Continuous flow strategies for glycerol valorization

Florian Barbaz,[1] Paolo Pescarmona,[2] Jean-Christophe M. Monbaliu[1,3]

[1] Center for Integrated Technology and Organic Synthesis (CiTOS), MolSys Research Unit, University of Liège, Belgium
[2] Engineering and Technology institute Groningen (ENTEG), University of Groningen, Netherland
[3] WEL Research Institute, Avenue Pasteur 6, Wavre, Belgium

This Project has received funding from the European Union (Marie Sklodowska-Curie Grant Agreement No 101073223)

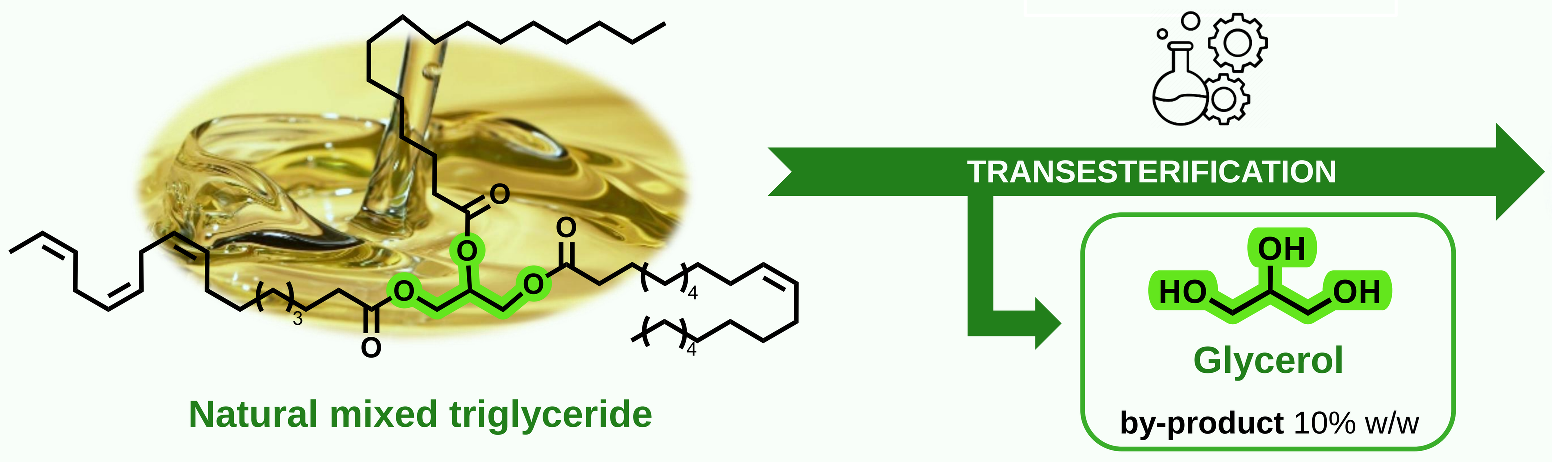
Flow Chemistry Europe 2025, Málaga

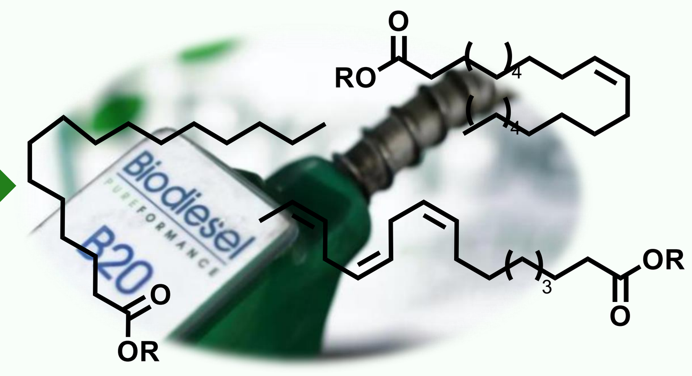
Abstract

Here, we summarize our work on the valorization of unrefined bio-based glycerol, a widely available and valuable C3-polyol.[1] With the assets of flow technology, bio-based glycerol is converted into high value-added 5-membered ring building blocks such as oxazolidinones. Specifically, our approach aims at maximizing potential chains of values with versatile intermediates that can be used in a wide range of applications.

