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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] > $[NO_3]$ > [Cl] > $[BF_4]$. 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.

HIGHLIGHTS

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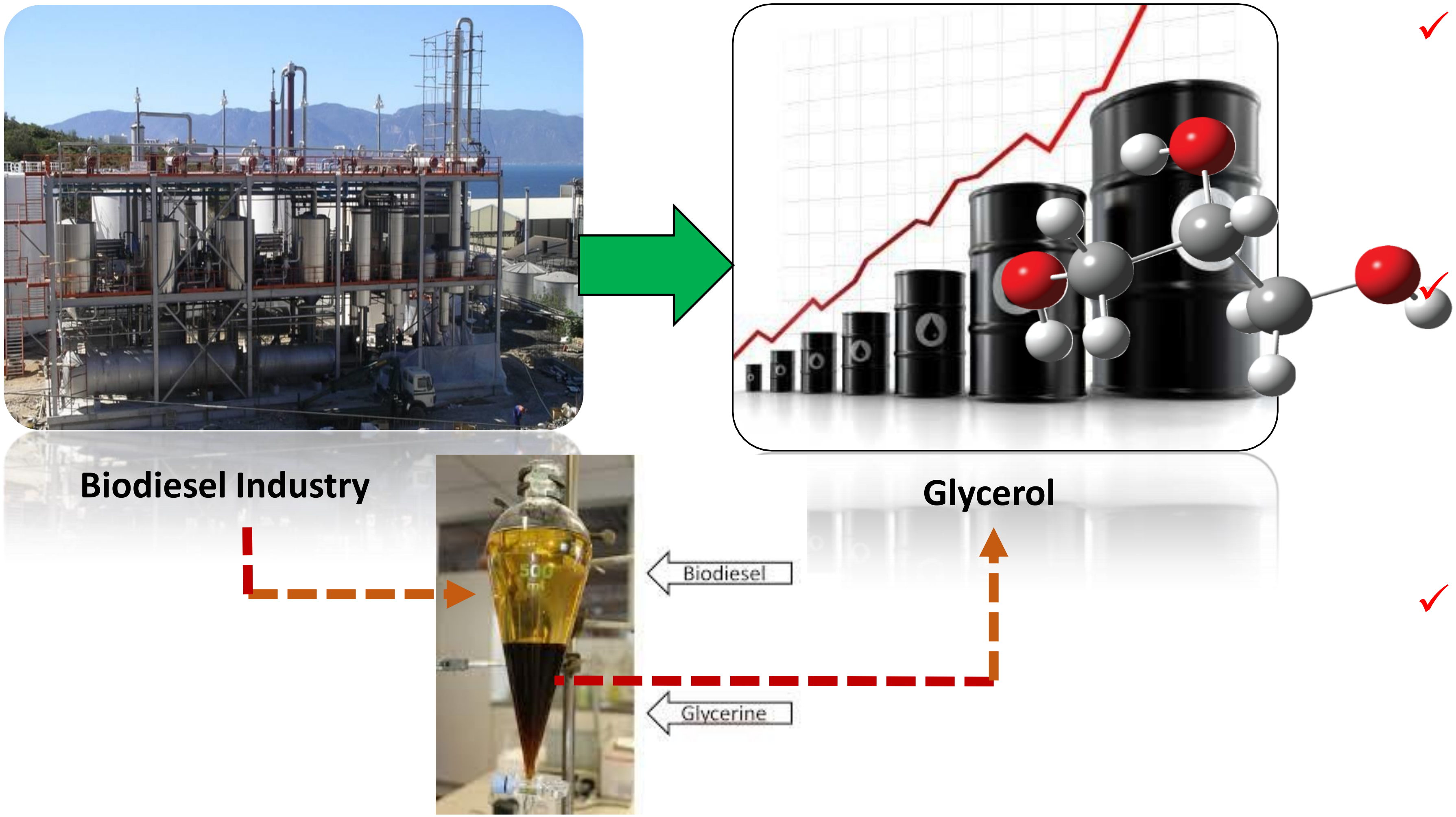
