SEPARATION ENHANCED REACTOR SYSTEMS FOR HIGH CARBON EFFICIENCIES: SEDMES

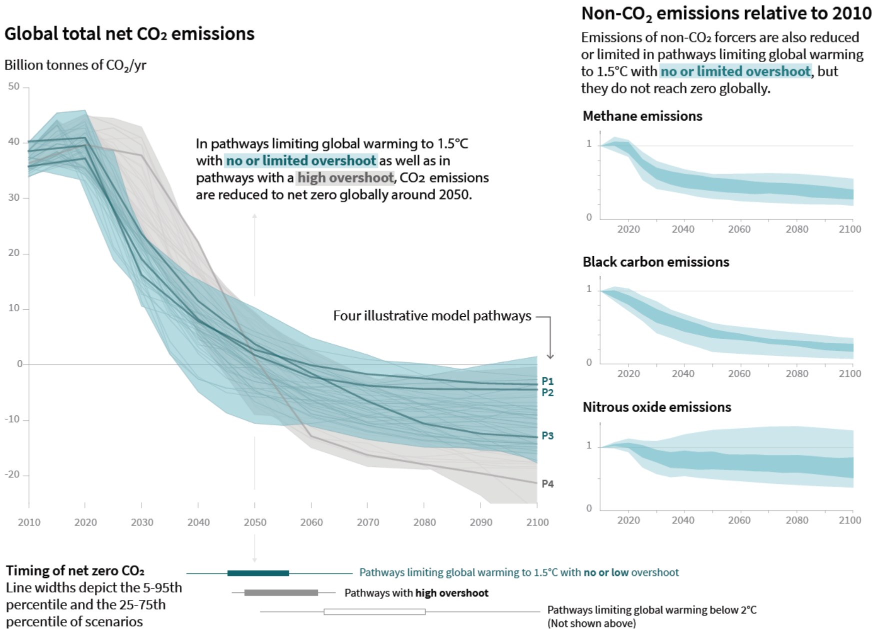
NPS 16 | J. van Kampen

TU/e

ECN

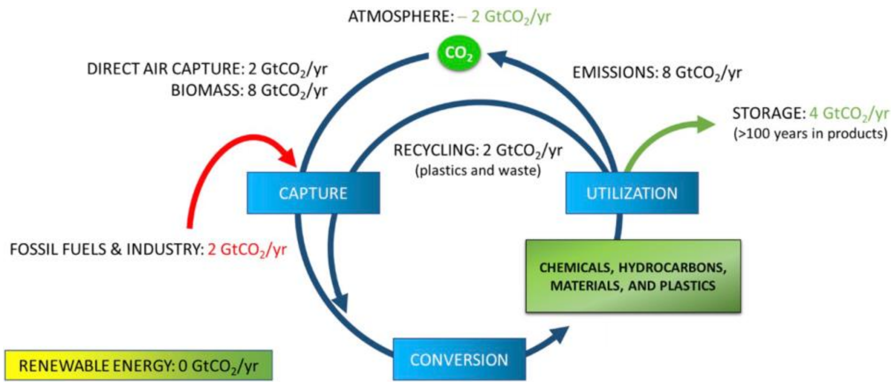
TNO innovation for life

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



Detz and van der Zwaan (2019), *Energy Policy.*

CO_2 AND H_2 TO PRODUCTS

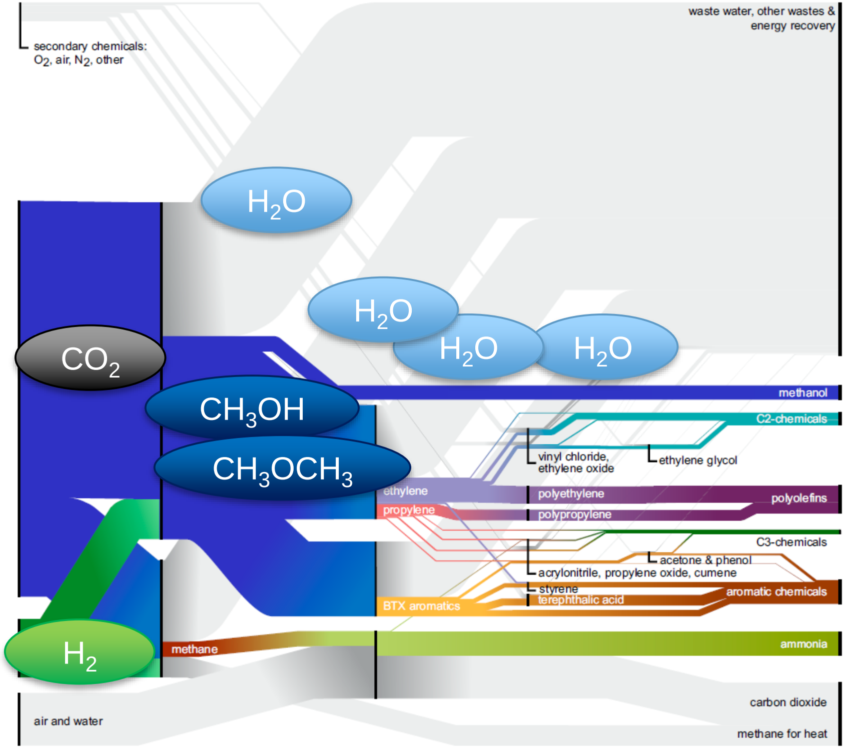
- Mass flows within the chemical industry (2030)

