VTT

# BECCU

bio-energy based $CO_2$ for polyols and fuels

VTT

# Fossil-free polycarbonate polyols from captured carbon dioxide and renewable hydrogen

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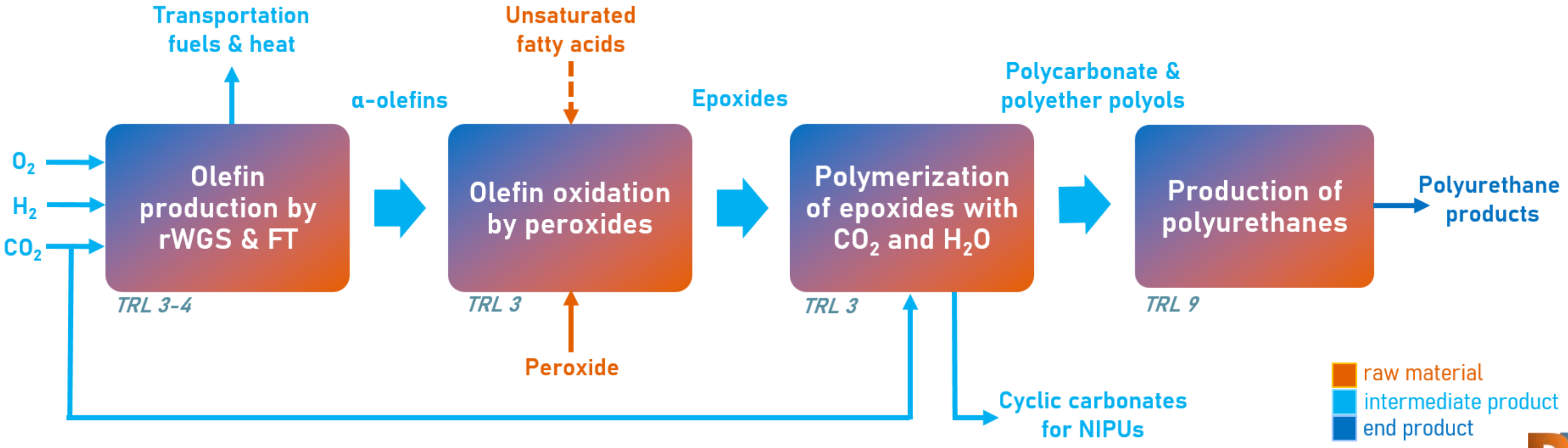
11.02.2022 VTT – beyond the obvious

BECCU

# Route to chemicals and polymers

- The process is based on the **production of olefins** through reverse water-gas shift (rWGS) and Fischer-Tropsch (FT) reaction steps
- The olefins are further converted to epoxides through oxidation reactions by peroxides and epoxides are polymerized together with $CO_2$ to obtain polyols
- The yield of C2-C4 olefins is maximized to be used in polyol production and higher hydrocarbons are utilized as energy carriers (waxes or fuels)

