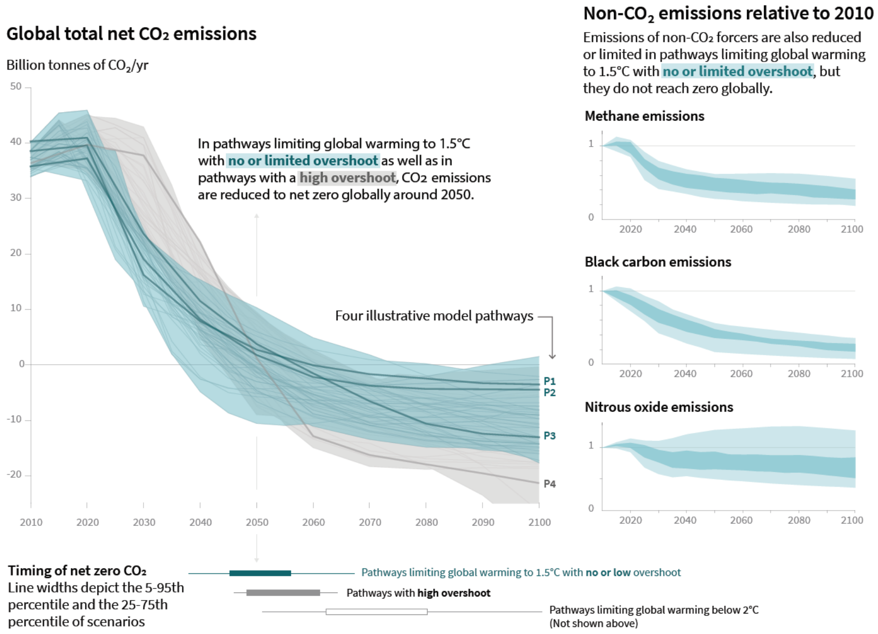
SEPARATION-ENHANCED PROCESSES FOR THE UTILISATION OF CO_2

ICCDU 2019 - Aachen, Germany | Jurriaan Boon

ECN › TNO innovation for life

CO_2 EMISSION REDUCTION!

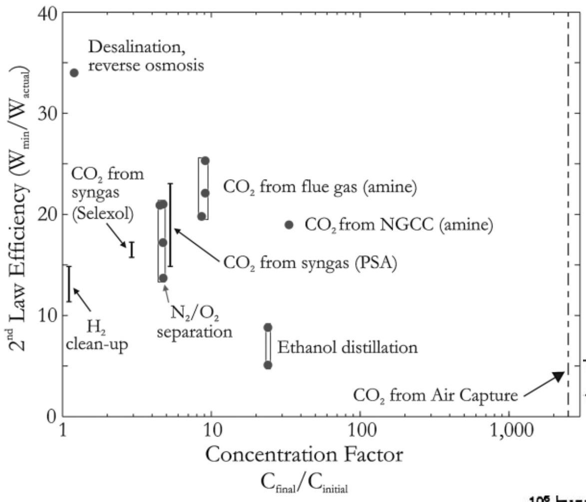


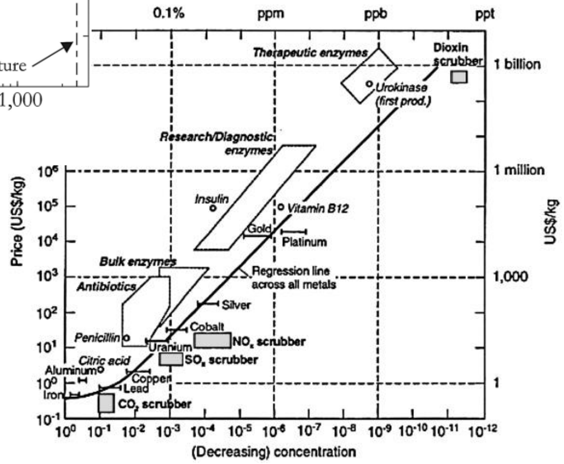
IPCC, 2018

- CCS (up to 1218 $GtCO_2$ until 2100)
- Fuels, chemicals, materials: CO_2 & energy
- CCS & CCUS & CCU – joint development
- Investing in technology relevant today, equally relevant in 2050
- Where possible, let CCU enable CCS

CO_2

- Concentrated streams first
  - $W_{min} \sim RT \ln(p_1/p_0)$
  - Processes:
    high 2nd law eff or concentration factor
  - Increasing cost for decreasing conc
- Captured CO_2, building on CCS development
  - Steel
  - Cement
  - Waste
- Utilisation of biogenic carbon

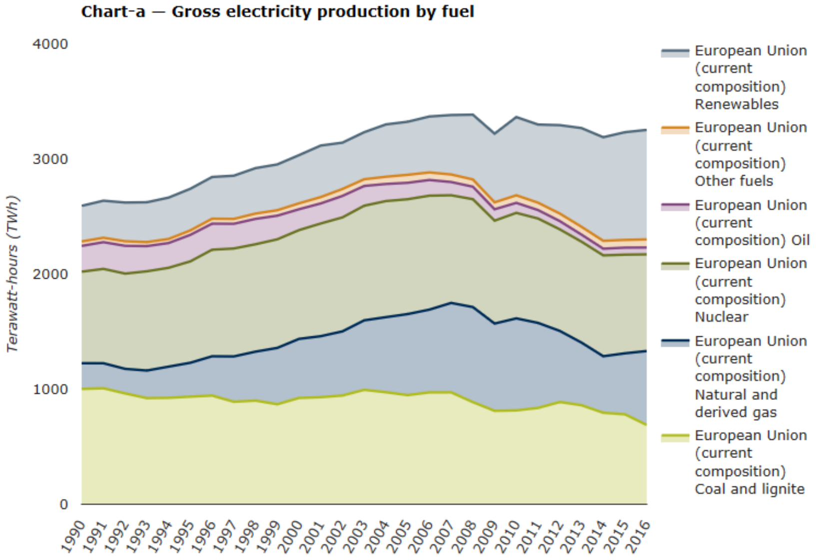




House et al. Proceedings of the National Academy of Sciences
Dec 2011, 108 (51) 20428-20433; DOI:10.1073/pnas.1012253108