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

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

- DME as simple, available, sustainable, low-emission, infrastructure compatible fuel https://www.aboutdme.org/

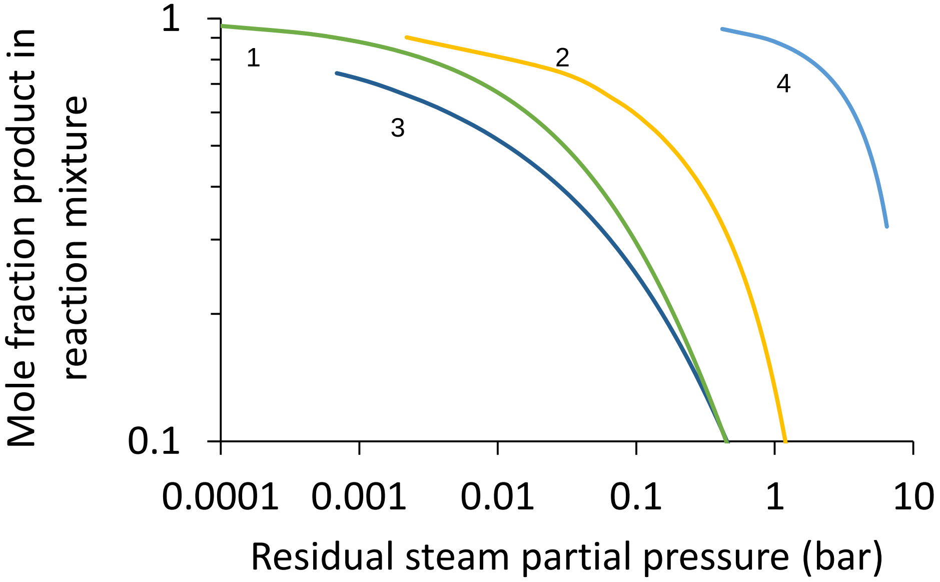
International DME Association
DME: 21st Century Energy



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

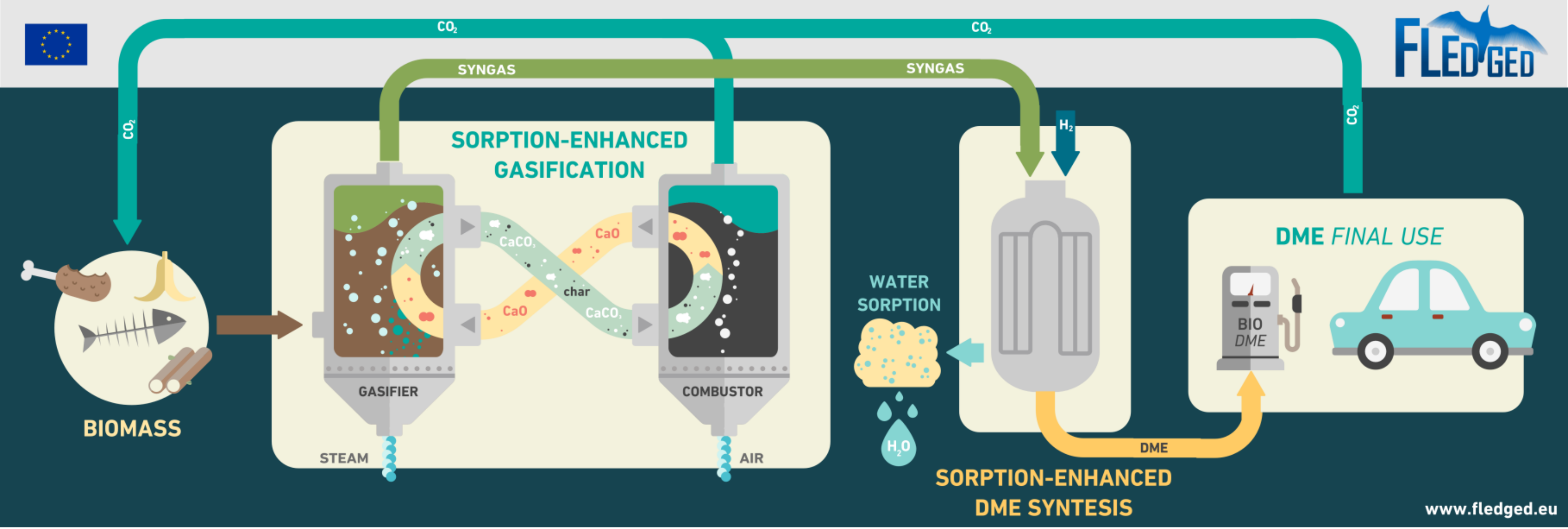
DIRECT SYNTHESIS FROM CO_2

- Steam separation enhancement: process intensification for CO_2 utilisation
- Reactions from CO_2:
  1. Reverse water-gas shift
  2. DME synthesis
  3. Methanol synthesis
  4. Methanation
- Reducing the steam partial pressure in situ
  - Adsorbents
  - Membranes