Context

- Vegetable oil
- Animal fat
- Waste cooking oil



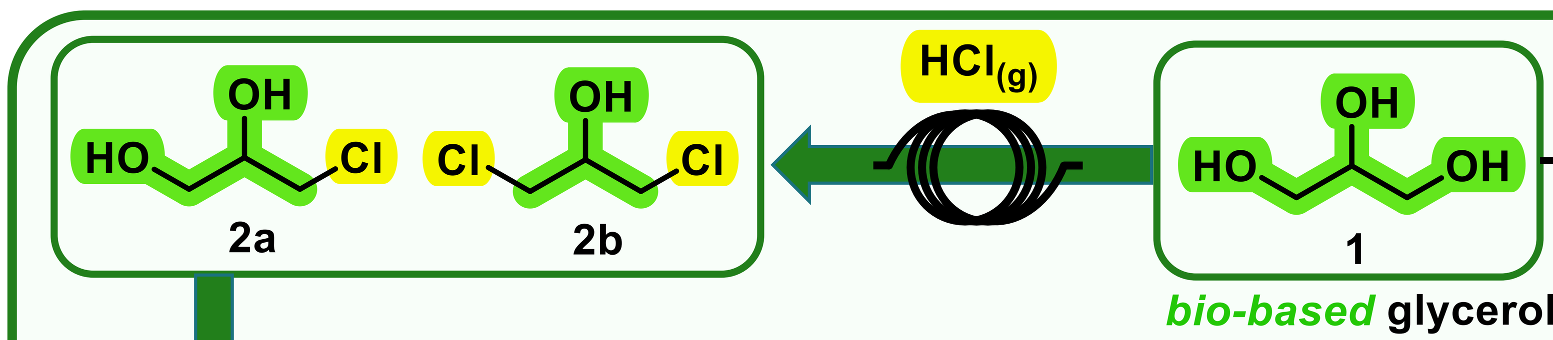


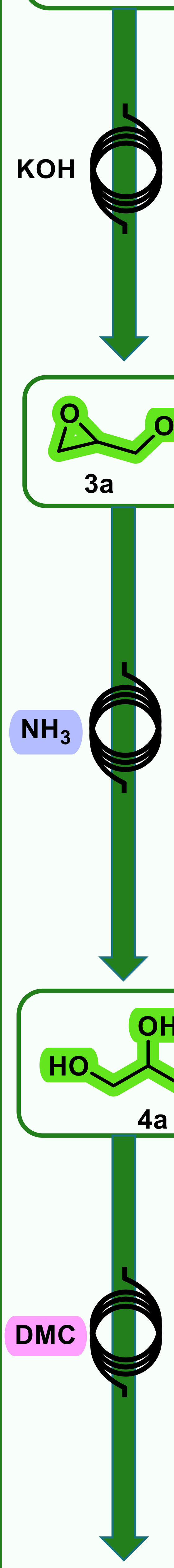
Urgent need for valorization

* S. Salunkhe et. al., Processes **2022**, 10, 2670

Results

Glycerol hydrochlorination / Williamson dechlorination 1

