Biobased acrylic acid production through Re-heterogeneous catalysis: towards process electrification

Maja Gabrič[1], Brigita Hočevar[1], Sašo Gyergyek[2], Blaž Likozar[1], Miha Grilc[1,*]

1 Department of catalysis & reaction engineering, National Institute of Chemistry, Hajdrihova 19, 1000 Ljubljana, Slovenia

2 Department for Materials Synthesis, Jožef Stefan Institute, Jamova 60, 1000 Ljubljana, Slovenia

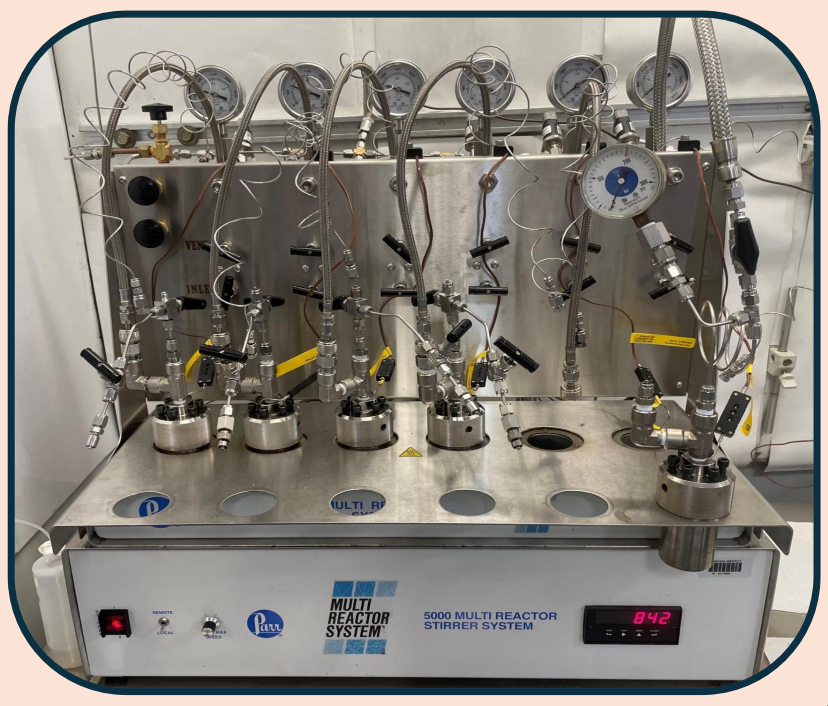
*Corresponding author: miha.grilc@ki.si

Introduction

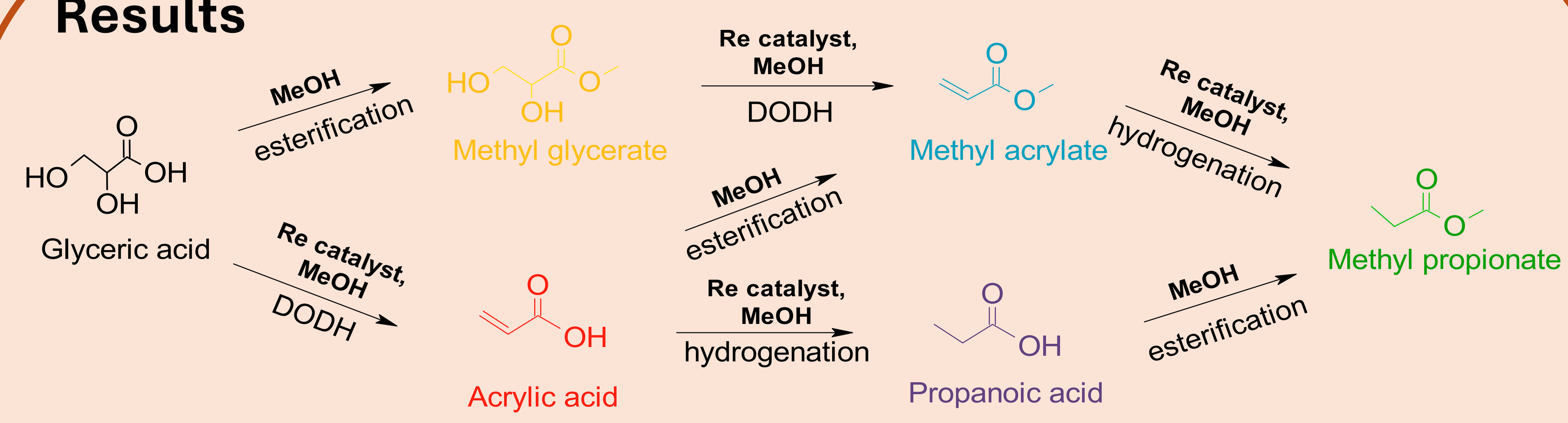
Biomass-to-value-added-product routes often rely on the catalytic removal of oxygen from feedstock using H_2 over supported metal catalysts, with recent attention focused on Re-catalyzed deoxydehydration (DODH). A notable example is the also catalytic route using a Re/C catalyst to convert glyceric acid to acrylic acid and its esters, which are highly sought-after chemical building blocks, especially for polymer production In the study we explored different supported Re catalysts regarding their catalytic behavior for DODH of glyceric acid. [1]