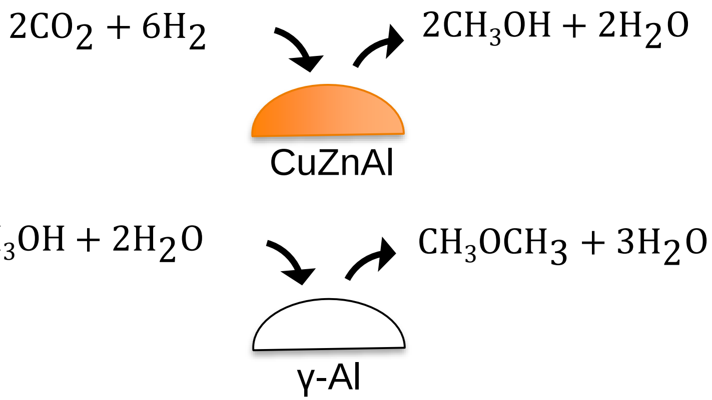
van Kampen et al. (2019), *Chemical Engineering Journal*. https://doi.org/10.1016/j.cej.2019.06.031

SEPARATION ENHANCEMENT: ADSORBENTS

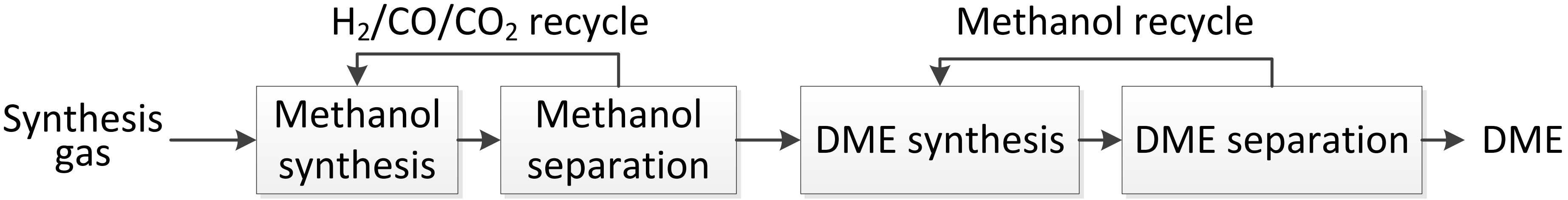


CO_2
CO_2
SYNGAS
SYNGAS
CO_2
CO_2
SORPTION-ENHANCED GASIFICATION
H_2
$CaCO_3$
CaO
char
CaO
$CaCO_3$
WATER SORPTION
DME *FINAL USE*
BIO DME
BIOMASS
GASIFIER
COMBUSTOR
STEAM
AIR
H_2O
DME
SORPTION-ENHANCED DME SYNTESIS
www.fledged.eu

CONVENTIONAL DME SYNTHESIS

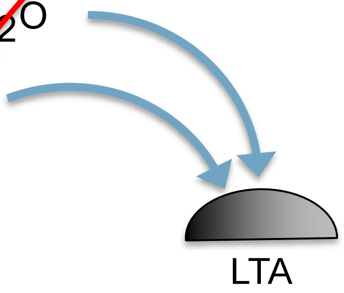


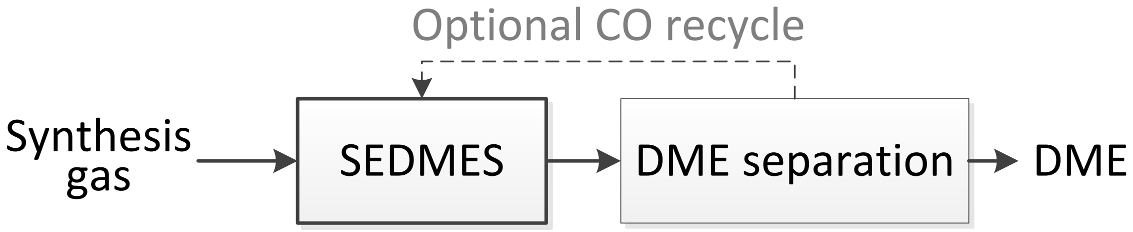
- Methanol synthesis: $CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O$
- Reverse water-gas shift: $H_2 + CO_2 \rightleftharpoons CO + H_2O$
- Methanol dehydration: $2\ CH_3OH \rightleftharpoons CH_3OCH_3 + H_2O$



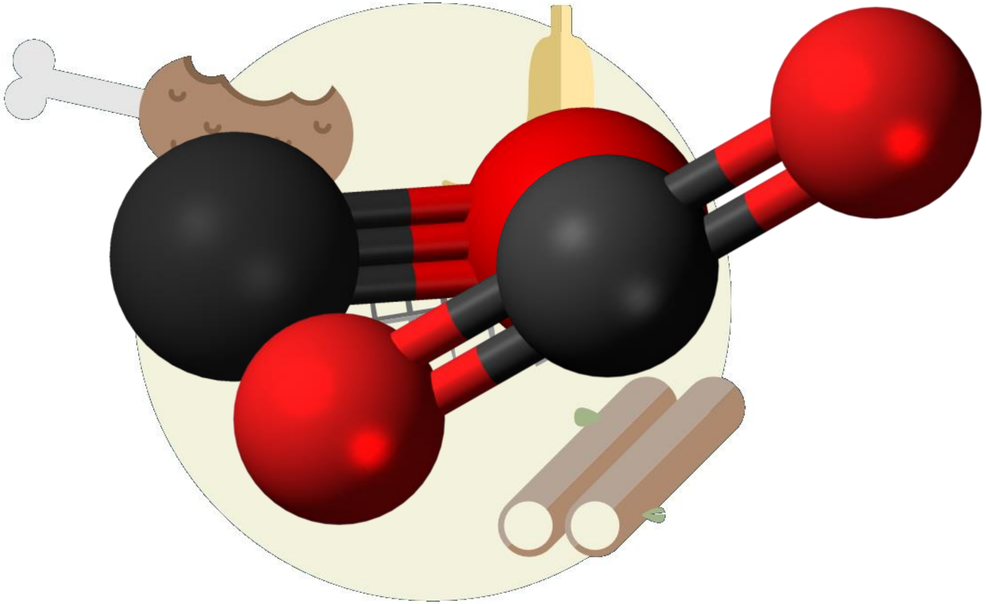
SORPTION ENHANCED DME SYNTHESIS (SEDMES)