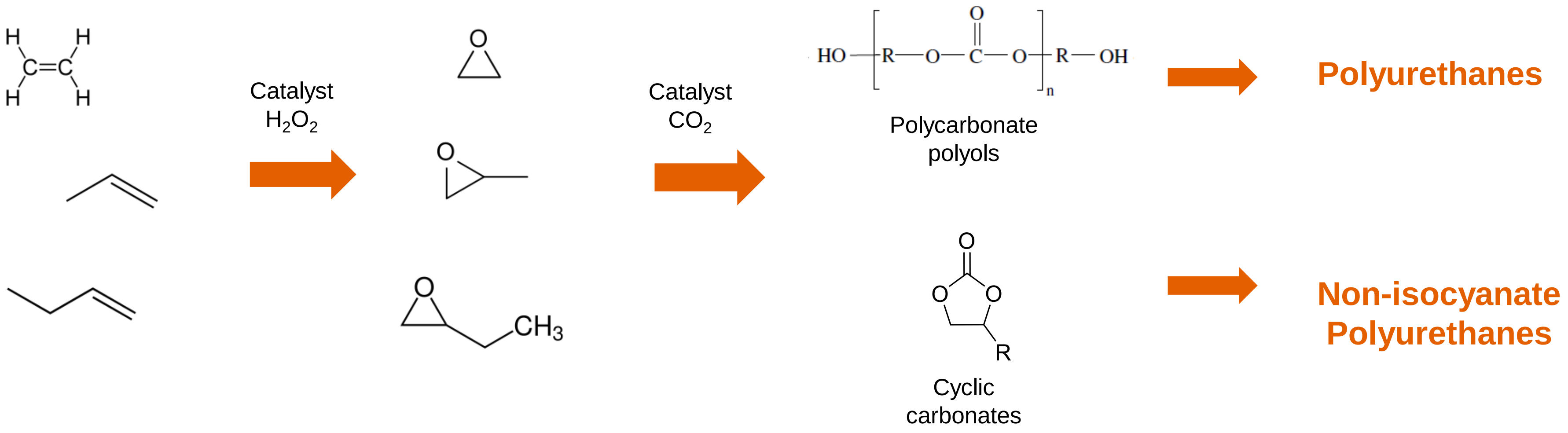


# Polyols from mixed C2-C4 olefins

## Mixed olefins

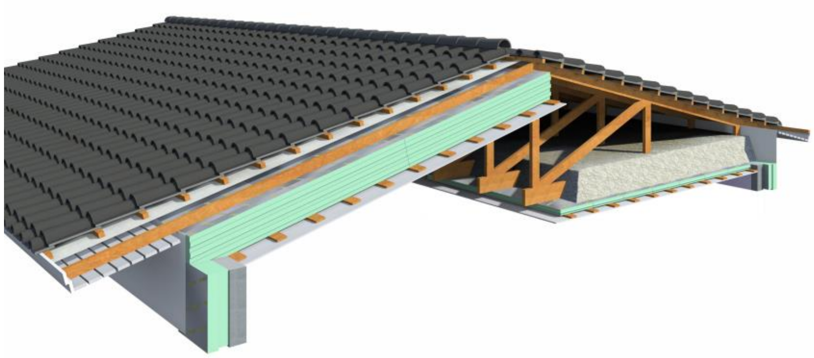
## Mixed epoxides

## Polyols from mixed epoxides



# Versatile polyurethanes in the spotlight

- Target chemical products in BECCU project are polyols, including polycarbonate and polyether polyols, being important raw materials for polyurethanes.
- Polyurethanes are used as either flexible or rigid foams (to be used in insulation materials, footwear, automotive parts etc.) and as adhesives (for such applications as woodworking glues and in abrasive papers).



*Polyurethane can be used in various long lifetime applications such as insulation materials*
*Figure: Finnfoam*

*Polyurethanes are widely used in adhesives for such applications as woodworking glues*
*Figure: Kiilto*

# Epoxidation and polyol synthesis R&D

## Epoxidation

- Epoxidation of mixed C2-C4 alkenes and fatty acids applying **hydrogen peroxide** as oxidating agent
- The reactions will be performed in gas-liquid system applying different alcohols (e.g. methanol) and water as solvent
- Co-operation with ÅA via two MSc theses (prof. Tapio Salmi)

## Polyol synthesis

- Polyols will be synthesized applying mixtures of Ethylene oxide (EO), propylene oxide (PO), butane oxide (BO)
- Experiment for the synthesis of polyether polyols will be performed in parallel with polycarbonate polyol synthesis
- Epoxidized fatty acids will be studied as co-feed for polyol syntheses

# …to polyurethanes and NIPUs

**Polyurethanes**

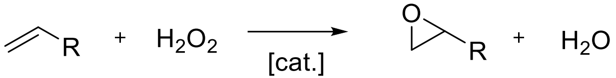
- Mixed C2-C4 polycarbonate and polyether polyols will be tested for different rigid and flexible foam and other polyurethane formulations together with company partners
- Application testing of polyurethanes will be performed for selected applications

**Non-isocyanate polyurethanes (NIPUs)**

- Cyclic polycarbonates obtained as by-product from polycarbonate polyol synthesis will be separated and applied to produce non-isocyanate polyurethanes
- Targeted polyurethane formulations and applications will be planned together with company partners

# Epoxidation

- Epoxidation of C2-C4 alkenes in liquid phase with hydrogen peroxide
  - Mild temperatures and liquid phase process increase safety
- Novelty in epoxidation of the mixture
  - Epoxidation of individual olefins compared to epoxidation of the mixture
- Epoxidation catalyst development
  - Heterogeneous catalysts enable continuous processing
  - Both commercial and in-house prepared catalysts studied