Methods

- High pressure stainless stell reactor sistem with magnetic bar stirrer
- $V_{reactor}$ = 75 mL
- Temperature from 120 °C to 180 °C
- 5 bar_g N_2 or H_2
- 800 rpm of stirring speed
- $m_{reactant}$ = 100 mg of Glyceric acid
- $m_{solvent}$ = 35 g of MeOH
- $m_{catalyst}$ = 140 mg of different Rhenium base catalyst with 5 wt. % of Re loading
- GC-MS for analysis of the products



Results



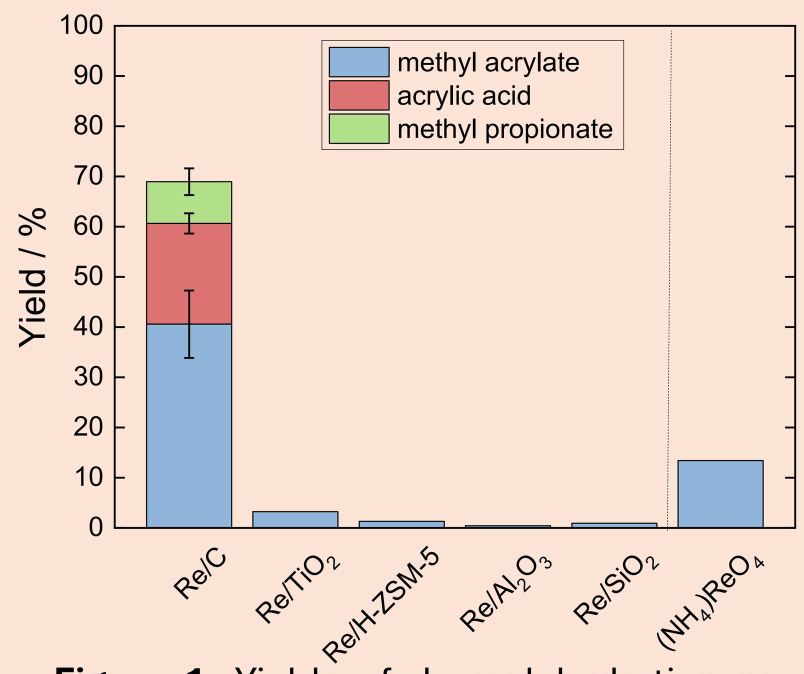


Figure 1: Yields of deoxydehydration products after 72 h over different supported Re catalysts in methanol at T = 150 °C, 5 bar_g, N_2 atmosphere.

