 and basic oxides (MgO and CaO) or mixed (Al/Mg, Al/Li) derived from hydrotalcites. From an economic point of view, ethylene carbonate is expensive even though it poses interesting physical properties (low toxicity, low evaporating rate, biodegradability, high solvency) and low reaction temperature of operation. Moreover, some difficulties could occur during the purification step of glycerol 1,2-carbonate due to high boiling point of the by-product diol.

Apart from that, glycerolysis reaction of glycerol and urea in the presence of a suitable catalyst has been recently developed. The reaction can be catalysed by zinc oxide, zinc sulphate, or c-zirconium phosphate. However, the reaction must be conducted at the pressure below 20-30 mbar, in order to remove the by-product which is high-quality ammonia and furthermore, the purification method is also complicated. The most widely studied transesterification reaction of glycerol 1,2-carbonate syntheses is through the reaction of glycerol with dialkyl carbonate such as diethyl carbonate or dimethyl carbonate. This attractive alternative reaction has been

used industrially; specifically in the manufacturing biodiesel. The use of dimethyl carbonate as a carbonate source results in methanol formation along the reaction. Dimethyl carbonate and methanol can be simply removed and easy purification of glycerol 1,2-carbonate can obviously overcome the limitation with respect to cyclic carbonate, ethylene carbonate or propylene carbonate. Indeed, the environmental-friendly nature of dimethyl carbonate can replace potentially hazardous chemicals like phosgene with ionic liquids as catalysts.

In addition, the researchers have recently shown an augmented interest in employing homogeneous [3] (inorganic metal salts, quaternary ammonium salts and ionic liquids) as well as heterogeneous [4] (metal oxides, mixed metal oxides, hydrotalcites, supported hydroxyapatite and Sn-complexes) catalysts for the transesterification reaction. Despite their high activity and easily separate, heterogeneous catalysts suffer from several major drawbacks including deactivation of catalysts 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.

Capability of ionic liquids to act as a solvent or perform excellently as a catalyst in chemical processes has never been argued. 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 ionic liquids. Moreover, dual function of ionic liquids 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. In view of that, many studies using homogenous basic ionic liquids have been reported as they showed a good catalytic activity for glycerol 1,2-carbonate formation [5]. The cation and anion of ionic liquids can cooperatively activate electrophiles and nucleophiles to catalyze various reactions which involve carbonyl activation. 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.

Therefore, the production of glycerol 1,2-carbonate from glycerol is certainly an attractive reaction that utilizes two inexpensive and readily available raw materials in a chemical cycle. Thus, in the present work, glycerol has been subjected to a transesterification reaction to produce glycerol 1,2-carbonate over several selected ammonium and imidazolium-based ionic liquids as catalyst. It is believed that the variation of catalytic performance were based on anion strength of ionic liquids which given by its hydrogen bond basicity reported by parameter β . The effect of different β value of anion on the glycerol and glycerol 1,2-carbonate - ionic liquids interaction were also discussed. The concentrations of the glycerol and glycerol 1,2-carbonate were obtained directly from their respective peak areas in the gas chromatograph. Activity of ionic liquids towards the transesterification reaction was based on conversion of glycerol as limiting substrate measured under standard conditions of reaction. The transesterification progress was monitored by thin layer chromatography. Effects of reaction temperature, time, diethyl carbonate (DEC)/glycerol molar ratio and catalyst loading on the glycerol conversion and glycerol 1,2-carbonate yield have comprehensively been analyzed. A time online analysis study with ATR-FTIR and ^{13}C NMR conducted in this study help to further understand the mechanism and theory of the reaction. The elucidation of proposed reaction mechanism provides an in-depth understanding towards the production process.

In determining the potential catalyst, a series of imidazolium and ammonium-based ionic liquids were selected with respect to the hydrogen bond basicity (β value) quantified by Kamlet and Taft parameter. Table 1 shows the list of ionic liquids used as catalysts together with the reported β value.