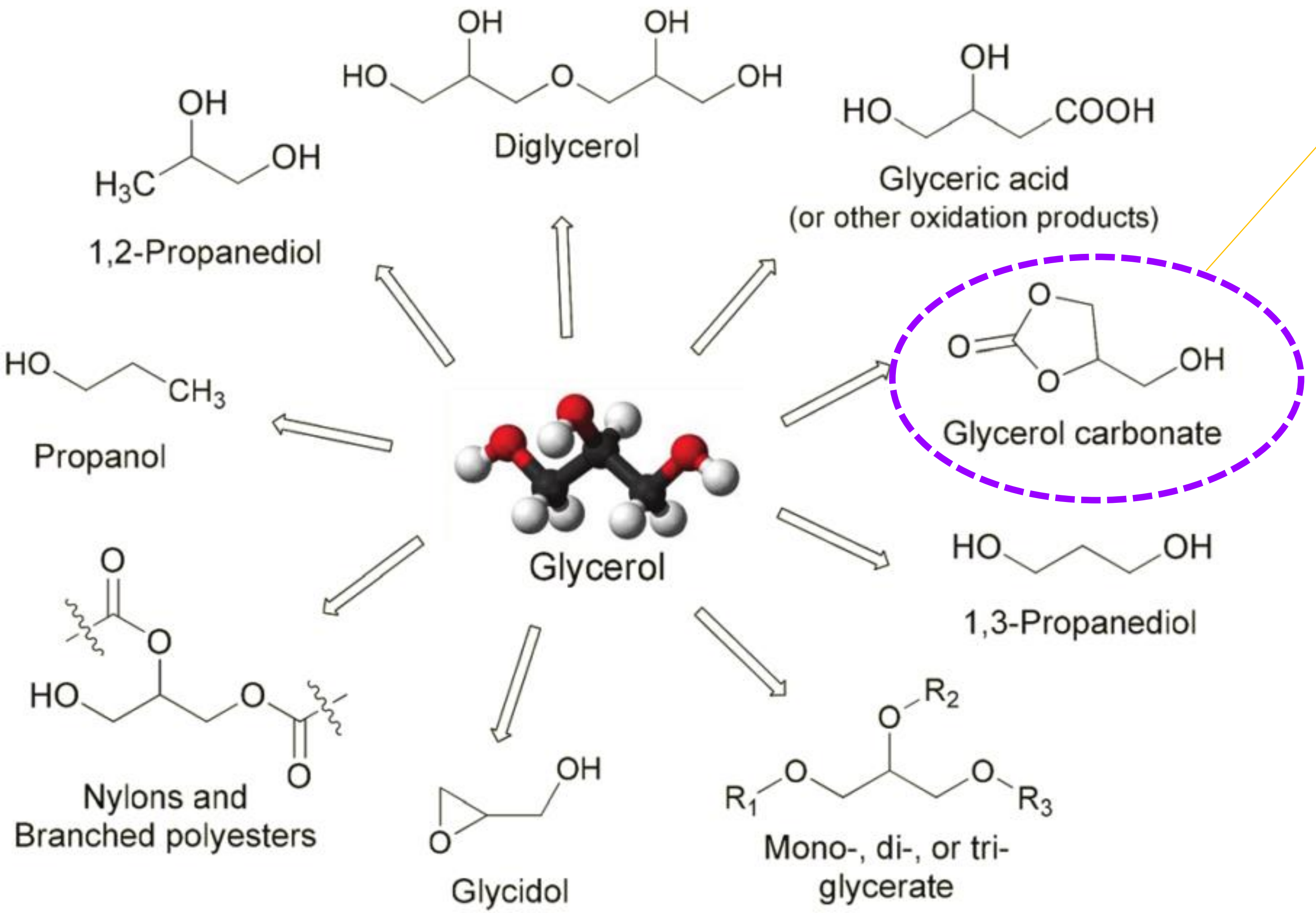
- The basic ionic liquid (emim[Ac]) showed best catalytic activity and recyclability.
- Detail understanding on the glycerol-catalysts and glycerol 1,2-carbonate-catalysts interactions has been well explored.