ENERGY

- Electricity: Direct electrochemistry, H_2 – not yet C-neutral
- H_2 from residual industrial gases
- H_2, syngas from biogenic sources



European Environment Agency
https://www.eea.europa.eu/data-and-maps/indicators/overview-of-the-electricity-production-2/assessment-4

CO_2 AND H_2 TO PRODUCTS

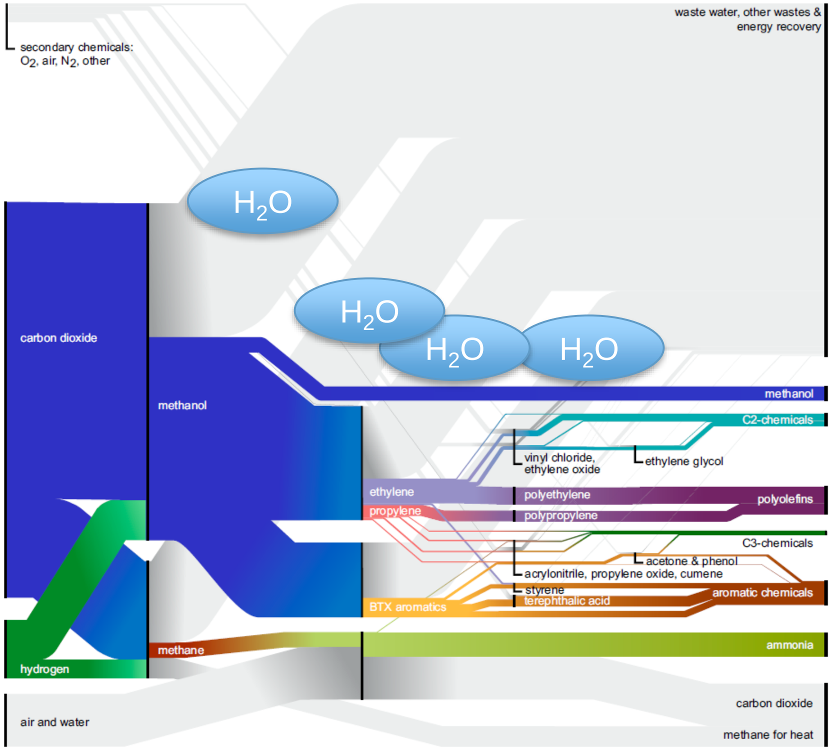
- Mass flows within the chemical industry (2030)

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O$$

$$2CO_2 + 6H_2 \longleftrightarrow \boxed{CH_3OCH_3} + 3H_2O$$

- DME as Simple, Available, Sustainable, Low-Emission, Infrastructure Compatible Fuel https://www.aboutdme.org/

International DME Association
DME: 21st Century Energy



Kätelhön et al. (2019). *Proceedings of the National Academy of Sciences*, *116*(23), 11187-11194.

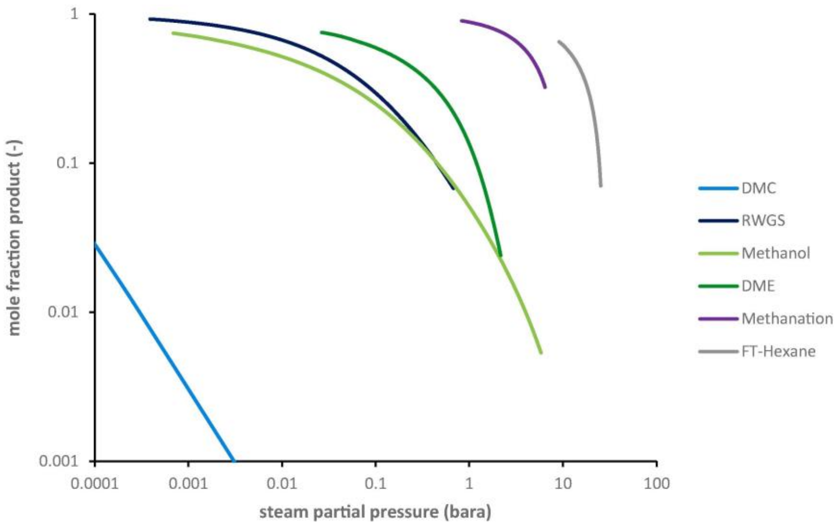
DME: DIRECT SYNTHESIS FROM CO_2

- Steam separation enhancement:
  process intensification for CO_2 utilisation

- DME synthesis from CO_2

$$2CO_2 + 6H_2 \longrightarrow CH_3OCH_3 (+3H_2O)$$

- Reducing the steam partial pressure in situ
  - Adsorbents
  - Membranes



van Kampen et al. (2019) *Chemical Engineering Journal*. https://doi.org/10.1016/j.cej.2019.06.031

SEPARATION ENHANCEMENT: ADSORBENTS

DIRECT DME SYNTHESIS

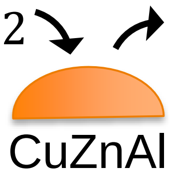
Methanol synthesis

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O$$

$$2CO_2 + 6H_2 \qquad 2CH_3OH + 2H_2O$$

Reverse water-gas shift (WGS)