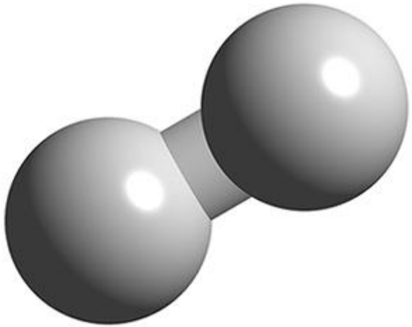
- Direct DME: $2\ CO_2 + 6\ H_2 \rightarrow CH_3OCH_3 + 3\ H_2O$
- Direct DME: $2\ CO + 4\ H_2 \rightarrow CH_3OCH_3 + H_2O$
- Adsorption: $H_2O\ (g) \rightarrow H_2O\ (ads)$





FEED FLEXIBILITY



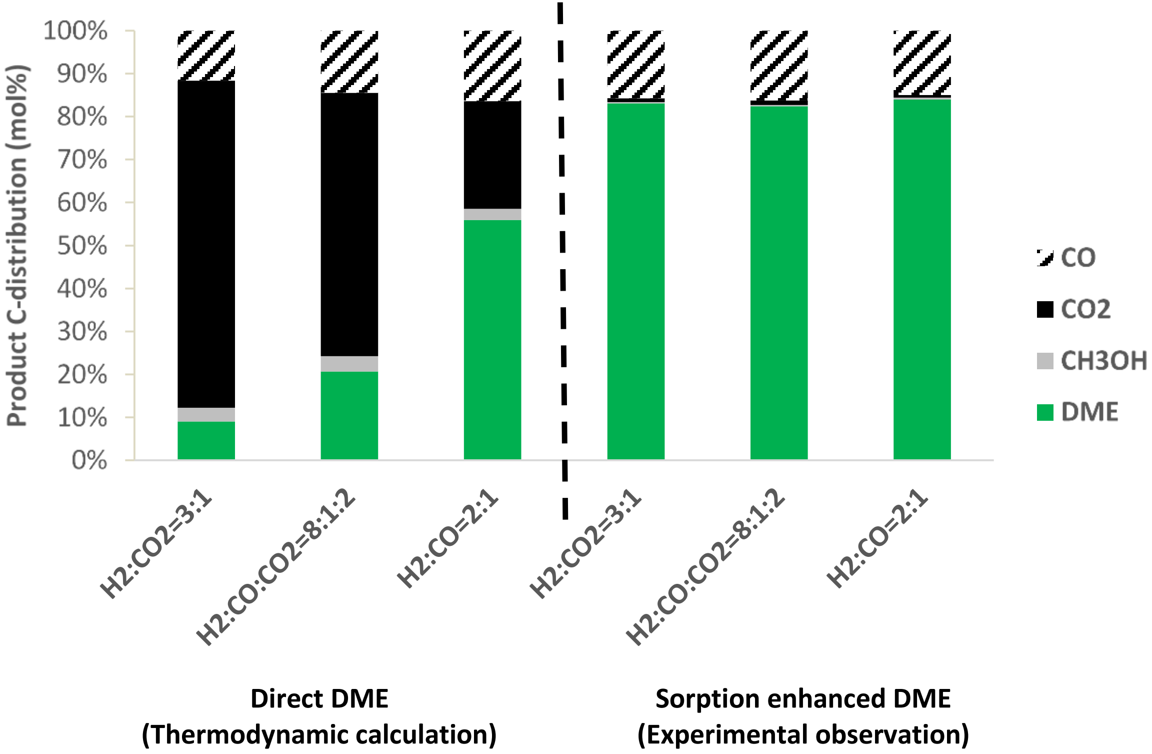


SEDMES FEED FLEXIBILITY

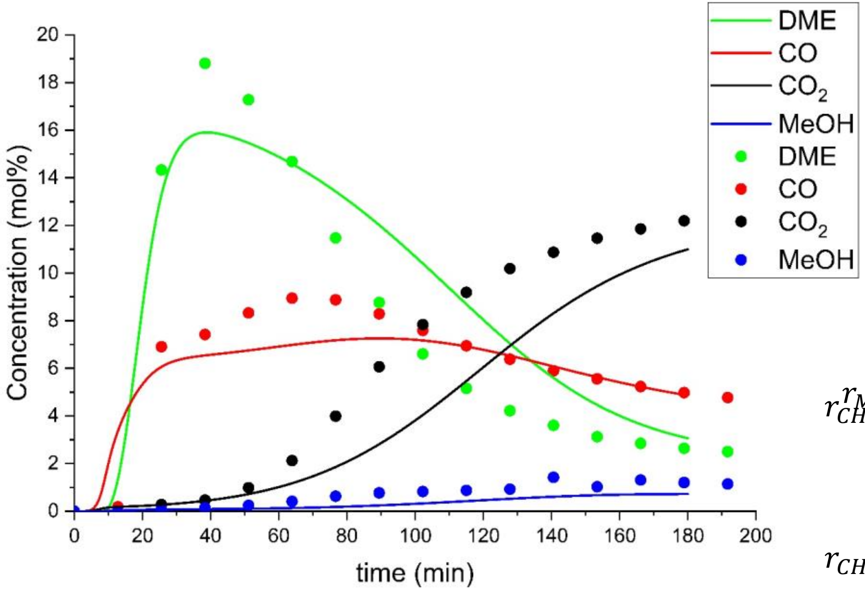
van Kampen et al., Chemical Engineering Journal 374 (2019) 1286–1303.