GLYCEROL



- One major drawback in the biodiesel industry – produce ~10 % w/w of undesired glycerol.
- Large surplus in the current glycerol market represents a waste that must be used or eliminated.
- Conversion of glycerol into value added products is essential to maintain the sustainability of biodiesel production.
- Glycerol carbonate can be synthesized via transesterification reaction of glycerol with carbonylating source

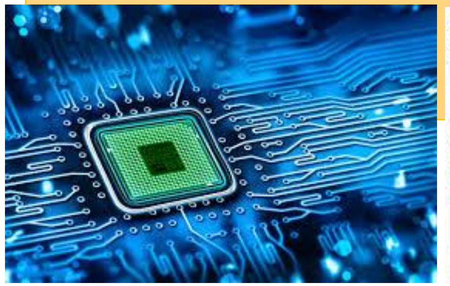
CONVERSION OF GLYCEROL



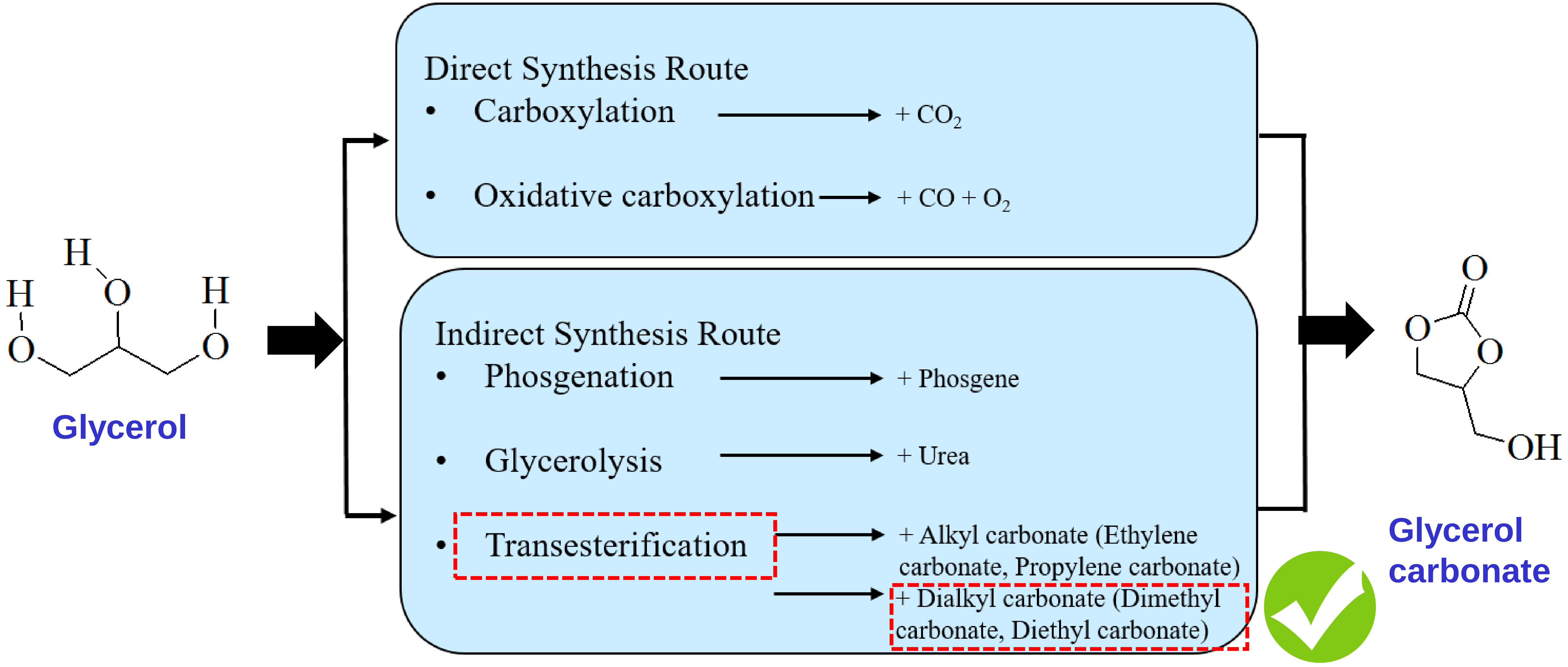
Glycerol as a platform for functional chemicals (Pagliaro et al., 2007)

Applications in industry

- ❑ Semiconductor
- ❑ Chemical
- ❑ Pharmaceutical
- ❑ Building and Construction
- ❑ Agricultural
- ❑ Cosmetic & Personal Care
- ❑ Polymer and Plastic




SYNTHESIS ROUTES

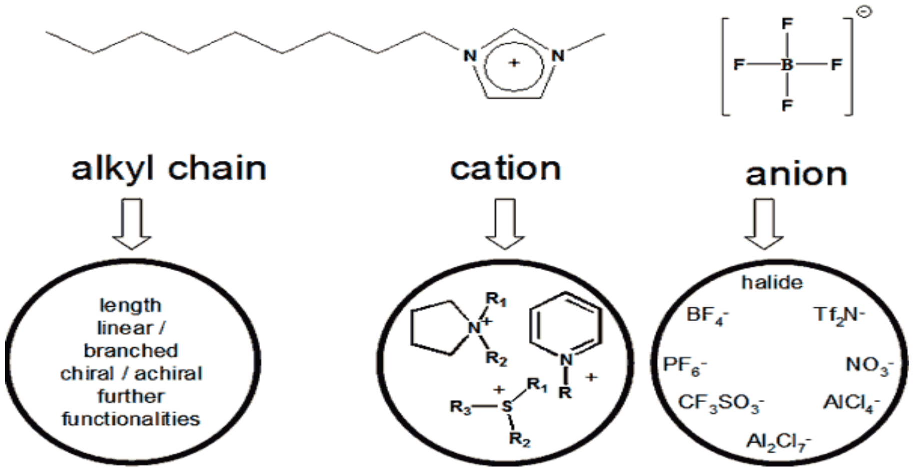


APPLICATIONS OF IONIC LIQUID

- Solvents
- Synthesis & Catalysis
- Process Engineering/ Separation
- Electrochemical
- Engineering fluids Performance Additives
- Biotechnology

Why considering IL?