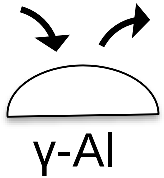
$$H_2 + CO_2 \rightleftharpoons CO + H_2O$$



Methanol dehydration

$$2CH_3OH \rightleftharpoons CH_3OCH_3 + H_2O$$

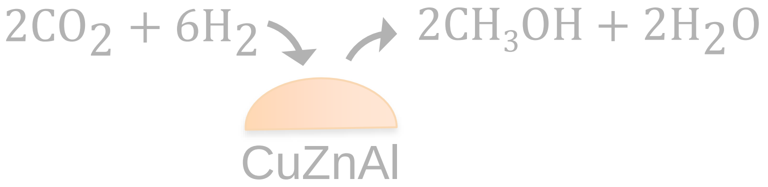
$$2CH_3OH + 2H_2O \qquad CH_3OCH_3 + 3H_2O$$



SEDMES: SORPTION-ENHANCED DME SYNTHESIS

Methanol synthesis

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O$$

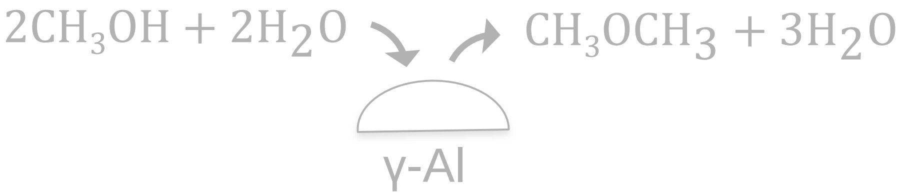


Reverse water-gas shift (WGS)

$$H_2 + CO_2 \rightleftharpoons CO + H_2O$$

Methanol dehydration

$$2CH_3OH \rightleftharpoons CH_3OCH_3 + H_2O$$



SEDMES: SORPTION-ENHANCED DME SYNTHESIS

Methanol synthesis

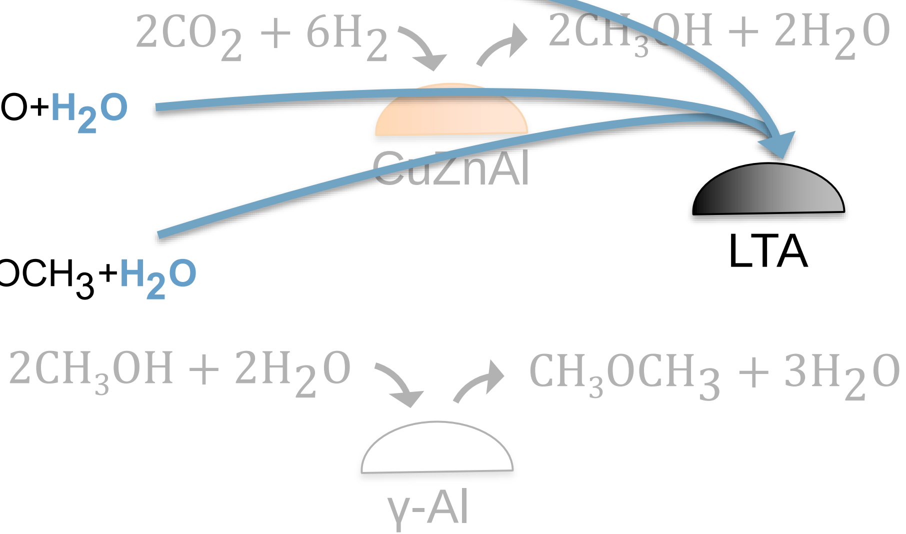
$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O$$

Reverse water-gas shift (WGS)

$$H_2 + CO_2 \rightleftharpoons CO + H_2O$$

Methanol dehydration

$$2CH_3OH \rightleftharpoons CH_3OCH_3 + H_2O$$

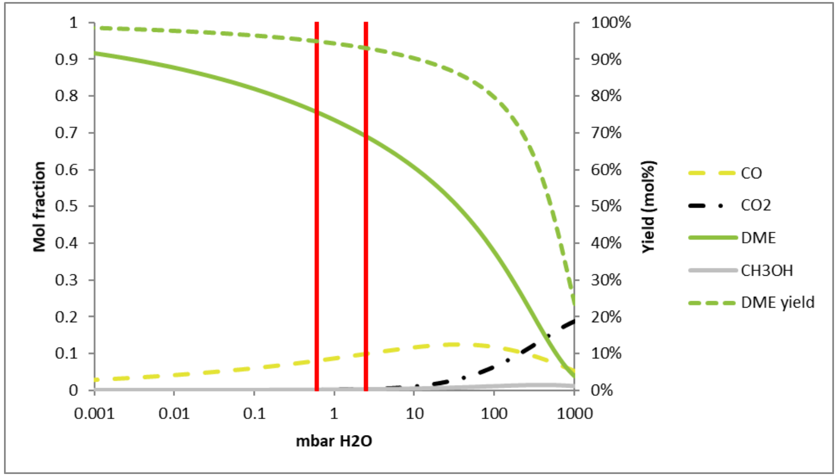


SEDMES MODELLING

- Equilibrium model with in situ water removal

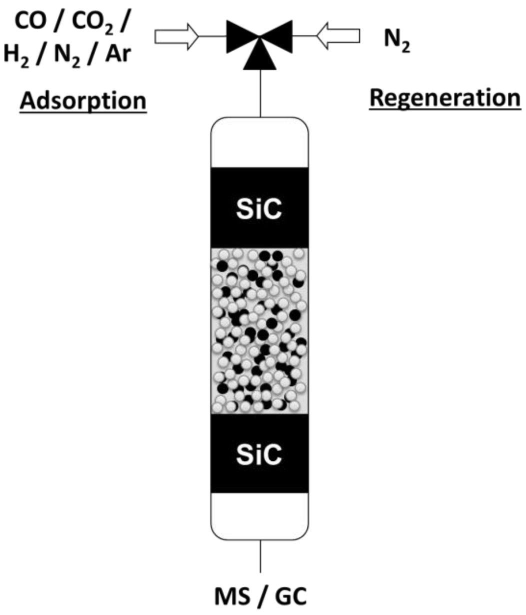
- Stoichiometric feed, 275 °C, 25 bar(a)