- Direct DME synthesis
- 275 °C & 40 bar(a), incl. 30% inert
- Carbon is found in CO / CO_2 / MeOH / DME

- Sorption enhanced DME synthesis
- 275 °C & 40 bar(a), incl. 30% inert
- Carbon is found in CO / ~~CO_2 /~~ ~~MeOH /~~ DME



SEDMES BREAKTHROUGH MODEL



Graaf et al., Chemical Engineering Science 43 (1988) 3185-3195.
Vanden Bussche et al., Journal of Catalysis 161 (1996) 1-10.

$$r_{CO} = \frac{k'_2 \varphi_{CO2}\left[1 - (1/K_{p2})\left(\varphi_{H2O}\varphi_{CO}/\varphi_{CO2}\varphi_{H2}\right)\right]}{\left(1 + K_2(\varphi_{H2O}/\varphi_{H2}) + \sqrt{K_3\varphi_{H2}} + K_4\varphi_{H2O}\right)}$$

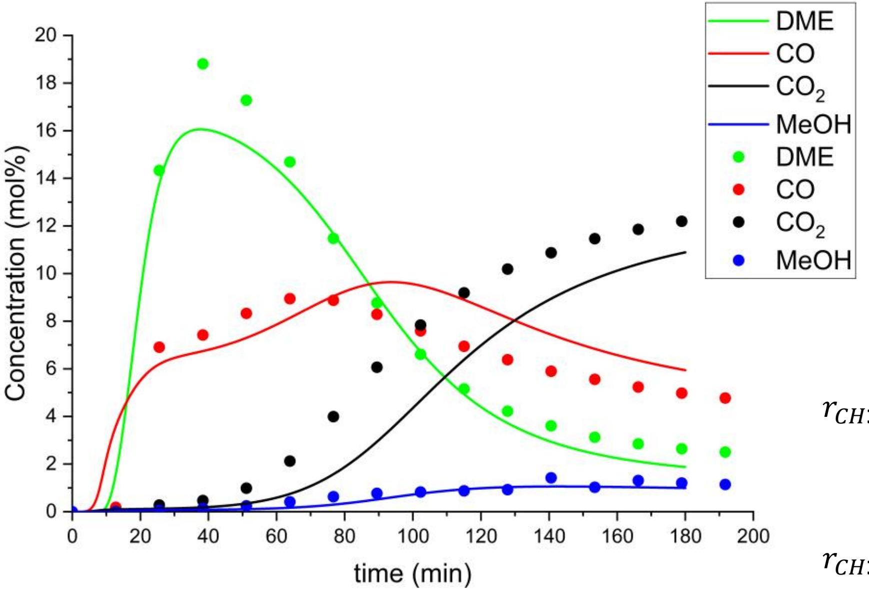
$$r_{RWGS} = \frac{k_2 K_{CO2}\left[\varphi_{CO2}\varphi_{H2} - \varphi_{H2O}\varphi_{CO}/K_{p2}\right]}{\left(1 + K_{CO}\varphi_{CO} + K_{CO2}\varphi_{CO2}\right)\left[\varphi_{H2}^{1/2} + \left(K_{H2O}/K_{H2}^{1/2}\right)\varphi_{H2O}\right]}$$

$$r_{MeOH} = \frac{k'_3 \varphi_{H2}\varphi_{CO2}\left[1 - (1/K_{p1})\left(\varphi_{CH3OH}\varphi_{H2O}/\varphi_{H2}^{3}\varphi_{CO2}\right)\right]}{\left(1 + K_2(\varphi_{H2O}/\varphi_{H2}) + \sqrt{K_3\varphi_{H2}} + K_4\varphi_{H2O}\right)^3}$$

$$r_{CH3OH,1} = \frac{k_1 K_{CO}\left[\varphi_{CO}\varphi_{H2}^{3/2} - \varphi_{CH3OH}/\left(\varphi_{H2}^{1/2}K_{p1}\right)\right]}{\left(1 + K_{CO}\varphi_{CO} + K_{CO2}\varphi_{CO2}\right)\left[\varphi_{H2}^{1/2} + \left(K_{H2O}/K_{H2}^{1/2}\right)\varphi_{H2O}\right]}$$

$$r_{CH3OH,2} = \frac{k_3 K_{CO2}\left[\varphi_{CO2}\varphi_{H2}^{3/2} - \varphi_{CH3OH}\,\varphi_{H2O}/\left(\varphi_{H2}^{3/2}K_{p3}\right)\right]}{\left(1 + K_{CO}\varphi_{CO} + K_{CO2}\varphi_{CO2}\right)\left[\varphi_{H2}^{1/2} + \left(K_{H2O}/K_{H2}^{1/2}\right)\varphi_{H2O}\right]}$$

SEDMES BREAKTHROUGH MODEL



Graaf et al., Chemical Engineering Science 43 (1988) 3185-3195.