Table 1: Ionic liquids used in this work and their reported hydrogen bond basicity (β value) of anion.

| No. | Ionic liquid | Abbreviation | β value |
|-----|--|----------------------|---------------|
| 1 | Methylammonium nitrate | MA[NO ₃] | 0.46 [6] |
| 2 | Ethylammonium nitrate | EA[NO ₃] | 0.46 [6] |
| 3 | 2-hydroxyethylammonium formate | HEA[Fmt] | 0.73 [7] |
| 4 | 1-ethyl-3-methylimidazolium dimethyl phosphate | emim[DMP] | 1.12 [8] |
| 5 | 1-butyl-3-methylimidazolium dicyanamide | bmim[Dca] | 0.59 [9] |

| | | | |
|---|---|------------------------|----------|
| 6 | 1-butyl-3-methylimidazolium chloride | bmim[Cl] | 0.95 [9] |
| 7 | 1-butyl-3-methylimidazolium tetrafluoroborate | bmim[BF ₄] | 0.55 [9] |
| 8 | 1-ethyl-3-methylimidazolium acetate | emim[Ac] | 1.20 [9] |

All ionic liquids screened were noted active (moderate to high glycerol conversion) for the reaction except for MA[NO₃], EA[NO₃], bmim[BF₄] (Table 2). These ionic liquids having non-coordinating anion and halide based ionic liquids (bmim[Cl]) giving less than 10 % conversion of glycerol and only traces amount of glycerol 1,2-carbonate was formed in the reaction. The glycerol conversion, yield and selectivity of glycerol 1,2-carbonate were followed the anion order of [Ac] > [Dca] > [Fmt] > [DMP] > [NO₃] > [Cl] > [BF₄].

Table 2: Catalyst screening of selected ionic liquids as catalyst for transesterification of glycerol. Reaction conditions: Temperature = 120 °C, Time = 2 Hours, Molar ratio of diethyl carbonate/glycerol = 2 and catalyst loading 0.5mol% based on limiting reactant.

| No. | Ionic liquid | Glycerol conversion (%) | Glycerol 1,2-carbonate yield (%) |
|-----|------------------------|-------------------------|----------------------------------|
| 1 | Blank | 5.0 | 5.0 |
| 2 | MA[NO ₃] | <10.0 | <10.0 |
| 3 | EA[NO ₃] | <10.0 | <10.0 |
| 4 | bmim[Cl] | <10.0 | <10.0 |
| 5 | bmim[BF ₄] | <5.0 | <5.0 |
| 6 | HEA[Fmt] | 24.0 | 24.0 |
| 7 | emim[DMP] | 22.2 | 22.0 |
| 8 | bmim[Dca] | 45.0 | 45.0 |
| 9 | emim[Ac] | 93.5 | 88.7 |

Interestingly, the ionic liquid, 1-ethyl-3-methylimidazolium acetate (emim[Ac]) shows best catalytic performance under solvent-free condition with conversion of glycerol and glycerol 1,2-carbonate yield attained highest at 93.50% and 88.70%, respectively under reaction temperature of 120°C reaction time of 2 hours, DEC/glycerol molar ratio of 2 and catalyst loading of 0.5 mol% with recyclability of the catalyst reached at least three times without any significant reduction in conversion, yield and selectivity. Hence, emim[Ac] was taken up for further investigations with the aim of improving the glycerol 1,2-carbonate yield and selectivity. The effect of reaction temperature, time of reaction, molar ratio of DEC/glycerol and catalyst loading were later evaluated in detail.

In general, increasing temperature of transesterification reaction should lead to a dramatic effect towards the conversion of glycerol. This is mainly due to the miscibility between hydrophobic diethyl carbonate and hydrophilic glycerol improves at higher temperatures. Figure 1 reveals a rapid increase of glycerol conversion and glycerol 1,2-carbonate yield were observed when temperature increase from 110 to 120 °C, possibly due to the increase of collision energy when temperature is increased. About 93.50% conversion of glycerol and 88.70% glycerol 1,2-carbonate yield was successfully synthesized at reaction temperature of 120 °C. Further increase of reaction temperature at 130 °C gives 95.87% glycerol conversion and glycerol 1,2-carbonate yield dramatically dropped to 64.17%. A rapid darkening of the reaction mixture was also observed as temperature of the reaction increase to more than 120 °C. The decreased of glycerol 1,2-carbonate yield at 130 °C resulted from increasing reactivity of its hydroxyl moiety with temperature. At high temperature, the acidic primary hydroxyl pendant group of glycerol could react with the anion of ionic liquid resulting in forming hydroxide ion which could initiate the glycerol 1,2-carbonate ring opening polymerization leading to a polymer. This incident lower conversion of glycerol to glycerol 1,2-carbonate.