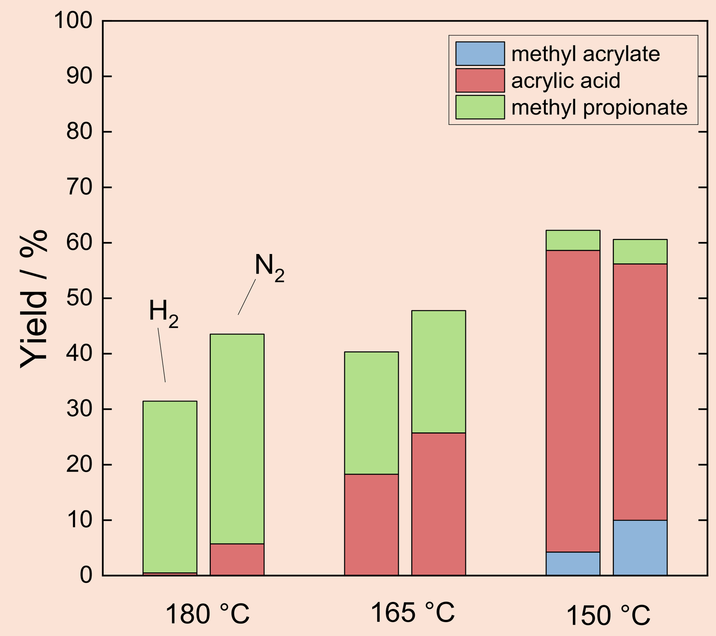


Figure 2: Yields of deoxydehydration products after 72 h over Re/C in methanol at different temperature at 5 bar_g N_2 or H_2 atmosphere.

ELECTRIFICATION OF REACTORS AND PROCESSES

To overcome the problem of temperature gradients in the reactor and ultimately promote or inhibit bulk-phase reactions or the breakdown of thermally unstable compounds, the suspended solid phase (catalyst or heat-carrier) can be selectively heated by magnetic heating of magnetic particles (Figure 3)[2]. For magnetic heating showcase our research team has effectively synthesized and applied a catalyst with magnetic nanoparticles (MN) coated by carbon and finely dispersed Re for the principle in DODH of biobased glyceric acid to acrylic acid.