$$r_{CO} = \frac{k_2 K_{CO2}\left[\varphi_{CO2}\varphi_{H2} - \varphi_{H2O}\,\varphi_{CO}/K_{p2}\right]}{\left(1 + K_{CO}\varphi_{CO} + K_{CO2}\varphi_{CO2}\right)\left[\varphi_{H2}^{1/2} + \left(K_{H2O}/K_{H2}^{1/2}\right)\varphi_{H2O}\right]}$$

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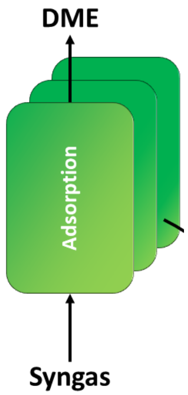
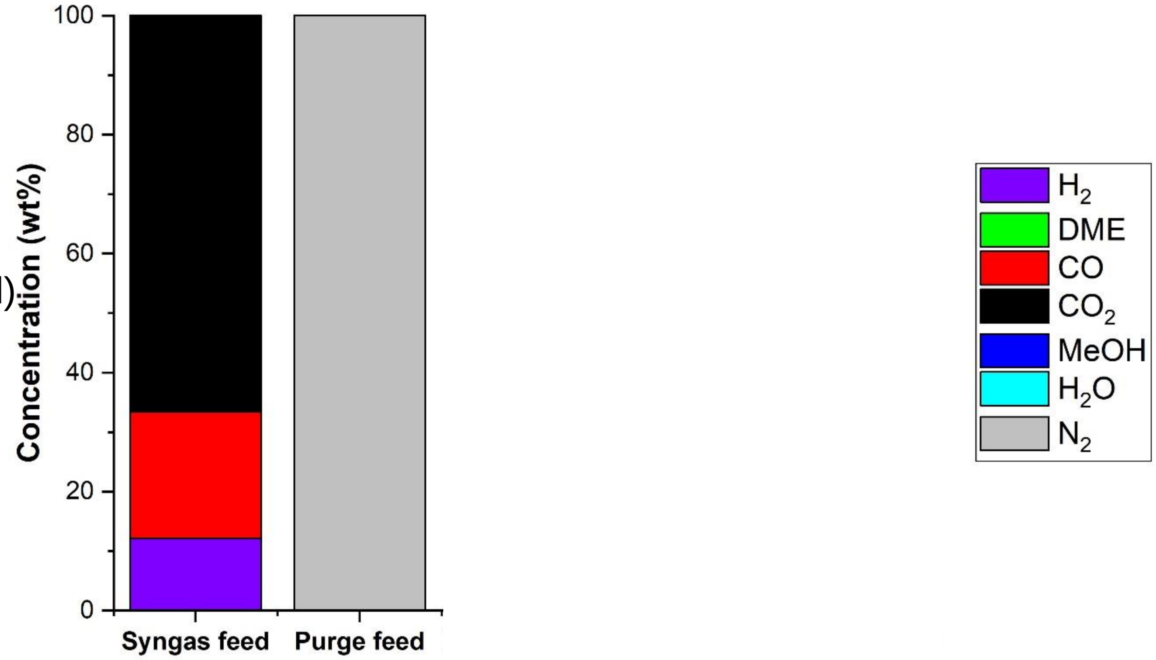
CYCLE DESIGN

- 3 column continuous process
- 4 step TPSA cycle:
  - Adsorption
  - Depressurization (Blowdown)
  - Purge
  - Repressurization



FEED & PRODUCT

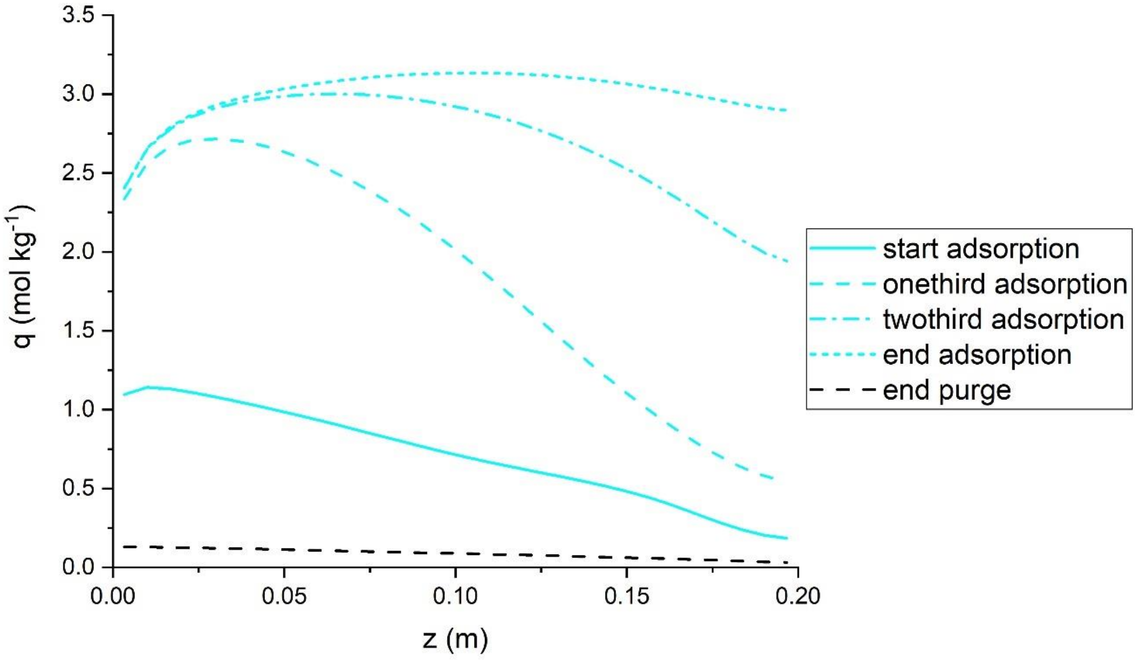
- Feed
  - CO_2:CO=2:1
  - M=2
- Product
  - 64% conversion (unoptimized)
  - Thermodynamically only 26%
- Purge product: N_2+H_2O
  - recycle