- Target
  - 90% DME yield
  - Small residual CO_2 concentration

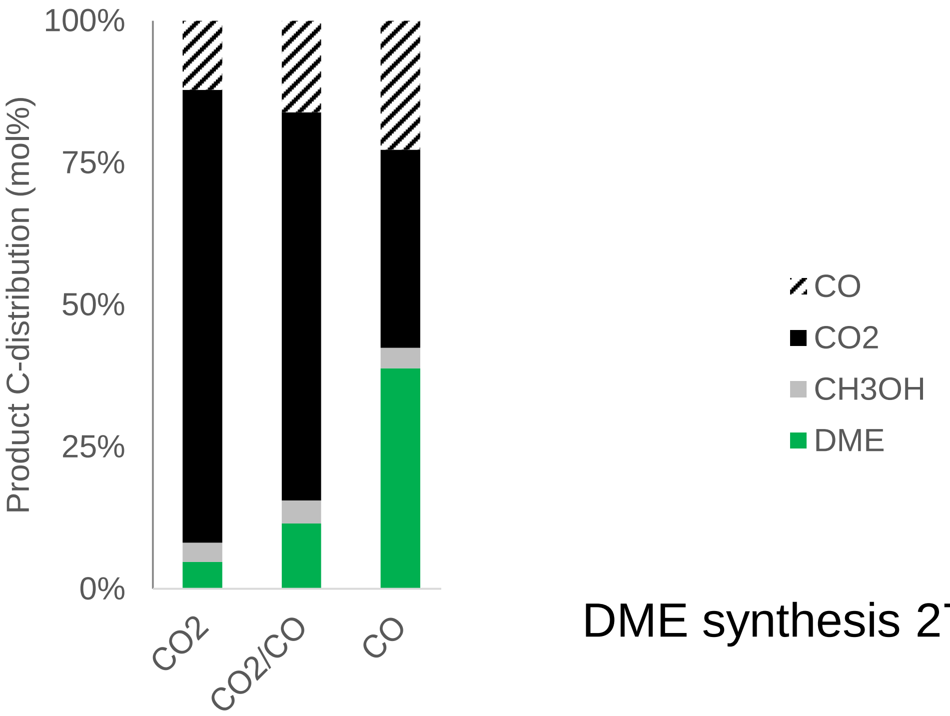


SEDMES EXPERIMENTS

- Adsorption at 275 °C & 40 bar(a)
- Regeneration at 275-400°C & 1-3 bar(a)
- Copper/Zinc Oxide/Alumina (CZA) catalyst
  Zeolite LTA adsorbent, well mixed
- Feed M = ([H2]-[CO2])/([CO]+[CO2]) = 2

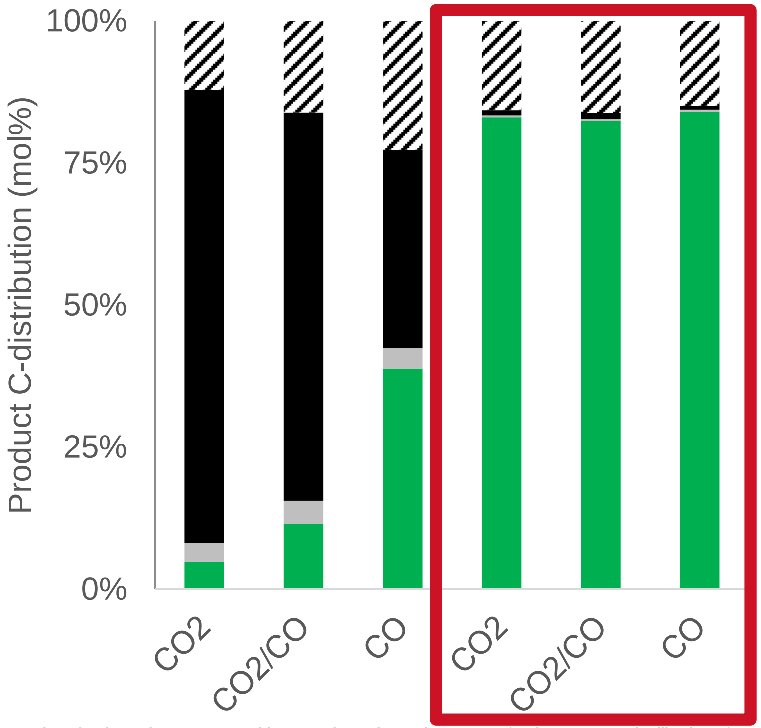


SEDMES: YIELD IMPROVEMENT



DME synthesis 275 °C & 40 bar(a)