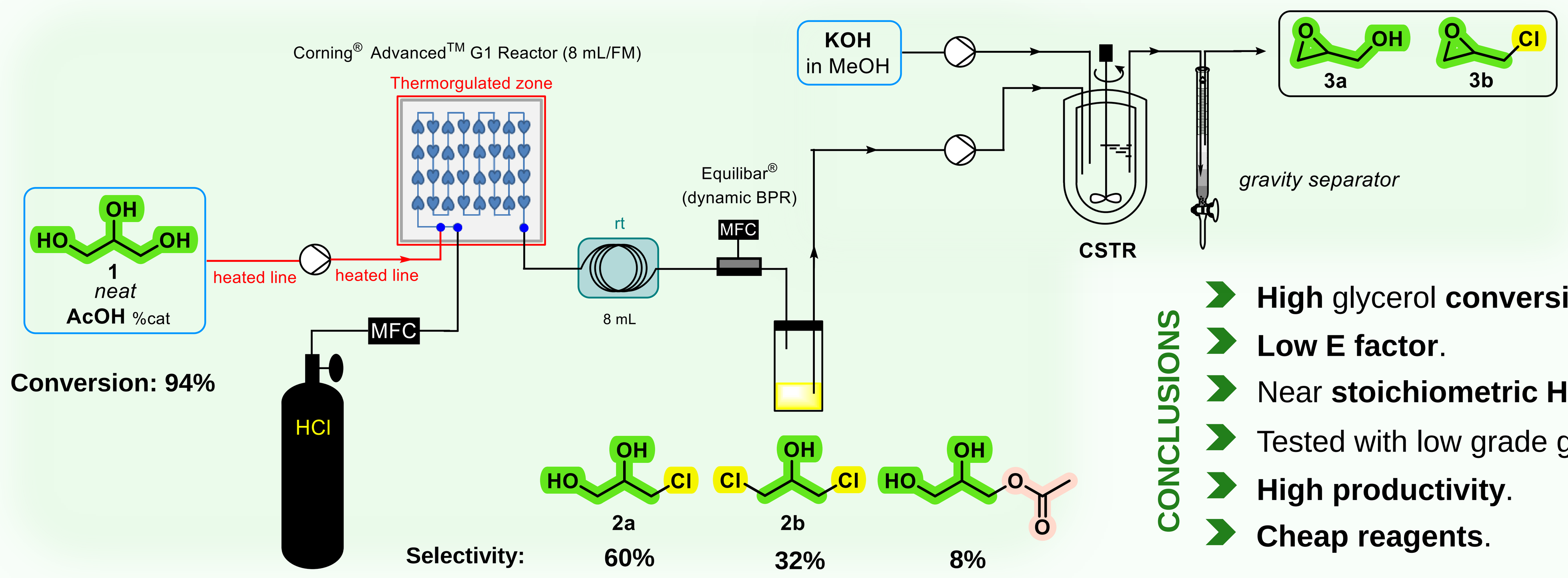




CHALLENGES

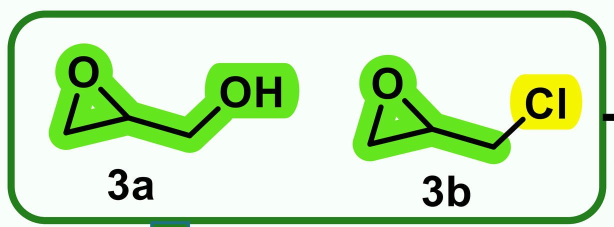
Glycerol hydrochlorination
- Safe handling of gas HCl.
- Glycerol high viscosity.
- Gas/Liquid medium.
- Intensification.

Dechlorination
- Salt precipitation (KCl).
- Solid particles handling in flow.
- Maximize **3a**/**3b** ratio.