☑ Higher thermal stability
☑ Adjustable polarity by cation and anion combination
☑ Tunability of acidity or basicity properties
☑ Recyclable
☑ Green catalysis
☑ Cation/anion has independent activity

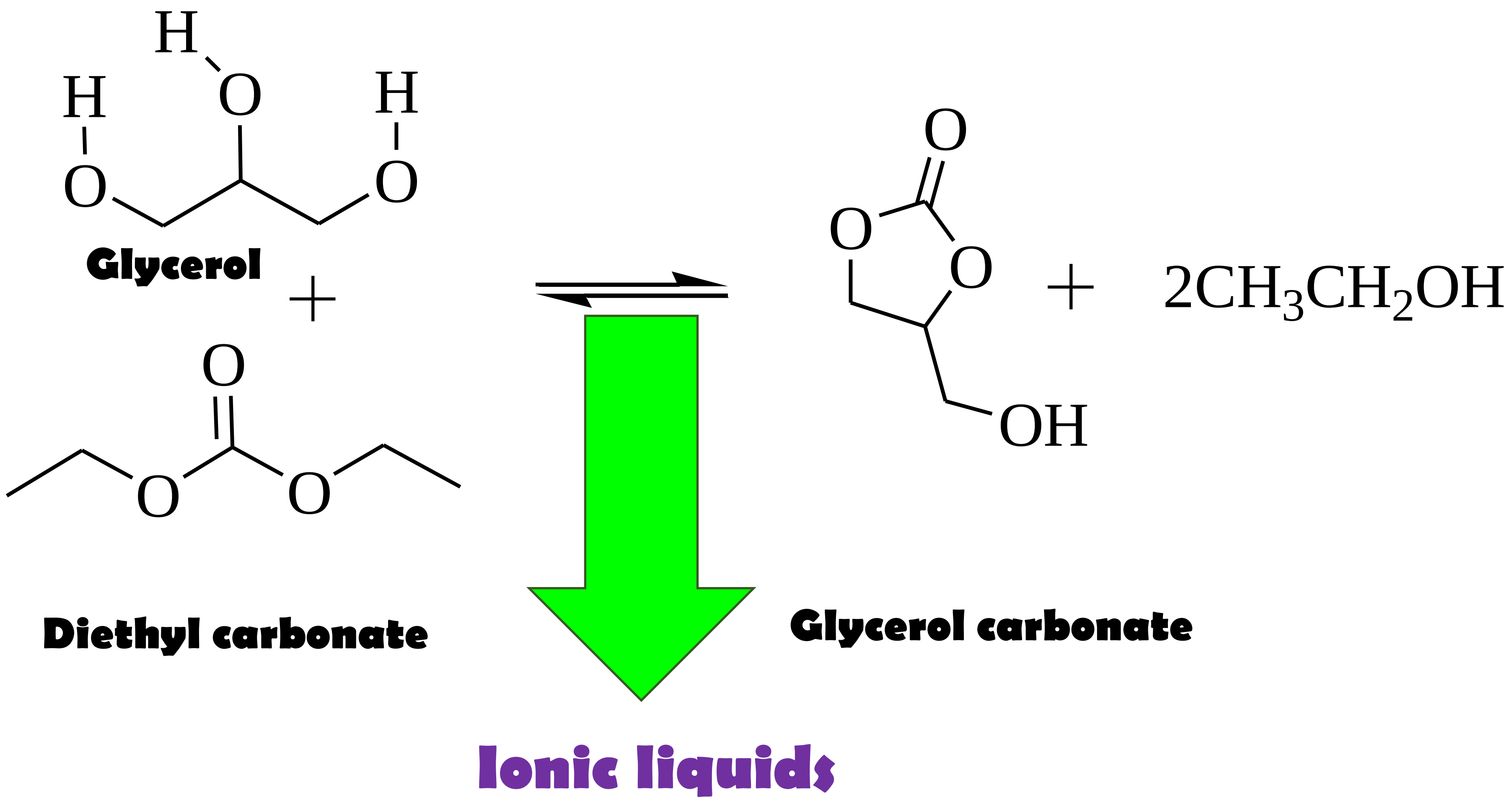


PREVIOUS STUDIES

Year	Ionic liquid	Temperature (ºC)	Time	Substrate molar ratio	Catalyst loading	Conversion/Yield	Reference
2014	[amim][Im]	70	30 min	1:2 (DMC)	10 mol%	C = 65.6, S = 100	Yi *et al.*, 2014
2012	TEA[OH]	80	90 min	1:3 (DMC)	0.217 mmol	C = 89, S = 56	Gade *et al.*, 2012
	TBA[OH]	80	90 min	1:3 (DMC)	0.217 mmol	C = 90, S = 47	
	TMA[OH]	80	90 min	1:3 (DMC)	0.217 mmol	C = 95, S = 47	
2012	$[Mor_{1,4}][N(CN)_2]$	120	13	1:3 (DMC)	0.17 mmol	C = 95	Chiappe *et al.* 2012

Research or **report** on ionic liquid as catalyst for transesterification reaction of glycerol are **still rare**.