SEDMES: YIELD IMPROVEMENT

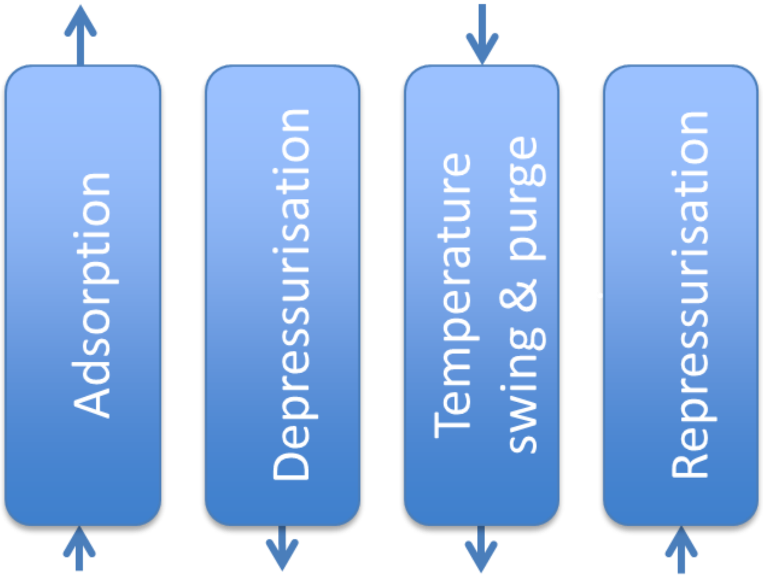


SEDMES 275 °C & 40 bar(a)

- ✓ increased yield of DME
- ✓ improved selectivity to DME over methanol
- ✓ strongly reduced CO_2 content in the product

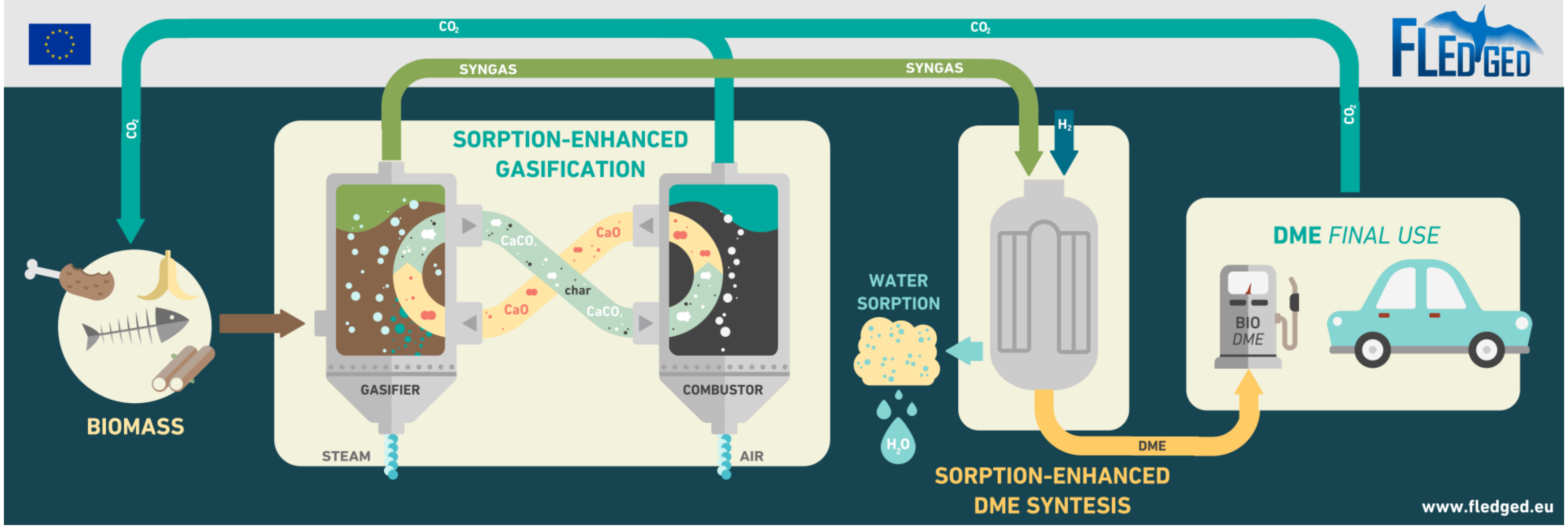
SEDMES: CYCLE DESIGN

- Example: 4-step TPSA cycle design
  - Adsorption
  - Depressurisation (blowdown)
  - Temperature swing & purge
  - Repressurisation