R=H, $CH_3$, $CH_2CH_3$

Comparison of Ti-MWW and TS-1 for the epoxidation of various linear alkenes[a].

| No. | Substrate | Ti-MWW (%) | | | TS-1 (%) | | |
|---|---|---|---|---|---|---|---|
| | | products yield[b] | $H_2O_2$ conv. | oxide sel. | products yield[b] | $H_2O_2$ conv. | oxide sel. |
| 1 | ethylene[c] | 6.6 | 8.1 | 99.6 | 13.0 | 13.2 | 14.5 |
| 2 | popylene[c] | 94.9 | 98.9 | 99.5 | 89.3 | 91.6 | 82.8 |
| 3 | 1-butene[c] | 64.3 | 68.0 | 99.8 | 48.5 | 52.0 | 92.2 |
| 4 | 1-pentene[d] | 35.5 | 39.1 | 99.5 | 22.4 | 30.4 | 87.6 |
| 5 | 1-hexene[d] | 26.9 | 29.1 | 99.3 | 15.6 | 20.2 | 92.4 |

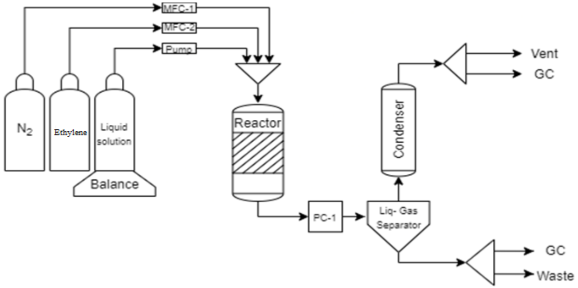
[a] MeCN as solvent for Ti-MWW and MeOH as solvent for TS-1.
[b] Including ethylene oxide and corresponding byproducts formed by hydrolysis or solvolysis.
[c] Reaction conditions: cat., 50 mg; alkene, 0.2 MPa; $H_2O_2$, 15 mmol; solvent, 10 g; temp., 40 °C; time, 2 h.
[d] Reaction conditions: cat., 50 mg; alkene, 15 mmol; $N_2$, 0.2 MPa; $H_2O_2$, 15 mmol; solvent, 10 g; temp., 40 °C; time, 2 h.

Lu *et al.* Applied Catalysis A: General 515 (2016) 51–59

# Epoxidation

- C2-C4 olefin epoxidation is studied in continuous flow reactor with hydrogen peroxide as oxidant
- Epoxidation studies were started with ethylene due to its reported lower reactivity compared to propylene and 1-butylene
- High selectivity to epoxide is prioritised over conversion
- Titanosilicate catalyst TS-1 applied as commercial catalyst
- Parameters studied
  - Temperature
  - Pressure
  - Gas and liquid flow rates
  - Water concentration
  - Mixture effect