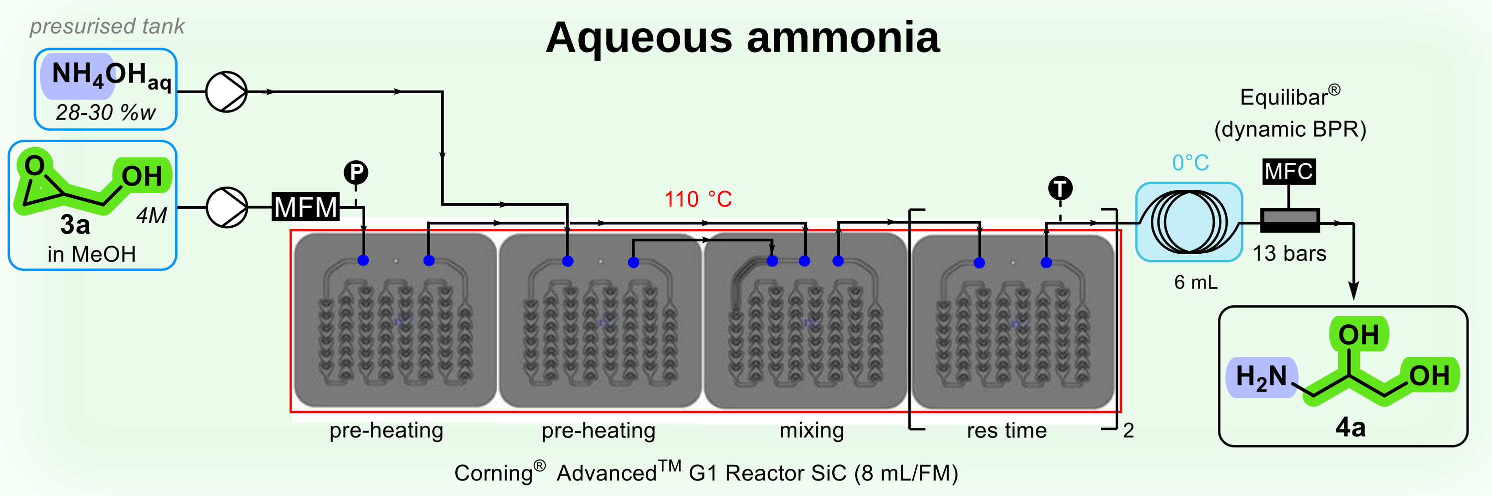


CONCLUSIONS
- **High** glycerol **conversion**.
- **Low E factor**.
- Near **stoichiometric HCl**.
- Tested with low grade glycerol.
- **High productivity**.
- **Cheap reagents**.