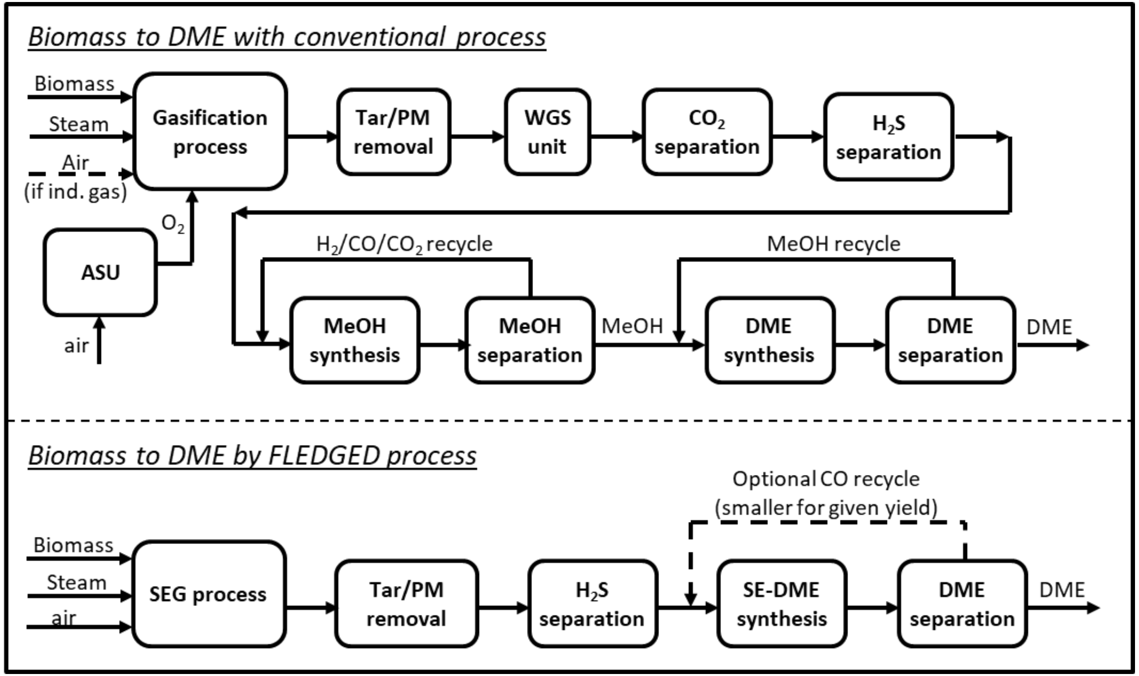


THE FLEDGED PROJECT

- The ***FLEDGED*** project will deliver a process for ***Bio-based dimethyl Ether (DME)*** production from **biomass** gasification, validated in ***industrially relevant*** environment (TRL5).