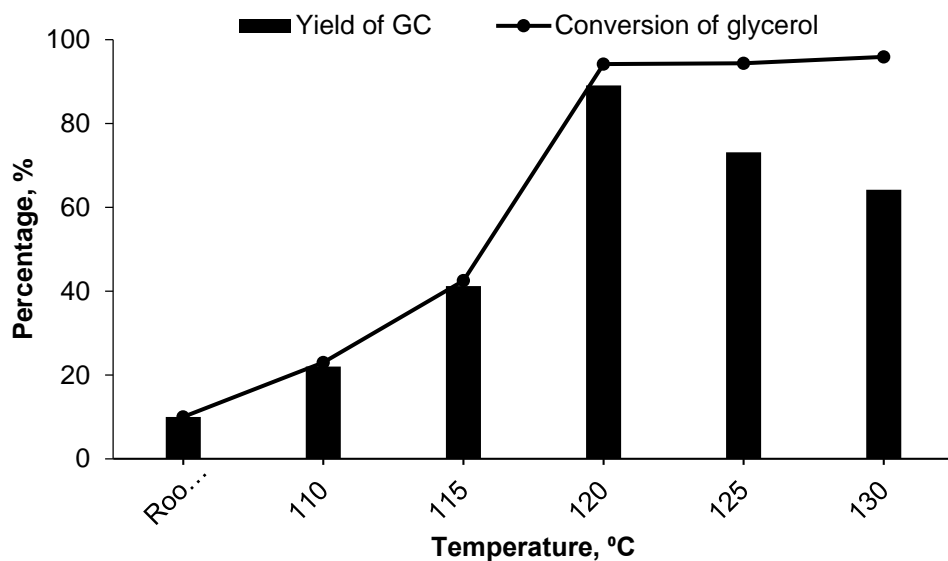


Figure 1: Effect of reaction temperature on the transesterification of glycerol with diethyl carbonate in the presence of emim[Ac] as catalyst. Reaction conditions: Reaction time = 2 hours, diethyl carbonate/glycerol molar ratio = 2 and emim[Ac] = 0.5mol% based on limiting reactant.

As the reaction temperature plays a very critical effect towards glycerol conversion and glycerol 1,2-carbonate yield, optimum reaction temperature for the transesterification was selected at 120 °C and was then used for checking the influence of the remaining reaction parameters.

Apparently, higher reaction time could be advantageous as it allows more time for the glycerol to react in the catalyzed reaction. Furthermore, the conversion rate of glycerol, selectivity and yield of glycerol 1,2-carbonate are expected to increase with reaction time. Figure 2 shows the influence of reaction time on the transesterification reaction catalyzed by emim[Ac], with respect to the glycerol conversion and glycerol 1,2-carbonate yield. Glycerol 1,2-carbonate yield is certainly improved from 42.4% to 88.7% when the reaction time had increased from 1 hour to 2 hours. However, the production is decreased to 68.0% over 4 hours of reaction. On the other hand, the glycerol conversion increased more than three-fold and achieved 93.5% conversion after 2 hours reaction and remains with the extended time of reaction.

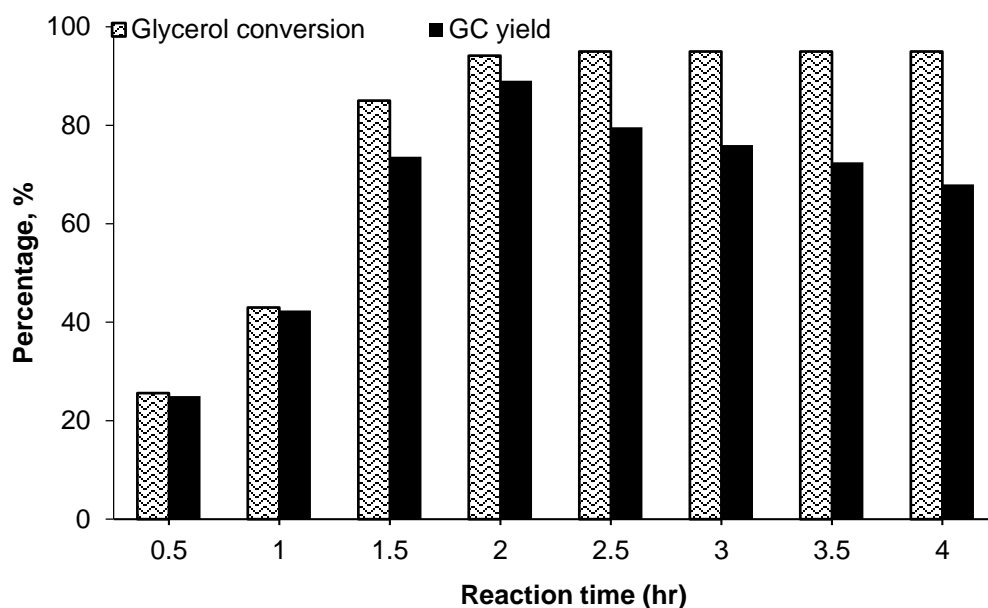


Figure 2: Effect of reaction time on the transesterification of glycerol with diethyl carbonate in the presence of emim[Ac] as catalyst. Reaction conditions: Temperature = 120 °C, Molar ratio of diethyl carbonate/glycerol = 2 and emim[Ac] = 0.5mol% based on limiting reactant.