WORKING CAPACITY

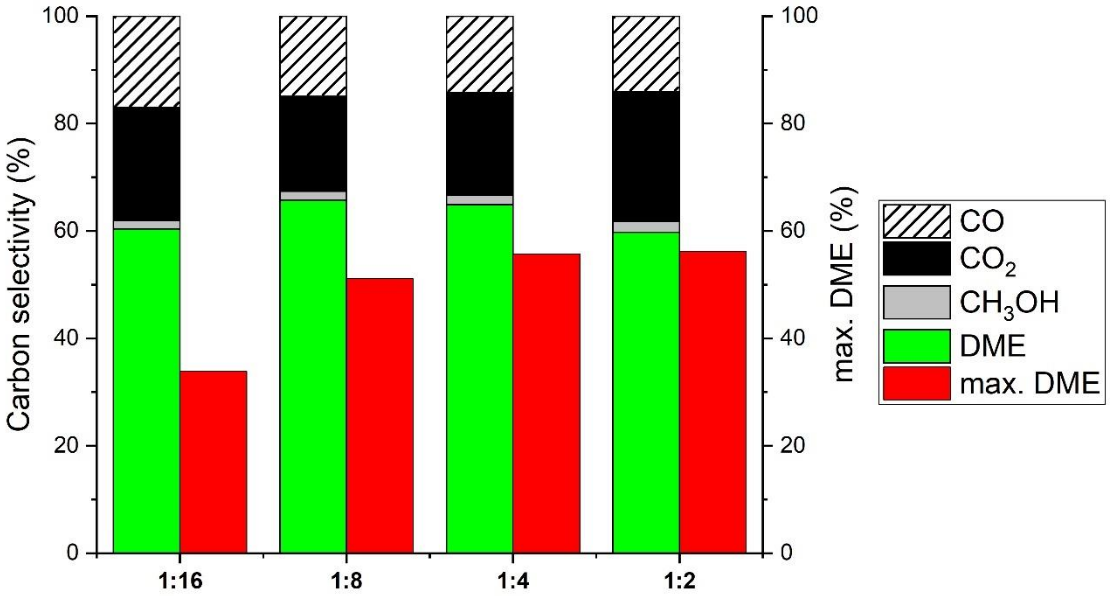
- Working capacity
  - adsorption
  - regeneration
- Determines conversion & yield
  - Limitation

- Depends on
  - Process conditions
  - **Regeneration**



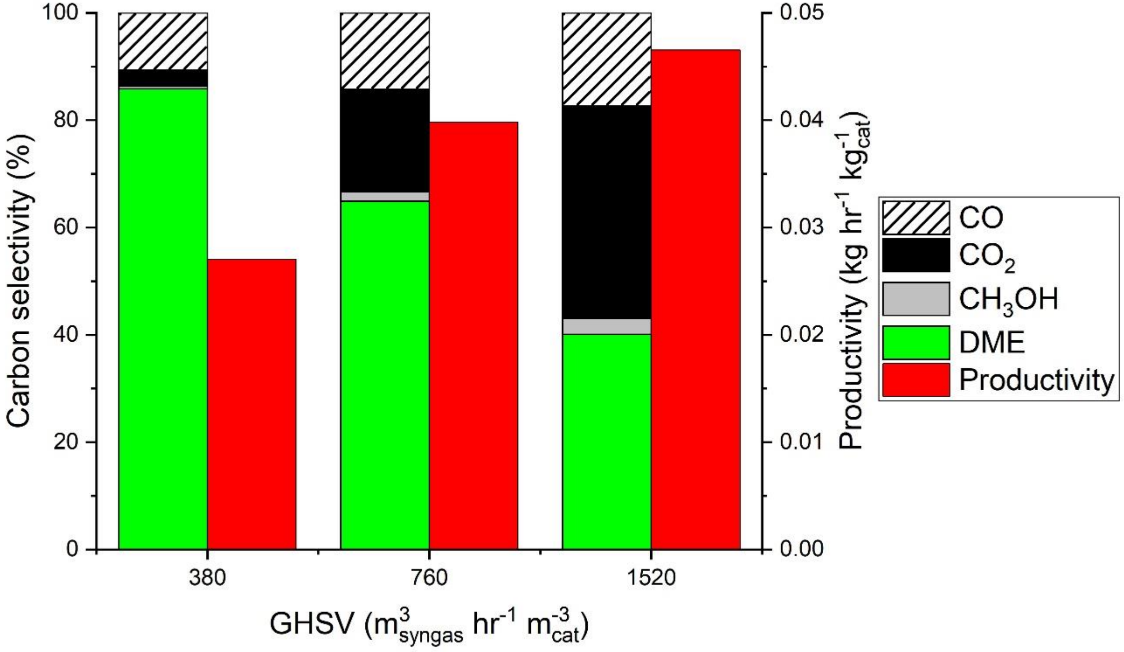
CATALYST VS. SORBENT

- Working capacity limited
- Increasing adsorbent beneficial
  - Penalty reducing catalyst