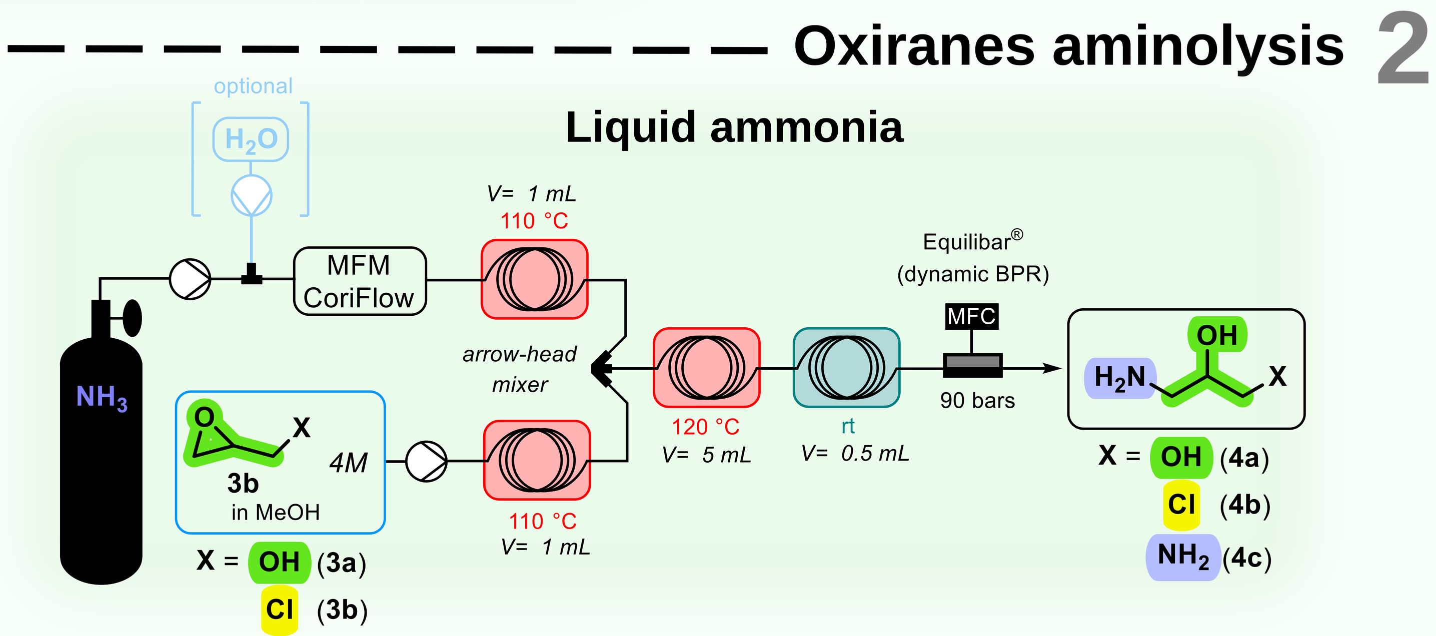
Oxiranes aminolysis 2



Aqueous ammonia



Liquid ammonia



Microfluidic optimization:

Substrat	Product	Temp (°C)	Res Time (min)	Oxiranes %conv	Product %select
3a	4a	120	0.5	>99	>98
3b	4b	60	1	84	64
3b	4c	100	1	>99	77

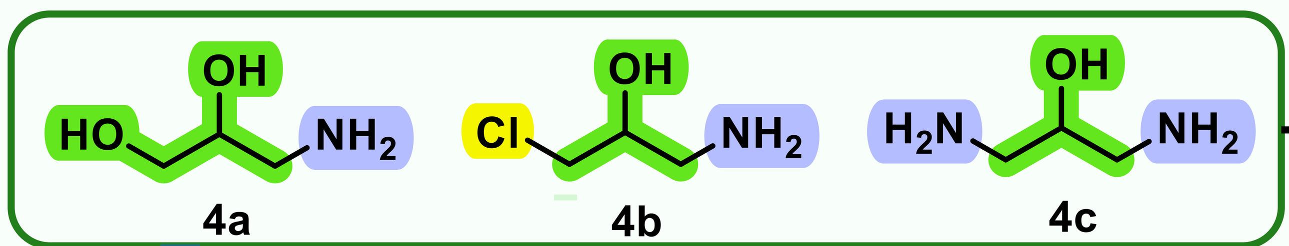
Pilot-scale:

CONCLUSIONS
- **>99% conversion, >98% selectivity**.
- **Res Time**: 30 s.
- **E factor**: 5.1
- **Output**: 3.978 kg.day-1.
- **STY** (Space Time Yield): 16,6 kg.day-1.L-1.

CONCLUSIONS
- **Less solvent** wasted.
- **Easier** downstream **purification**.
- Higher **4b** selectivity.
- Lower **3a** conversion.
- The addition of water has a positive impact on **3a** conversion.