FLEDGED: BIOMASS TO DME



FLEDGED

www.fledged.eu/

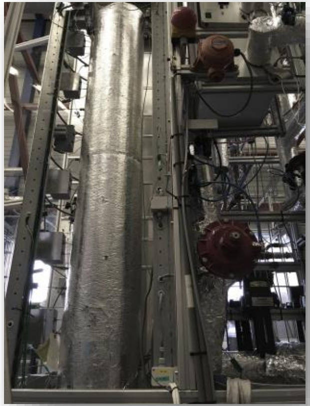
YouTube

https://youtu.be/JEn39Zi_aCg

SEDMES: SCALE-UP

0.9 × 20 cm

- ✓ Materials selection
- ✓ Process conditions



3.8 × 200 cm

Counter-current regeneration
Heat effects

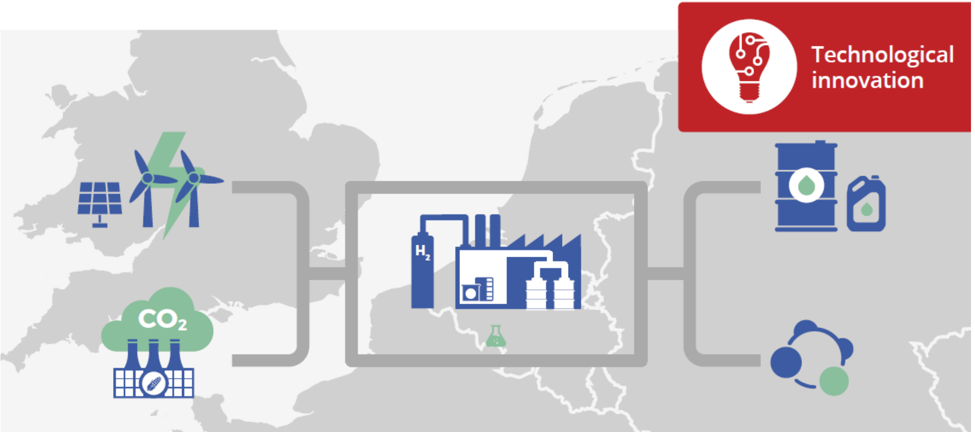
3.8 × 600 cm

Cycle design & optimisation

EU INTERREG E2C PROJECT

Interreg
EUROPEAN UNION
2 Seas Mers Zeeën
European Regional Development Fund

Electrons to High Value Chemical Products

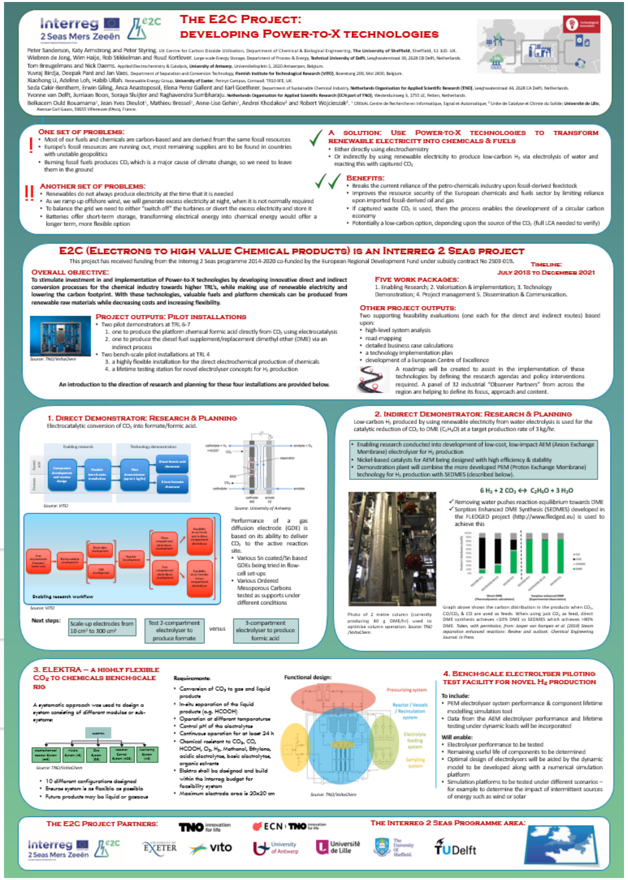


http://www.voltachem.com/E2C

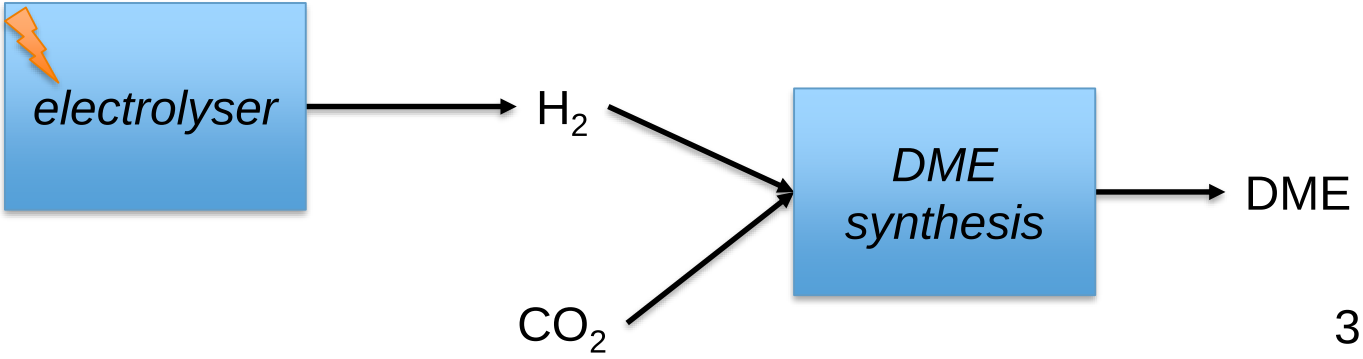
THE E2C PROJECT

- Developing power-to-X technologies
- Poster: Peter Sanderson et al.

Poster title	Developing Power-to-X Technologies: The E2C Project
Poster code	P 58

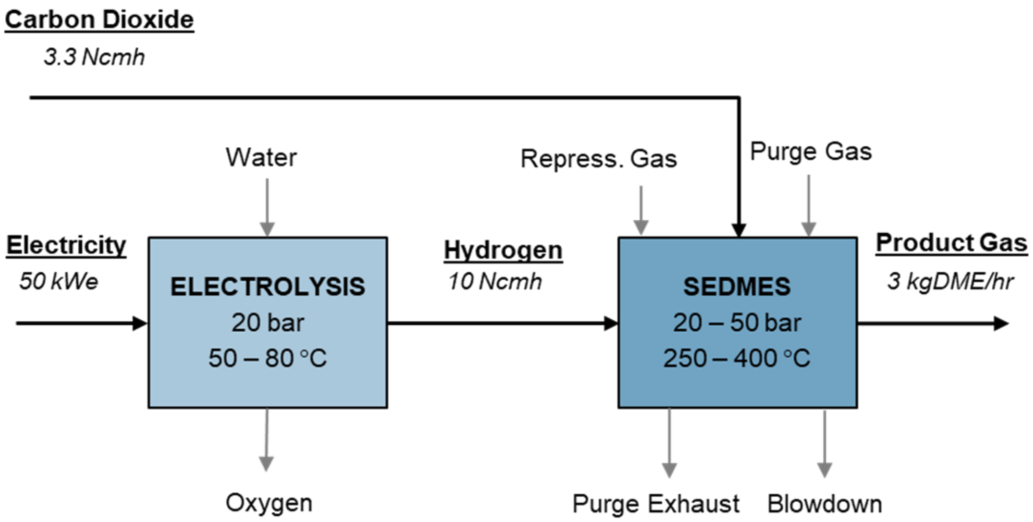


E2C PILOT DEMONSTRATOR: CO_2 TO DME



3 kg/hr demonstrator (2021)

E2C PILOT DEMONSTRATOR: CO_2 TO DME



EU INTERREG E2C PROJECT

Interreg
EUROPEAN UNION
2 Seas Mers Zeeën
European Regional Development Fund

e2c

Electrons to High Value Chemical Products

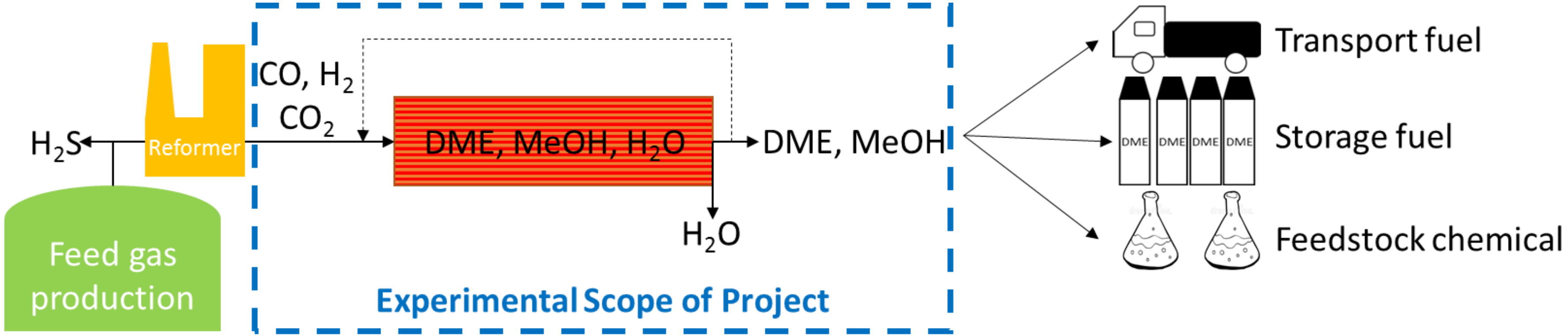
International open innovation platform, open to additional industrial partners during and after the project