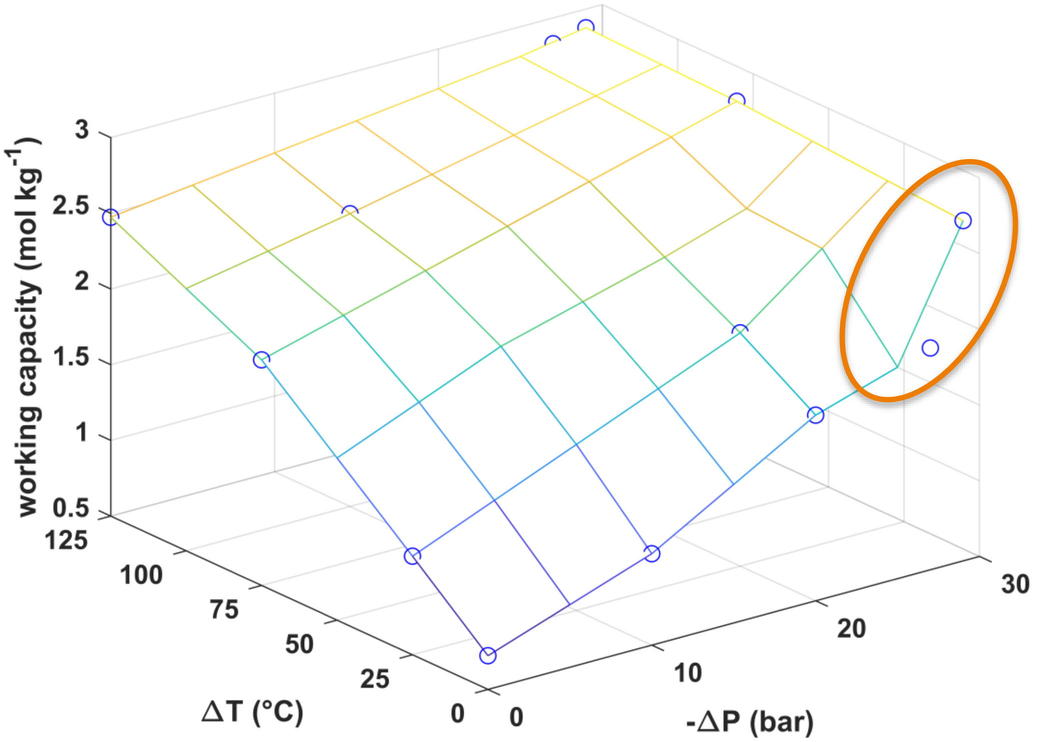
SELECTIVITY VS. PRODUCTIVITY

- Lower GHSV, lower steam content
- Trade-off
  - Higher conversion & selectivity
  - Lower productivity



REGENERATION STRATEGY

- Temperature swing
- Pressure swing
  - Faster cycling
  - Higher productivity
- Window for PSA?

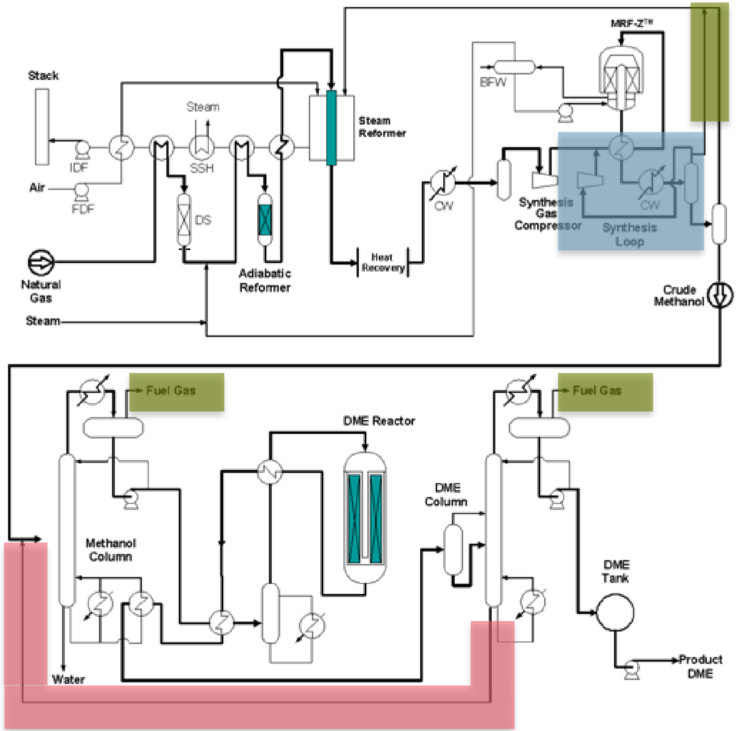


CONCLUSION

- Sorption enhanced DME synthesis (SEDMES):
  - Proof-of-concept
  - High DME yield
  - Feed flexibility
    - CO_2 not as product but as reactant

  - 3 column cycle design (TPSA)
  - Temperature swing regeneration to 400 °C
    - Improves DME yield pre and post steam breakthrough
    - Adsorbent capacity increases
  - Window for pressure swing regeneration?
    - Increased productivity

OUTLOOK



- Methanol route (indirect)
- Thermodynamic limitations result in:

Syngas recycle in methanol part

Methanol recycle in DME synthesis

Avoidable fuel gas production

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

THANK YOU FOR YOUR ATTENTION

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https://youtu.be/JEn39Zi_aCg

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