TRANSESTERIFICATION REACTION



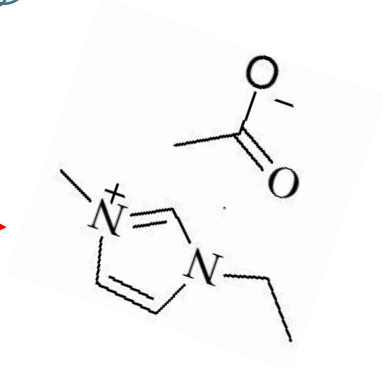
Screening of potential ionic liquid as catalyst towards the reaction

No.	Ionic liquid	β value	Glycerol conversion (%)	GC yield (%)
1	Blank	-	5.00	5.00
2	$MA[NO_3]$	0.46	<10.00	<10.00
3	$EA[NO_3]$	0.46	<10.00	<10.00
4	bmim[Cl]	0.95	<10.00	<10.00
5	$bmim[BF_4]$	0.55	<5.00	<5.00
6	HEA[Fmt]	0.73	24.08	24.00
7	emim[DMP]	1.12	22.20	22.00
8	bmim[Dca]	0.596	45.00	45.00
9	**emim[Ac]**	1.201	**93.50**	**88.70**

OUR FINDINGS

Table 1: Catalyst screening of selected ILs as catalyst for transesterification of glycerol. Reaction conditions: Temperature = 120 ^{o}C, Time = 2 Hours, Molar ratio of DEC/glycerol = 2 and catalyst loading 0.5 mol% based on limiting reactant.

Hypothesis….
Anion strength is measured by hydrogen bond basicity (β value).



1-ethyl-3-methylimidazolium acetate (emim[Ac])

Screening of reaction conditions

Effect of Temperature

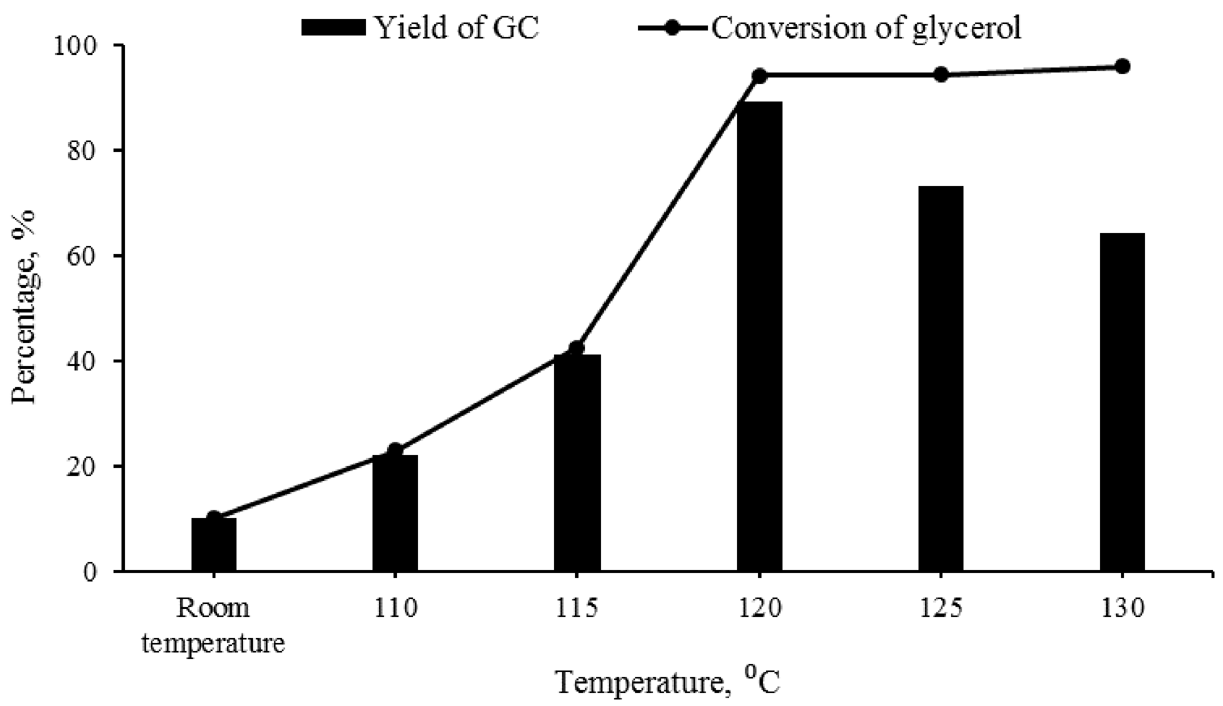
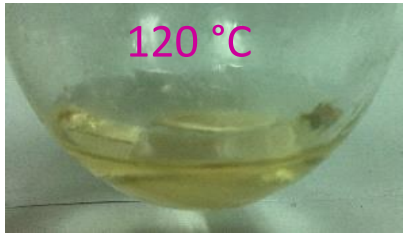
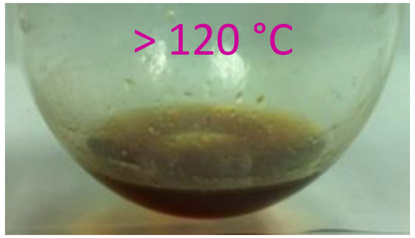


Fig. 1. Effect of reaction temperature on the transesterification of glycerol with DEC in the presence of emim[Ac] as catalyst. Reaction conditions: Reaction time = 2 Hours, DEC/glycerol molar ratio = 2 and emim[Ac] = 0.5 mol% based on limiting reactant.