Since the rate of reaction can be manipulated by varying the amount of one reactant, the molar ratio of substrates is an important parameter affecting the course of reaction. According to the stoichiometric calculations, the ratio for transesterification reaction requires only 1 mol of carbonates and 1 mol of glycerol to produce 1 mol of glycerol 1,2-carbonate and 2 mol of relevant by-product. However it was reported that type of catalyst and reaction conditions strongly affect the mechanism of reaction. In the transesterification between the hydrophilic glycerol and hydrophobic carbonate source, the reactants are not miscible and the reaction is reversible which is in need of an excess carbonate source to give positive effect on the conversion and yield. The prevention of two-phase formation between the reactants can be achieved either by applying excessive amount of carbonate source over the glycerol moiety to act as reactant and solvent or by adding organic solvent. It is worth to note that, emim[Ac] can also serves as solvent in this reaction as it possess dual function.

As tabulated in Table 3, low conversion and glycerol 1,2-carbonate yield was observed when equimolar of reactants was used in the transesterification giving 28.9% and 28.0%, respectively. The glycerol 1,2-carbonate yield was increased when the diethyl carbonate/glycerol ratio is raised beyond 2 and keep slightly decreased at molar ratio of 3. Further increased in the amount of diethylcarbonate beyond the molar ratio of 3 led to adverse effect on the yield and selectivity of glycerol 1,2-carbonate. This circumstance would incur additional cost for the reactants. It can be seen that, conversion of glycerol was slightly decreased to 92.9% and also glycerol 1,2-carbonate yield decreased to 72.9% at molar ratio of 4. This is expected due to dilution of reaction by diethyl carbonate or further reaction of glycerol 1,2-carbonate with an excess of diethyl carbonate to form glycerol dicarbonate. This glycerol dicarbonate synthesis could not be prevented and glycidol was additionally obtained in yields of 6–10% with respect to some parameters effect. Therefore, the molar ratio was fixed at 2 for further experiments.

Table 3: Effect of diethyl carbonate/glycerol molar ratio on conversion of glycerol and glycerol 1,2-carbonate yield and selectivity. Reaction conditions: Temperature = 120 °C, Reaction time = 2 hours and emim[Ac] = 0.5mol% based on limiting reactant.

| Diethyl carbonate/ Glycerol ratio | Glycerol conversion , % | Glycerol 1,2- carbonate yield, % | Glycerol 1,2-carbonate selectivity, % |
|--------------------------------------|----------------------------|-------------------------------------|--|
| 1 | 28.9 | 28.0 | 96.9 |
| 2 | 93.5 | 88.7 | 94.6 |
| 3 | 96.0 | 78.1 | 81.4 |
| 4 | 92.9 | 72.9 | 78.5 |

Increment of catalyst loading led to a gradual increase in the production of glycerol 1,2-carbonate. Therefore, a larger number of glycerol molecules potentially catalyzed in the desired reaction. The effect of catalyst loading on conversion, yield and selectivity were investigated in a range of 0.1 to 10 mol% keeping other parameters constant (Figure 3). It is observed that low emim[Ac] loading (0.1 mol%) led to a very slow reaction with 65.0% conversion and glycerol 1,2-carbonate yield was 64.8 %, thus giving 87.1% glycerol 1,2-carbonate selectivity. About 93.5% conversion of glycerol and 88.7% glycerol 1,2-carbonate yield was observed in 2 hours reaction time at emim[Ac] loading of 0.5 mol%. Increment of emim[Ac] loading to 10 mol% has slightly increased the conversion but reduced the glycerol 1,2-carbonate yield to 70.0%. Rising of catalyst concentration is believed to promote glycerol dicarbonate formation or glycerol decarboxylation as described in ATR-FTIR and NMR studies. Therefore, the use of 0.5 mol% of the emim[Ac] was acceptable for glycerol 1,2-carbonate synthesis in this reaction.