http://www.voltachem.com/E2C

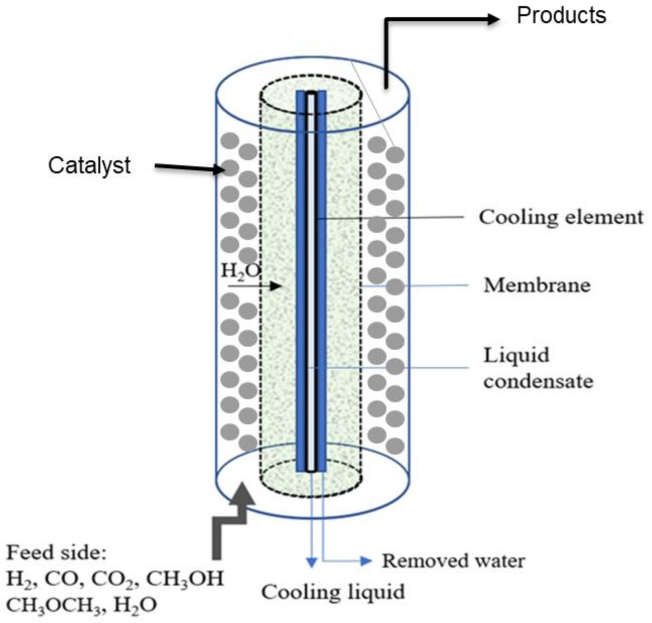
SEPARATION ENHANCEMENT: MEMBRANES

BIODIME

- New process concept to produce DME from CO_2 rich gasses such as biogas

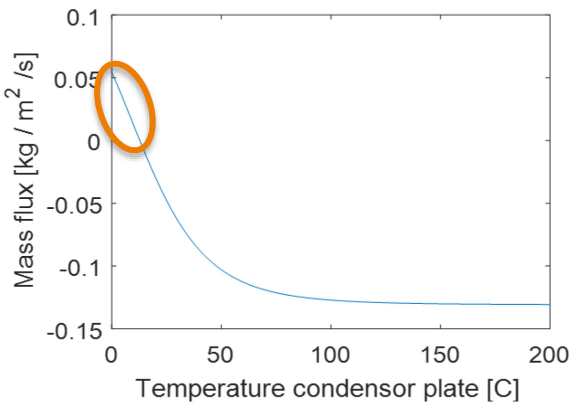


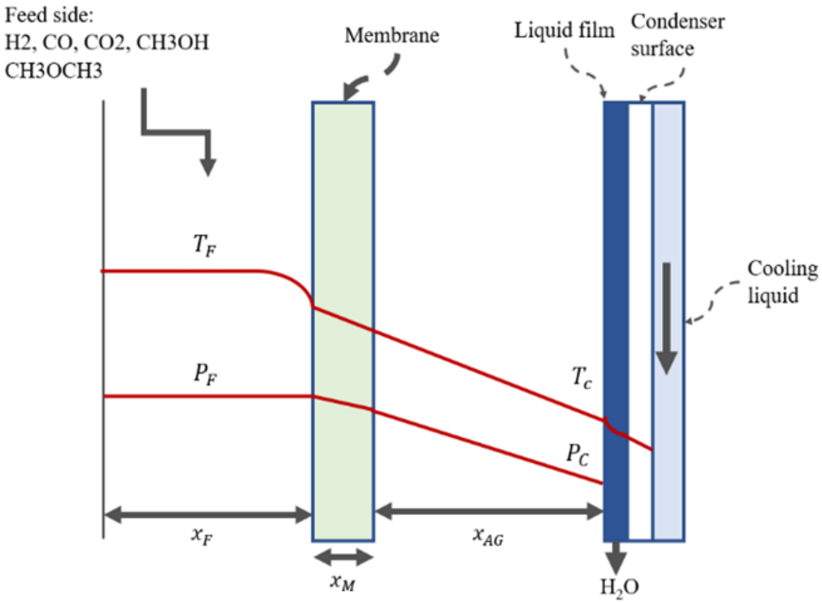
PERMEATION-ENHANCED DME SYNTHESIS: REACTOR CONCEPT



REACTOR MODEL

- Mass transfer model with reactor kinetics for estimation of DME production
- 50% increase in single-pass DME yield





EXPERIMENTAL MEMBRANE REACTOR SETUP

SEPARATION-ENHANCED PROCESSES FOR THE UTILISATION OF CO_2

- Steam separation enhancement promising process intensification for CO_2 utilisation
- Complex interplay of catalysis and removal
- In situ steam removal to be assessed case specifically (not only theoretically)
- Fledged: Sorption-enhanced DME synthesis (SEDMES) from biobased syngas scaled up to TRL5
- E2C: Pilot demonstrator, electrolysis and SEDMES for 3 kg/hr DME
- BioDiME: Development of membrane-enhanced DME synthesis

ACKNOWLEDGEMENTS

- ECN part of TNO
  - Biomass & Energy Efficiency, Petten, The Netherlands
  - Sustainable Process & Energy Systems, Delft, The Netherlands

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 727600.

This project has received funding from the European Union's Interreg 2 Seas programme under grant agreement No 2S03-019 E2C.


THANK YOU FOR YOUR ATTENTION
TNO.NL/ECNPARTOFTNO
ECN
TNO innovation for life