- Less than 10% of the glycerol conversion at room temperature.
- A rapid increase of glycerol conversion and GC yield - when temperature increase from 110 to 120 ^{o}C.
- About 93.50% conversion of glycerol and 88.70% GC yield was successfully synthesized at reaction temperature of 120 ^{o}C.
- Further increase of reaction temperature at 130 ^{o}C give 95.87% glycerol conversion and GC yield dramatically dropped to 64.17%.





Effect of Time

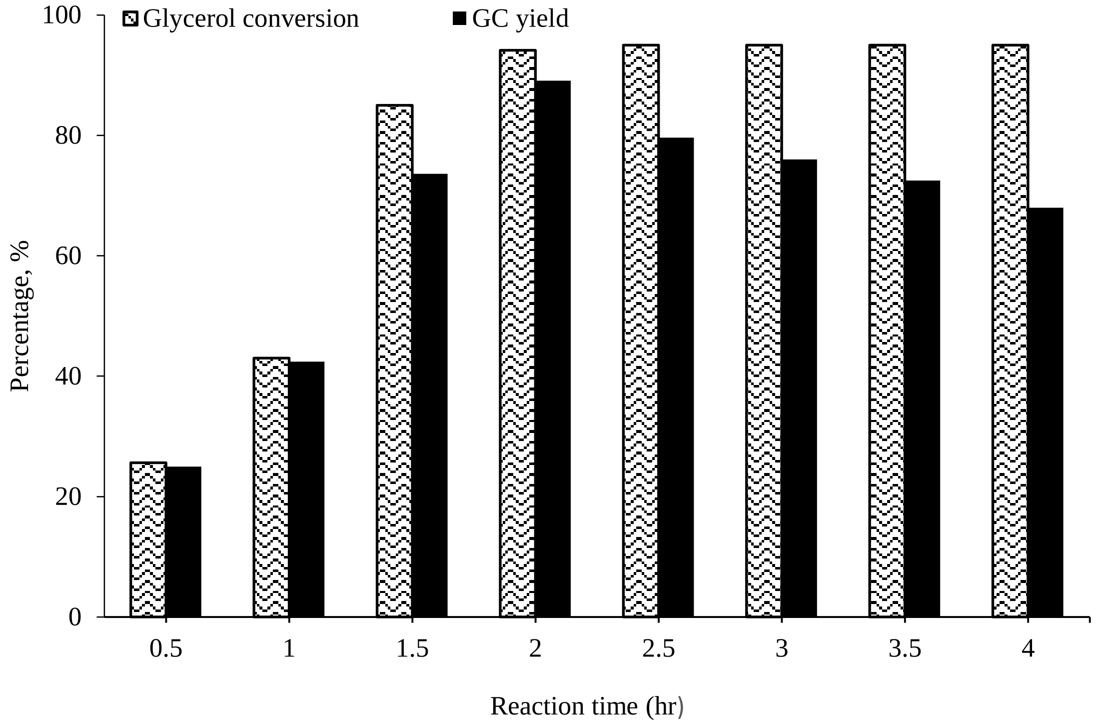


Fig. 2. Effect of reaction time on the transesterification of glycerol with DEC in the presence of emim[Ac] as catalyst. Reaction conditions: Temperature = 120 ^{0}C, Molar ratio of DEC/glycerol = 2 and emim[Ac] = 0.5 mol% based on limiting reactant.

- The GC yield is improved from 42.40% to 88.70% when the reaction time had increased from 1 to 2 hours
- then decreased over an extended time of reaction.
- However, time of reaction was very crucial as GC selectivity drop to 68.00% when the reaction time is prolonged up to 4 hours.
- The formation of GDC and glycidol was expected to decrease the GC selectivity whereas, glycerol conversion was slightly enhanced with extended time of reaction.

Effect of DEC/glycerol molar ratio

DEC/Glycerol ratio	Glycerol conversion, %	GC yield, %	GC selectivity, %
1	28.90	28.00	96.90
2	93.50	88.70	94.90
3	96.00	78.10	81.40
4	92.91	72.92	78.50

Table 1: Effect of DEC/glycerol molar ratio on conversion of glycerol and GC yield and selectivity. Reaction conditions: Temperature = 120 ^{0}C, Reaction time = 2 Hours and emim[Ac] = 0.5 mol% based on limiting reactant.

- low conversion and GC yield - equimolar of reactants (1:1) was used in the transesterification giving 28.90% and 28.00%, respectively.
- The GC yield was increased when the DEC/glycerol ratio is raised beyond 2 and keep slightly decreased at molar ratio of 3.
- Conversion of glycerol was slightly decreased to 92.91% and also GC yield decreased to 72.92% at molar ratio of 4.