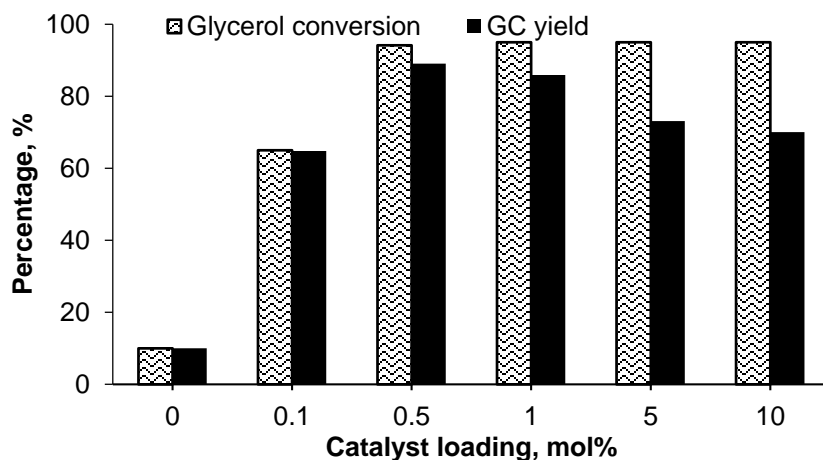


Figure 3: Effect of catalyst loading on the transesterification of glycerol with diethyl carbonate in the presence of emim[Ac] as catalyst. Reaction conditions: Temperature = 120 °C, Time = 2 hours, Molar ratio of diethyl carbonate/glycerol = 2.

Obviously, there is a need to reuse the catalyst after every cycle. Thus, reusability study was critically essential for the economic feasibility of reaction. The possibility of recycling emim[Ac] was also investigated under the optimal reaction conditions. The performance of emim[Ac] is shown in Figure 4. From the results, it revealed that the emim[Ac] could be recycled three times with only a slight reduction in the conversion of glycerol, yield and selectivity of glycerol 1,2-carbonate. The loss in activity and decrease in percent conversion may be due to slight mass loss of emim[Ac] during the catalyst recovery process. It is necessary to note that, electrostatic force between the cation and anion in ionic liquid is stronger than Van-der Waals force, thus give stable molecular structure of emim[Ac] and also good reusability.

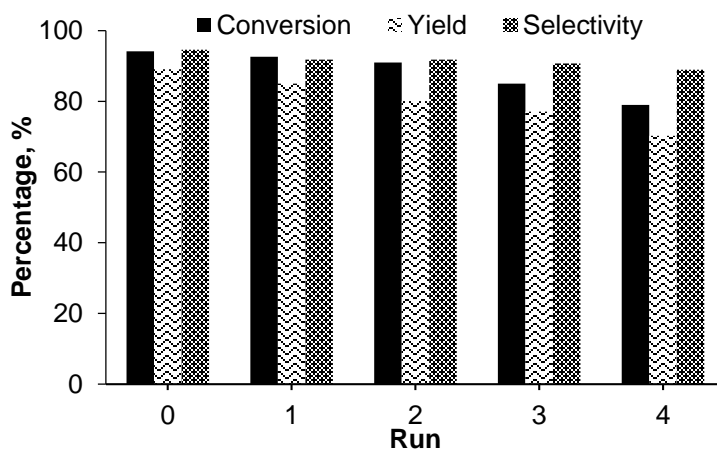


Figure 4: Recycling of emim[Ac]. Reaction conditions: Temperature = 120 °C, Time = 2 hours, Molar ratio of diethyl carbonate/glycerol = 2 and emim[Ac] = 0.5mol% based on limiting reactant.

In order to clearly understand the interaction of screened ionic liquids with glycerol or glycerol 1,2-carbonate, ATR-FTIR analysis was conducted to corroborate with GC-FID analysis. From ATR-FTIR studies, it can be concluded that, the interaction of the anion of the ionic liquid (β value >1.0, neglecting the complexity of ionic liquid's structure) with glycerol should be strong enough and the interaction of anion with glycerol 1,2-carbonate must be sufficiently weak in order to obtain high glycerol conversion, glycerol 1,2-carbonate yield and selectivity. Stability of emim[Ac] at working temperature (120 °C) were confirmed by ^1H and ^{13}C NMR analyses. No significant shiftment of chemical shifts were observed in both ^1H and ^{13}C NMR spectra, indicating that, emim[Ac] ionic liquid has not undergo any decomposition during transesterification reaction took place and it is applicable to be reused several time.

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