Intensified Continuous Flow Process for the Scalable Production of Bio-based Glycerol carbonate

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OH

+ catalyst

in MEK

CO

pre-heating

loop

GLY

IS

Low flow reactor (13,5 mL)

Clogging issue

85% GLC

0,79 min and 150 °C,

Superior heat

transfer and mixing

beneficial to G-L

reactions

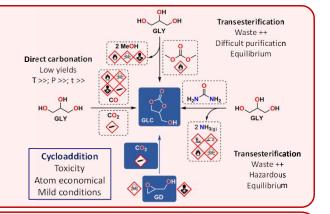
at 150 °C, 2 min

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Context

- The current escalation of greenhouse gas emissions is now undeniably identified as one of the main drivers for precipitating climate change
- CO₂ stands theoretically as an ideal feedstock at our disposal, because of its wide availability and low cost
- Among reachable linear and cyclic carbonates involving CO₂ as reagent, glycerol carbonate (GLC) is a very appealing building block with a plethora of applications comprising battery electrolytes, monomers and green solvent to name a few
- Current industrial processes toward GLC display a very poor atom economy and a global low process efficiency
- Over the last years, research efforts were mainly focused on the carbonation of epoxides and especially, the engineering of solutions to overcome the thermodynamic barrier of CO₂



GLC

GL Y

GD

GLC

Scale-up of GD carbonation with 1 mol% of BB

100%

60%

40%

20%

16 mL min⁻

GD 1.8M

BB 1 mol% in MEK

MFC

52%

0.79

GLC yield (%

Off-line NMF

150 °C

140 °C

GLC

130 °C

120 °C

2

78% GLC

28 sec and 140 °C

1

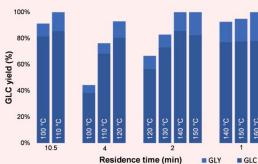
Residence time (min)

FM 1 - mixing FM 1 - residence

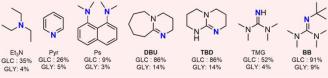
56 mL of internal volume

Results

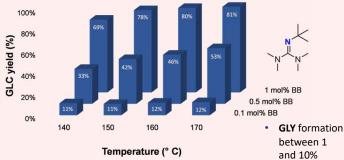
- Preliminary optimization highlighted the promotion of GLC and GLY formations with increasing temperature
- Determination of 1 equiv. of CO₂ as the most adequate flow rate to enhance GD conversion alongside with 10 bar of counter pressure
- 1,5,7-Triazabiscyclo[4,4,0]dec-5-ene as model catalyst



Catalyst screening at 5 mol% in respect to GD (2 min, 140 °C, 10 bar)



- All catalysts screened showed an unneglectable activity
- DBU and TBD displayed 86% of GLC yield
- Barton's base achieved highest conversion and selectivity toward GLC



Conclusion

- Development of a continuous flow process for the efficient and fast production of high added-value GLC with minor formation of GLY
- Identification of Barton's base as innovative and highly selective organocatalyst for **GD** carbonation at low catalyst loading
- Successful transposition to pilot reactor using an Corning[®] Advanced-Flow[™] G1 reactor offering an greener alternative to current industrial processes
 Angew. Chem. Int Ed., 2024,e202319060

Metrics

CO2

Production output : 3,6 kg day⁻¹

0.65 L_N min⁻¹

pre-heating loop

- Space time yield : 2,7 kg h⁻¹L⁻¹
- E-factor : 1,99

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