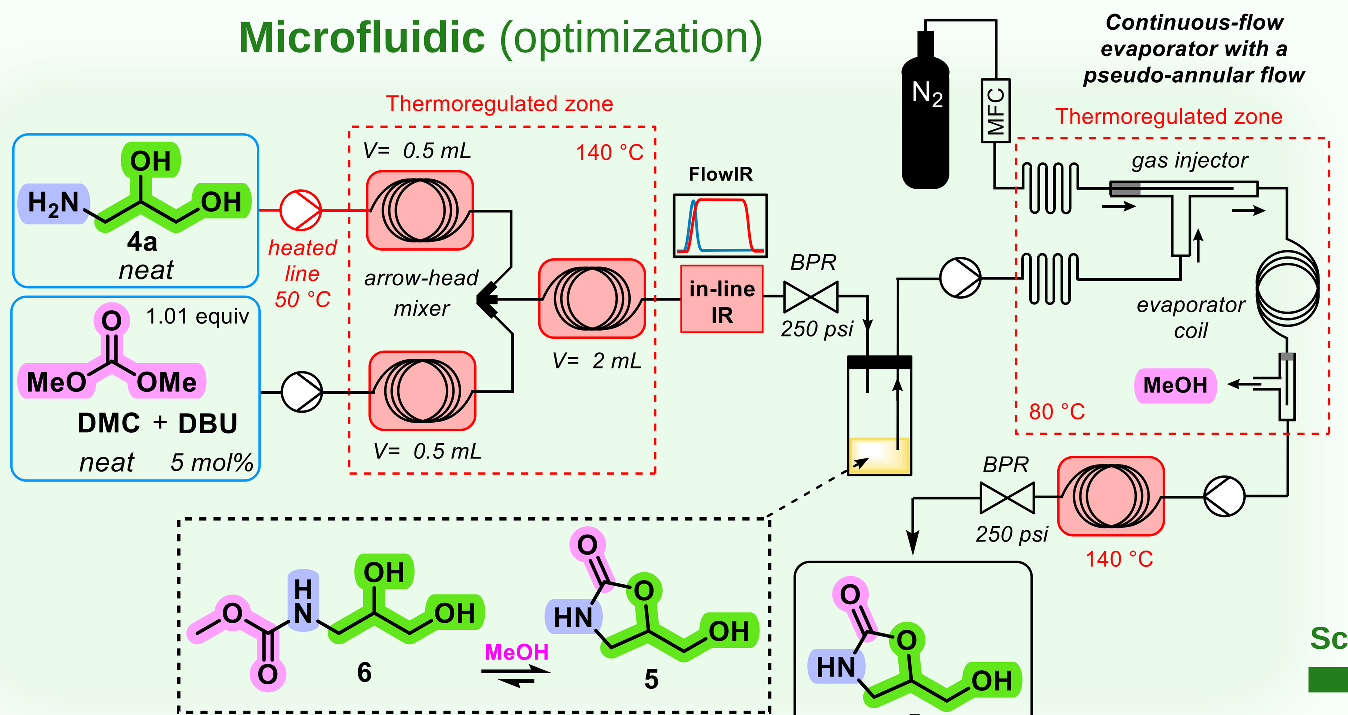
Substrat	Product	Res Time (min)	Oxiranes %conv	Product %select
3a	4a	2	44	94
3b	4b	2	95	72
3b	4c	4	>99	76

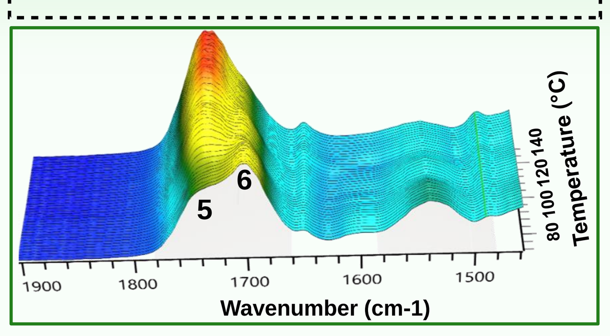
5-(hydroxymethyl)oxazolidinone synthesis 3