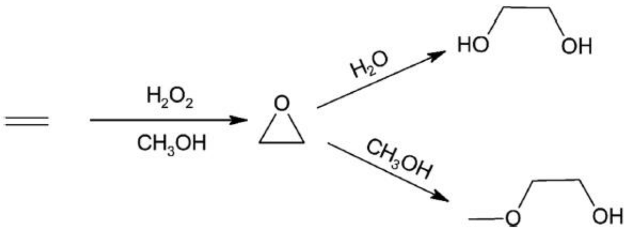
Åbo Akademi

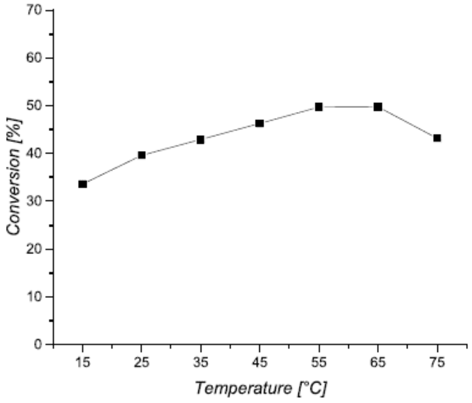


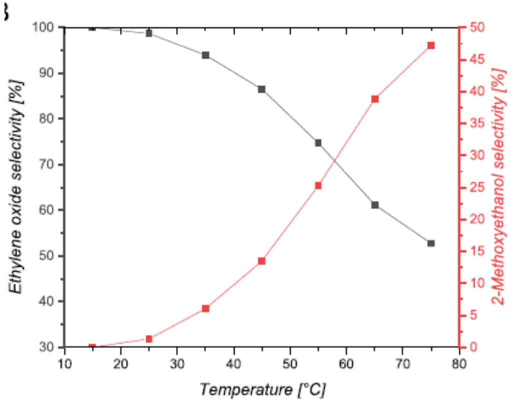
# Ethylene epoxidation

TS-1 catalyst, 4.5 bar
Ethylene flow 0.22 mmol/min
$H_2O_2$ flow 0.24 mmol/min

- Industrial process Ag-catalysed in gas phase
- Low selectivities or conversions reported in liquid phase oxidation
- Continuous process enables recycling of unreacted olefins



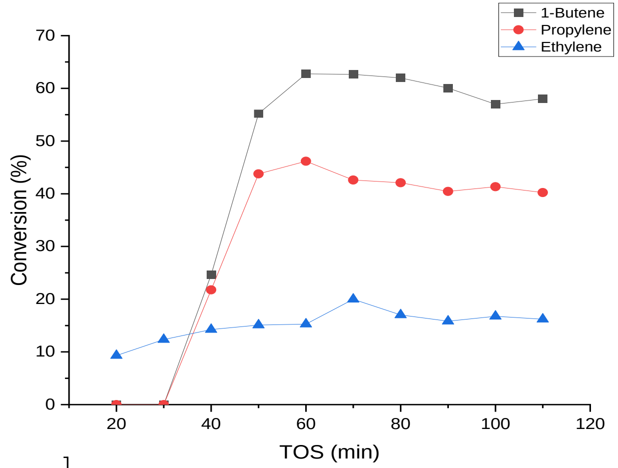



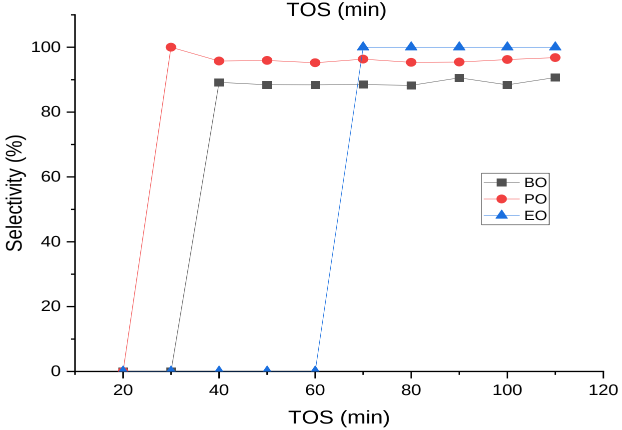

Alvear *et al.*, Ind. Eng. Chem. Res. 2021, 60, 26, 9429–9436

# Epoxidation of individual olefins

- Very high selectivity to epoxides >90% was achieved in continuous flow reaction
- Reactivity of the olefins in epoxidation increases in order ethylene<propylene<1-butene

| T | P | Liquid Flow | Olefin Molar Flow | Total Gas Flow (N2+olefin) | wt% $H_2O_2$ |
|---|---|---|---|---|---|
| 45 °C | 1 bar | 0.5 mL/min | 0. 223 mmol/min | 0.446 mmol/min | 2 |