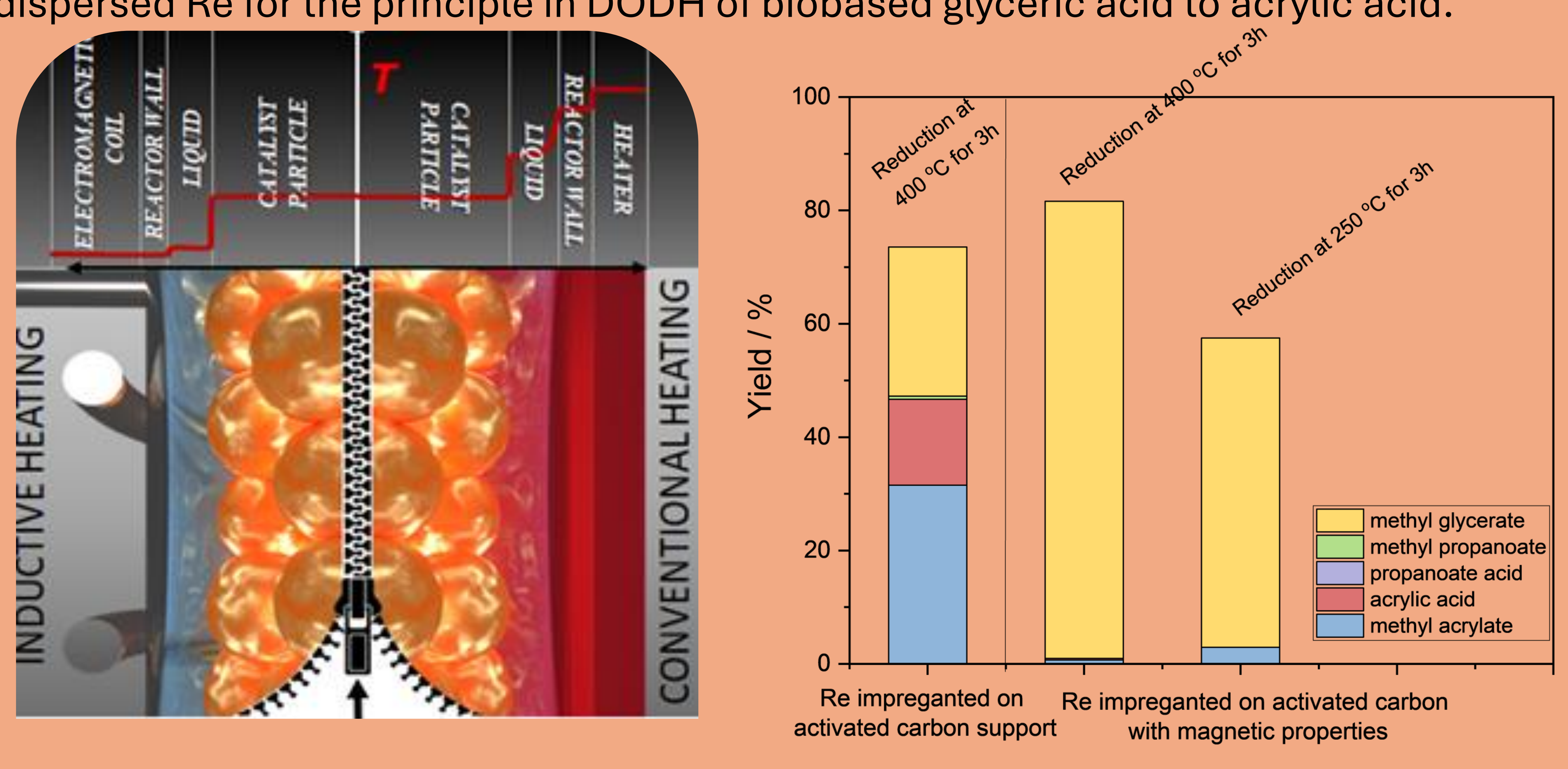


Figure 3: A schematic representation of a temperature profile in magnetic-and conductive-heated reactor[2] or electrified fluidized bed reactor and a comparison of Re-impregnated on commercial C-support with ferrimagnetic maghemite nanoparticles (MN), At T = 150 °C, 5 bar_g, N_2 atmosphere.

Similarly, (catalyst) **particles can be heated directly** via electrical resistant heating, while electrical current flows through the conductive bed material fluidized by the gas stream as demonstrated in e-CODUCT project. The electrothermal-fluidized-bed-reactor (ETFBR) technology has been demonstrated on a pilot scale with 2 kg/h capacity in Slovenia. The pilot unit is designed to convert greenhouse gases (such as CO_2) and acid gases (such us H_2S) into sulfur and methanol. The latter is used as a reactive solvent in DODH process.