Effect of catalyst loading

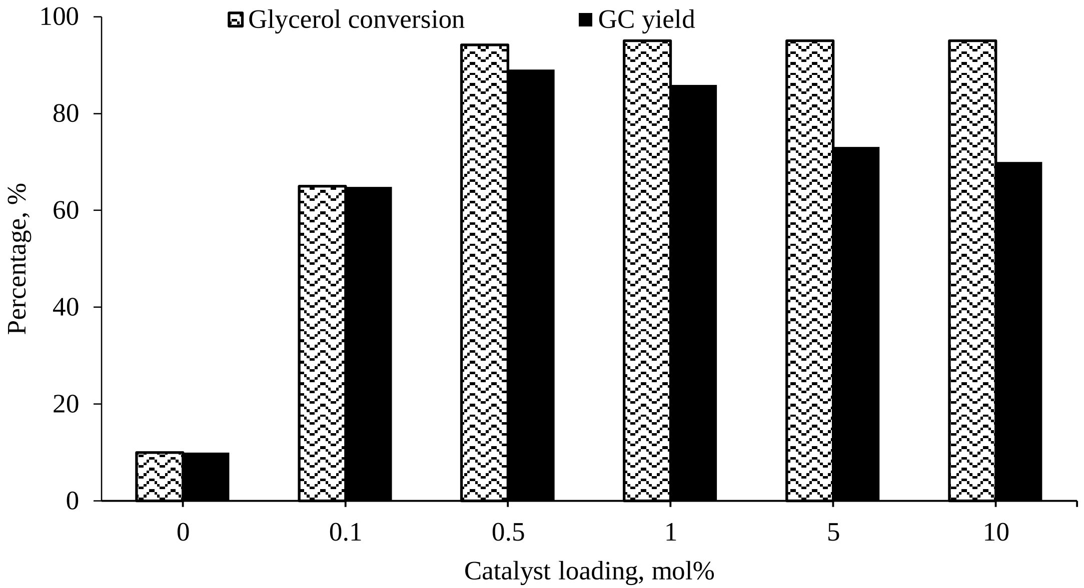
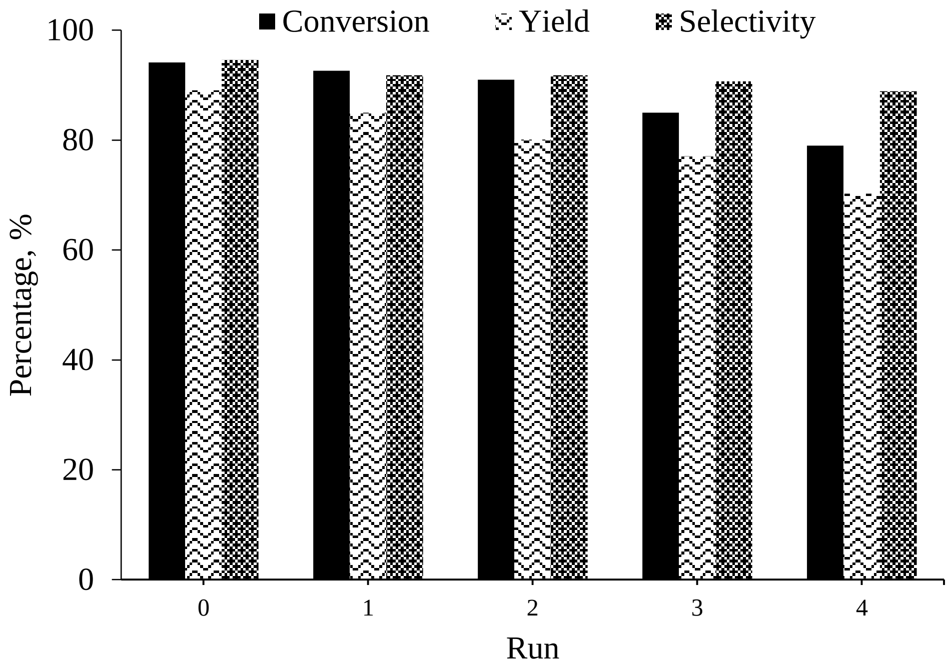


Fig. 3. Effect of catalyst loading on the transesterification of glycerol with DEC in the presence of emim[Ac] as catalyst. Reaction conditions: Temperature = 120 ^{0}C, Time = 2 Hours, Molar ratio of DEC/glycerol = 2.

- 0.1 mol% - too slow reaction with 65.00% conversion and GC yield was 64.82 %, thus giving 87.10% GC selectivity.
- 0.5 mol%. - 93.50% conversion of glycerol and 88.70% GC yield was observed in 2 hours reaction time.
- Increase of emim[Ac] loading to 10 mol% has increased the conversion slightly and GC yield had decreased to 70.03%.