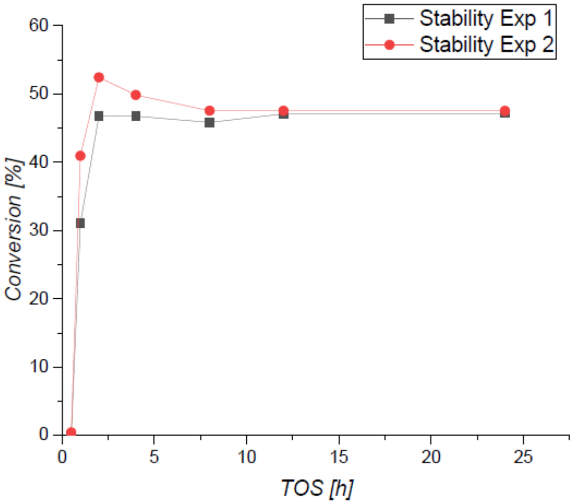


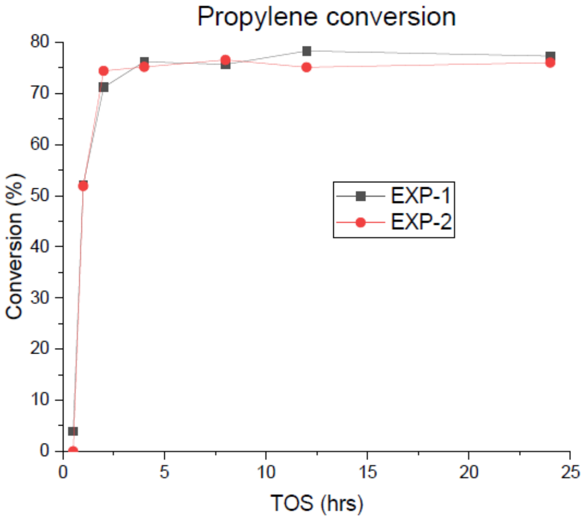

Federica Orabona

# Catalyst stability studies

## Ethylene




## Propylene

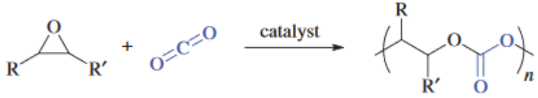



- TS-1 catalyst shows good stability in ethylene and propylene epoxidation
- Same catalyst batch has been used continuously by washing between the experiments
- Neglible deactivation has been noticed in 25 hrs run

Michele Fortunato & Matias Alvear/ÅA

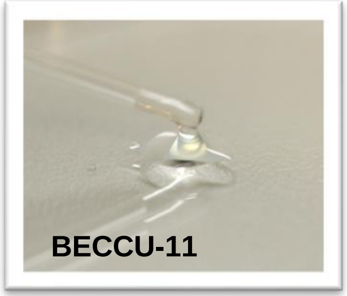
# Polycarbonate polyol synthesis

- PO and BO copolymerization with $CO_2$
- Heterogeneous catalysts applied
- Varying Mw of the product by changing process conditions and starter polyol concentration
- Application tests for polyurethane formulations starting









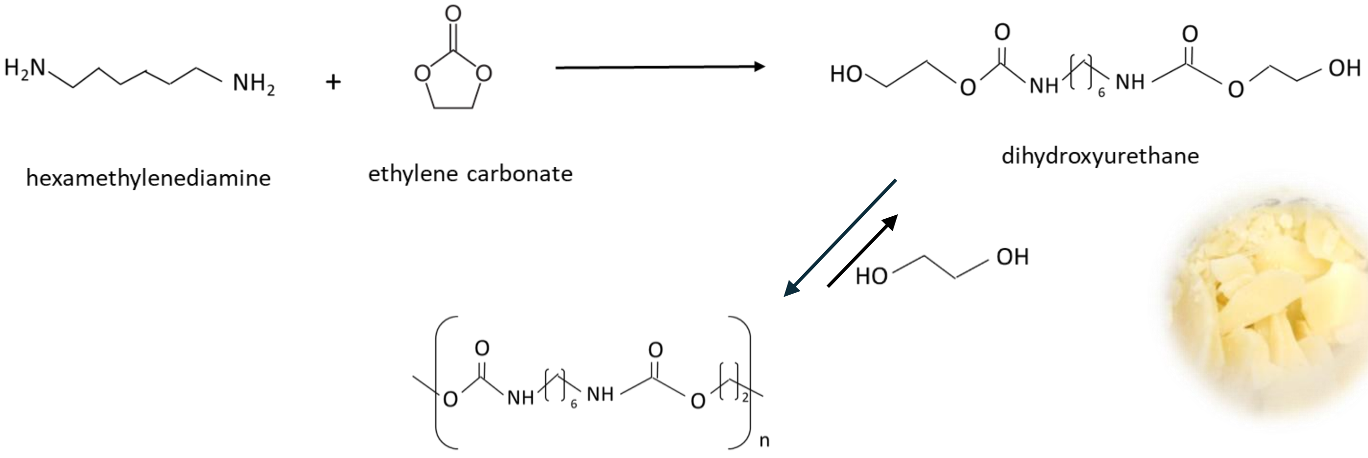


**Products based on BO**

**Products based on PO**

# Non-isocyanate polyurethanes (NIPUs)

- Cyclic carbonates formed as side products are utilised for NIPUs




[6,2]polyurethane

# Acknowledgements

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- WP leader Juha Lehtonen

# beyond the obvious

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