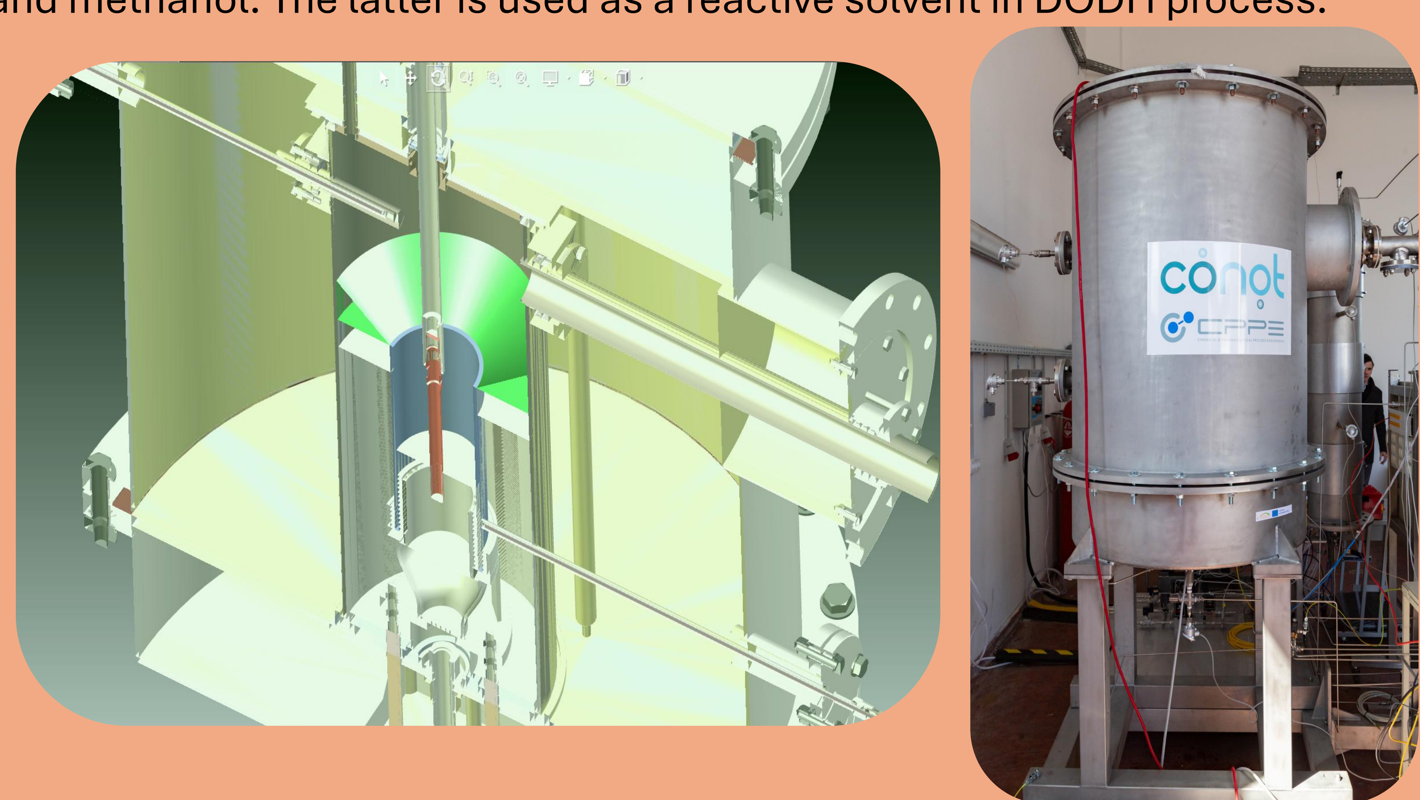


Figure 4: A 3D model of the ETFBR reactor core with center and radial electrodes clearly visible. Pilot reactor diameter is significantly larger (due to thermal insulation) then the fluidized-bed zone, as the latter is being heated upto 1200 C.

Conclusion

- The commercial Re/C catalyst showed by far the highest catalytic activity (**60.6% yield of methly acrylate and acrylic acid**) of all catalysts tested with the most optimal condition: **150°C in methanol after 72 hours in N2**
- Also magnetic catalyst showcased catalytic activity (5% yield)
- **Future work**: the catalyst will be tested in the batch induction-heated reactors to evaluate the activity, stability, selectivity under conditions that minimize transport limitations.
- **Electrification** of reactors and processes boosts the energy efficiency and flexibility of chemical processes.

References

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Acknowledgments

This research was funded by the Slovenian Research and Innovation Agency (P2–0152). The authors also acknowledge projects funded under Horizon Europe Grant Agreement, e-CODUCT (n°101058100) and Storming (n° 101069690), for their financial support.