SEPARATION-ENHANCED PROCESSES FOR THE UTILISATION OF CO₂

ICCDU 2019 - Aachen, Germany | Jurriaan Boon





CO₂ EMISSION REDUCTION!

Global total net CO₂ emissions



Non-CO₂ emissions relative to 2010

Emissions of non-CO2 forcers are also reduced or limited in pathways limiting global warming

- CCS (up to 1218 GtCO₂ 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



CO₂

- 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 CO₂, 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

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ENERGY

- Electricity: Direct electrochemistry, H₂
 not yet C-neutral
- > H₂ from residual industrial gases
- > H₂, syngas from biogenic sources



Chart-a - Gross electricity production by fuel

European Environment Agency

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

CO₂ AND H₂ TO PRODUCTS

Mass flows within the chemical industry (2030)

 $CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O$

 $2CO_2 + 6H_2 \leftrightarrow CH_3OCH_3 + 3H_2O$

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







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Kätelhön et al. (2019). *Proceedings of the National Academy of Sciences*, *116*(23), 11187-11194. ^{25 June 2019}



DME: DIRECT SYNTHESIS FROM CO₂

- Steam separation enhancement: process intensification for CO₂ utilisation
- > DME synthesis from CO_2 $2CO_2 + 6H_2 \rightarrow CH_3OCH_3(+3H_2O)$
- > 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

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DIRECT DME SYNTHESIS

Methanol synthesis

Reverse water-gas shift (WGS)

 $H_2 + CO_2 \rightleftharpoons CO + H_2O$

 $CO_2+3H_2 \rightleftharpoons CH_3OH+H_2O$

Methanol dehydration

 $\text{2CH}_3\text{OH} \rightleftharpoons \text{CH}_3\text{OCH}_3\text{+}\text{H}_2\text{O}$

 $2CH_{3}OH + 2H_{2}O \longrightarrow CH_{3}OCH_{3} + 3H_{2}O$

CuZnAl

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

SEDMES: SORPTION-ENHANCED DME SYNTHESIS

Methanol synthesis

 $\text{CO}_2 + 3\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH} + \text{H}_2\text{O}$

Reverse water-gas shift (WGS)

 $H_2+CO_2 \rightleftharpoons CO+H_2O$

Methanol dehydration

 $\text{2CH}_3\text{OH} \rightleftharpoons \text{CH}_3\text{OCH}_3\text{+}\text{H}_2\text{O}$

 $2CH_{3}OH + 2H_{2}O \longrightarrow CH_{3}OCH_{3} + 3H_{2}O$

CuZnAl

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

SEDMES: SORPTION-ENHANCED DME SYNTHESIS





SEDMES MODELLING

- > Equilibrium model with in situ water removal
- > Stoichiometric feed, 275 °C, 25 bar(a)

- Target
 - > 90% DME yield
 - > Small residual CO₂ 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





SEDMES: YIELD IMPROVEMENT



SEDMES 275 °C & 40 bar(a)

- CO
- CO2
- CH3OH
- DME

✓ increased yield of DME
 ✓ improved selectivity to DME over methanol
 ✓ strongly reduced CO₂ 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).



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FLEDGED: BIOMASS TO DME







https://youtu.be/JEn39Zi_aCg

SEDMES: SCALE-UP



0.9 × 20 cm

✓ Materials selection✓ Process conditions



3.8 × 200 cm



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 3.8×600 cm

Cycle design & optimisation

Counter-current regeneration Heat effects



EU INTERREG E2C PROJECT



Electrons to High Value Chemical Products



http://www.voltachem.com/E2C

THE E2C

- Developing pov >
- Poster: Peter Sanderson et al. >



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

PROJECT	
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E2C PILOT DEMONSTRATOR: CO₂ TO DME





Technological

innovation

EU INTERREG E2C PROJECT

Lezc



Electrons to High Value Chemical Products

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

CO

http://www.voltachem.com/E2C

SEPARATION ENHANCEMENT: MENBRANES



BIODIME

New process concept to produce DME from CO₂ 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





ECN • TNO innovation EXPERIMENTAL MEMBRANE REACTOR SETUP



28 | Towards a circular carbon economy with separation-enhanced processes for the capture and utilisation of CO2



SEPARATION-ENHANCED PROCESSES FOR THE UTILISATION OF CO₂

- > Steam separation enhancement promising process intensification for CO₂ 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



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THANK YOU FOR YOUR ATTENTION

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