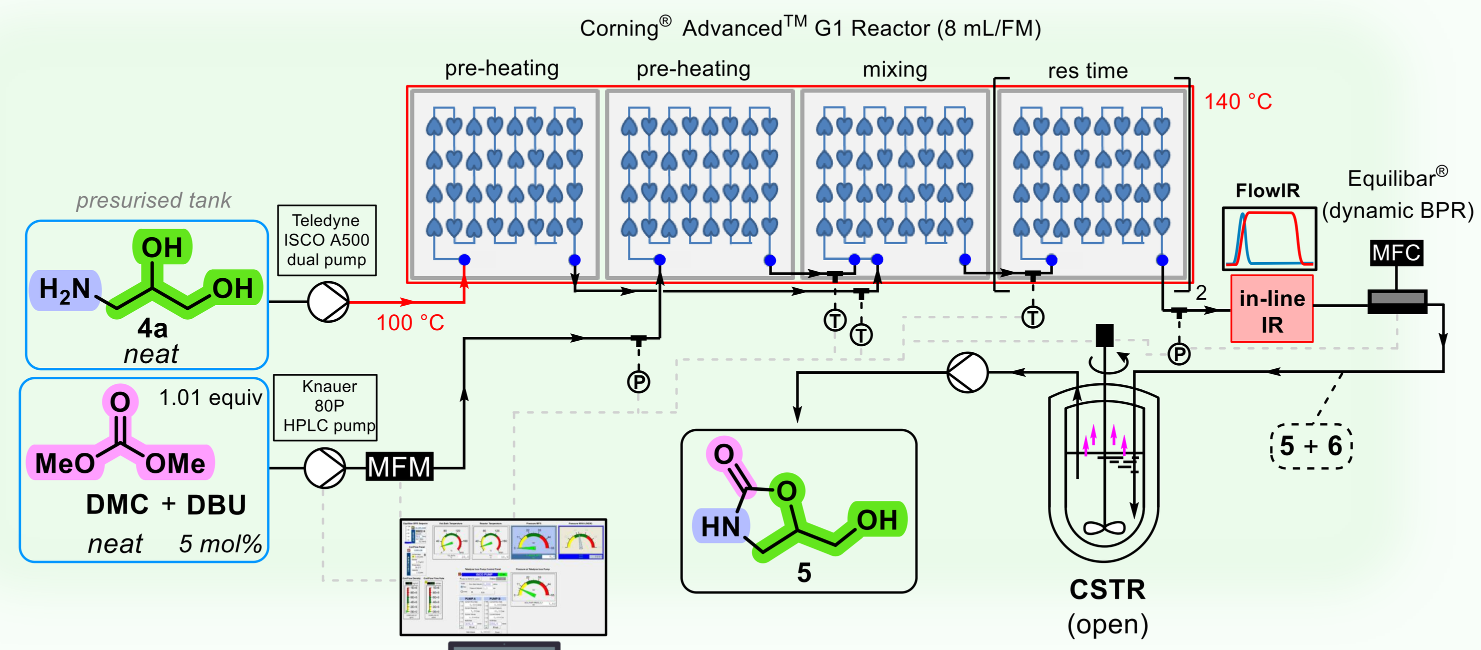
CHALLENGES
- **4a** high viscosity.
- Balance shift from **6** to **5**.
- Continuous methanol removal.

Microfluidic (optimization)

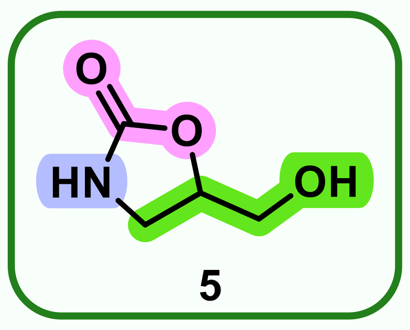




Pilot-scale



Scale-up



- DMC **green reagent**..
- **Solvent free**.
- **Stoechiometric** amount of reagent.
- Widely available catalyst.

- **Continuous-flow MeOH evaporator** module developed.
- Complete **6** conversion into **5** at the end of the process.
- High selectivity toward **5**.

- Intensified process.
- **In-line IR** monitoring.
- Centralized monitoring (HITEC Zang Lab Manager).

CONCLUSIONS
- **>99 conversion, >90% selectivity**.
- **Res Time**: 1min (flow) + 5 min (batch).
- **E factor**: 0.55
- **Output**: 23.2 kg.day-1.
- **STY**: 89.3 kg.day-1.L-1.

Conclusion

- Glycerol was successfully converted into value-added compounds (chlorohydrins, amino-alcohols, oxazolidinone).
- Intensified flow processes with low environmental footprint have been developed.

Perspectives

- Concatenation of the different steps.
- Recovery and valorization of the by-product (NH_3, MeOH).
- Implementation of in-line purification.

Acknowledgements

LIÈGE université · MARIE CURIE ACTIONS · CARBONIZE · CORNING · university of groningen