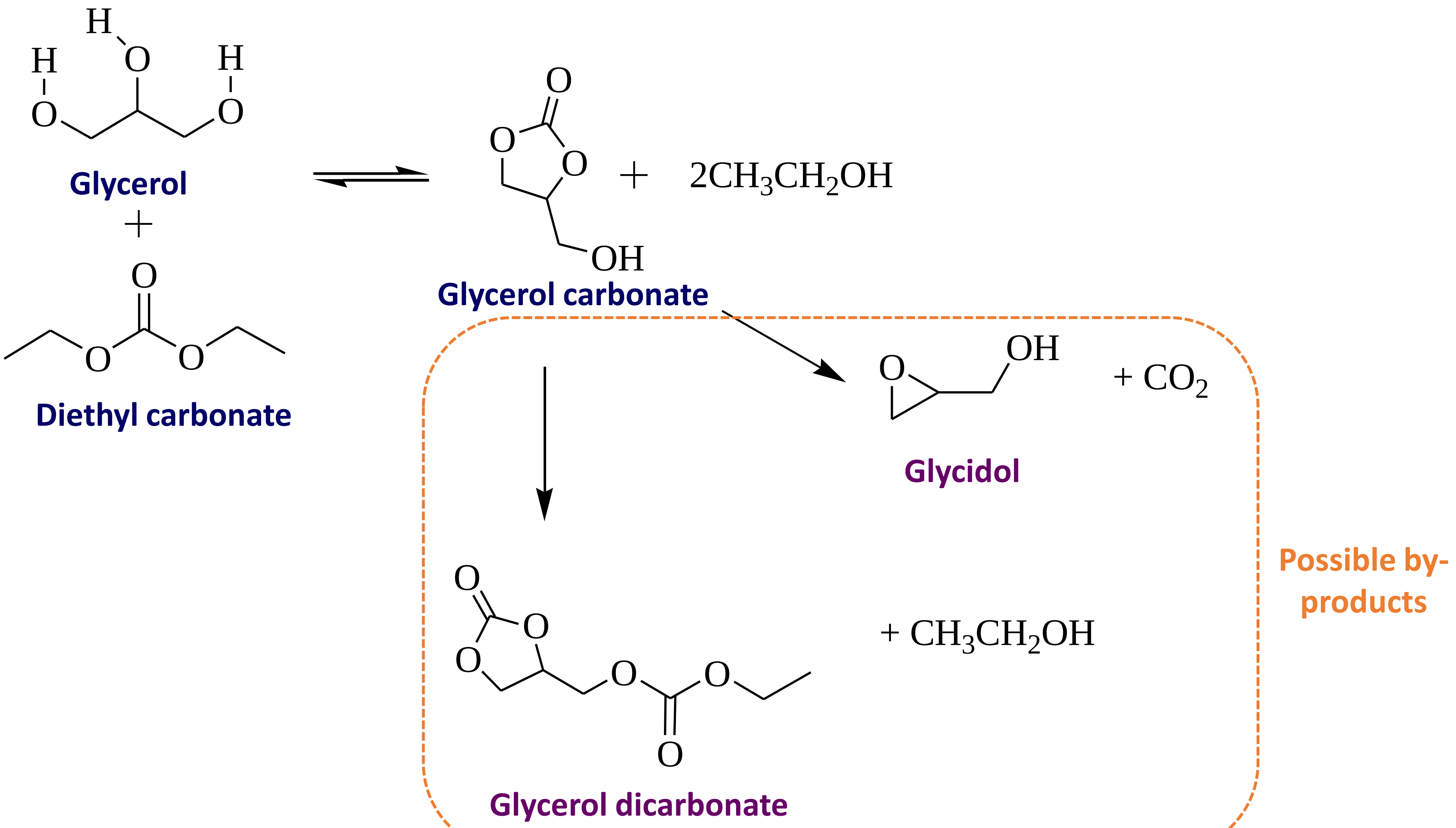
Recyclability study of ionic liquid



Run	Conversion, %	Yield, %
0	93.5	88.7
1	92.6	85.0
2	91.0	80.1
3	85.0	77.1
4	79.0	70.3

- ❑ Liquid-liquid extraction method with chloroform
- ❑ Emim[Ac] can be reused up to three cycles with insignificant reduction of glycerol conversion and glycerol carbonate yield.
- ❑ The loss in activity and decrease in percent conversion may be due to slight mass loss of emim[Ac] during the catalyst recovery process

REACTION PATHWAY



Bai *et al.*, 2013
Alvarez *et al.*, 2013

Comparison of the different catalytic systems

	Homogeneous system	Heterogeneous system
Example of catalyst	Ionic liquids	CaO, ZnO, MgO, mixed metal oxides derived from hydrotalcite
Reaction temperature	70-120 °C	60-140 °C
Reaction time (hour)	0.5-13	0.5-10
Substrate molar ratio (glycerol: carbonate)	1:1 – 1:3.2	1:1 – 1:17
Catalyst loading	0.1 – 0.217 mmol 0.01 – 10 mol%	0.1 - 54 wt% 3 – 15 mol%
Performance (Y/C/S)(%)	C = 11-100 S = 33 - 100	Y = <5 - 100
Formation of by-products	Yes	Yes
Calcination	No	Yes
Catalyst recovery	Moderate step of recovery	Simple step of recovery

CONCLUSIONS

- ✓Catalytic **transesterification** of glycerol is a **simple and efficient** route to produce GC.
- ✓**Ionic liquid shows good catalytic activity** towards transesterification reaction of glycerol.
- ✓**The effect of the operating parameters on the GC production are closely dependent on the type of catalyst applied.**
- ✓To have feasible GC production at industrial scale, process optimization of the production route and improved product isolation techniques are essential.

THANK YOU

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