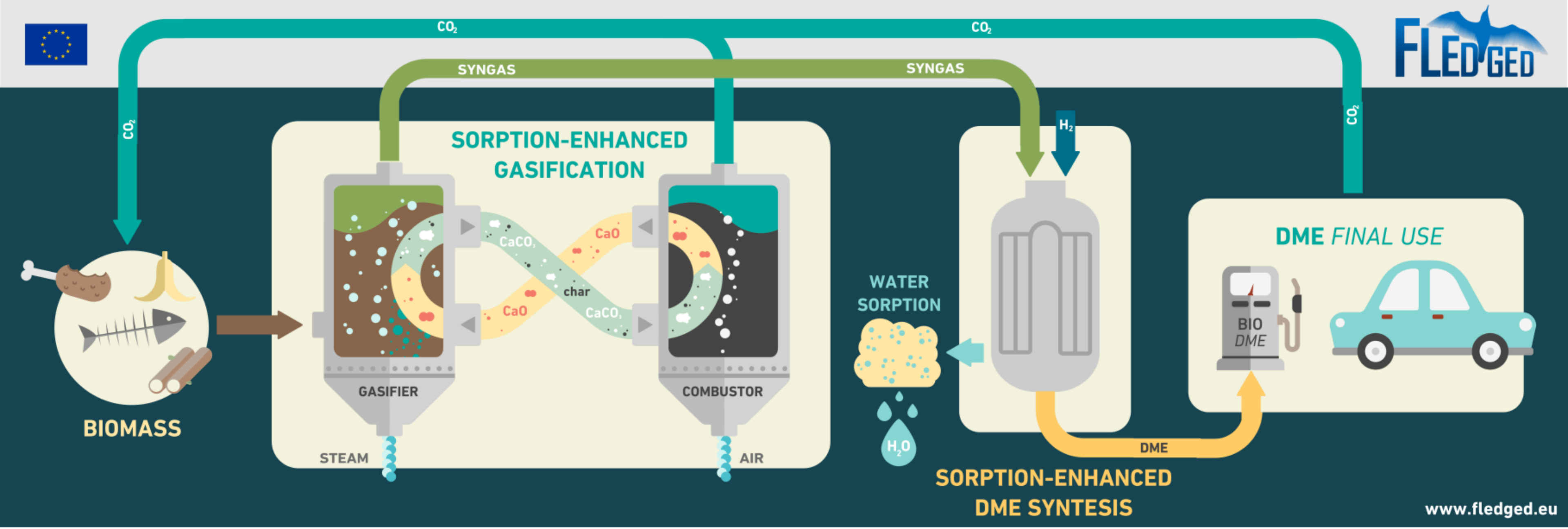
SORPTION ENHANCED DME SYNTHESIS FOR HIGH CARBON EFFICIENCIES

ECCE 12| J. van Kampen


CO$_2$
CO$_2$
SYNGAS
SYNGAS
CO$_2$
CO$_2$
SORPTION-ENHANCED
GASIFICATION
CaCO$_3$
CaO
char
CaO
CaCO$_3$
GASIFIER
COMBUSTOR
STEAM
AIR
BIOMASS
H$_2$
WATER
SORPTION
H$_2$O
DME
SORPTION-ENHANCED
DME SYNTESIS
DME FINAL USE
BIO
DME
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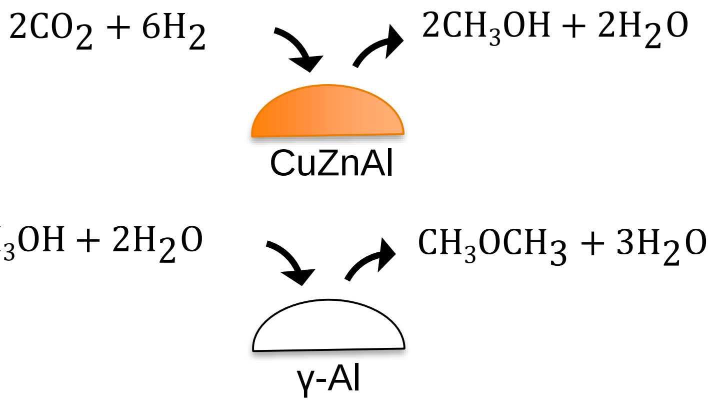
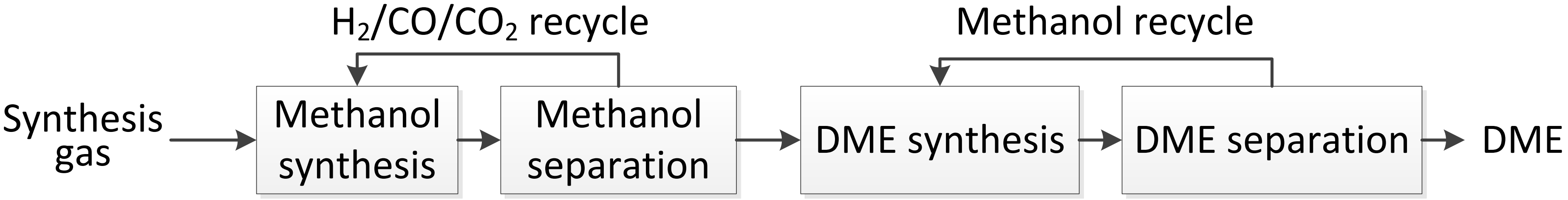
CONVENTIONAL DME SYNTHESIS

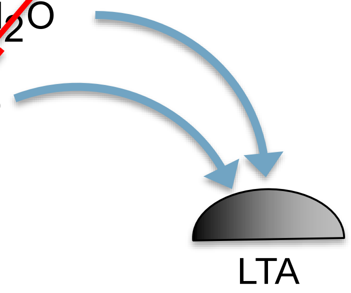


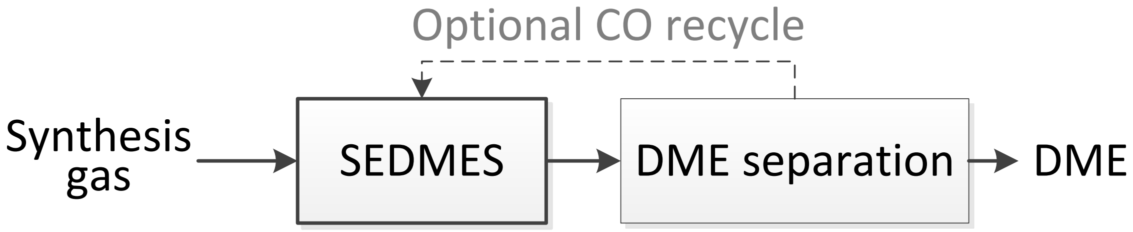
- Methanol synthesis: $CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O$
- Reverse water-gas shift: $H_2 + CO_2 \rightleftharpoons CO + H_2O$
- Methanol dehydration: $2\ CH_3OH \rightleftharpoons CH_3OCH_3 + H_2O$



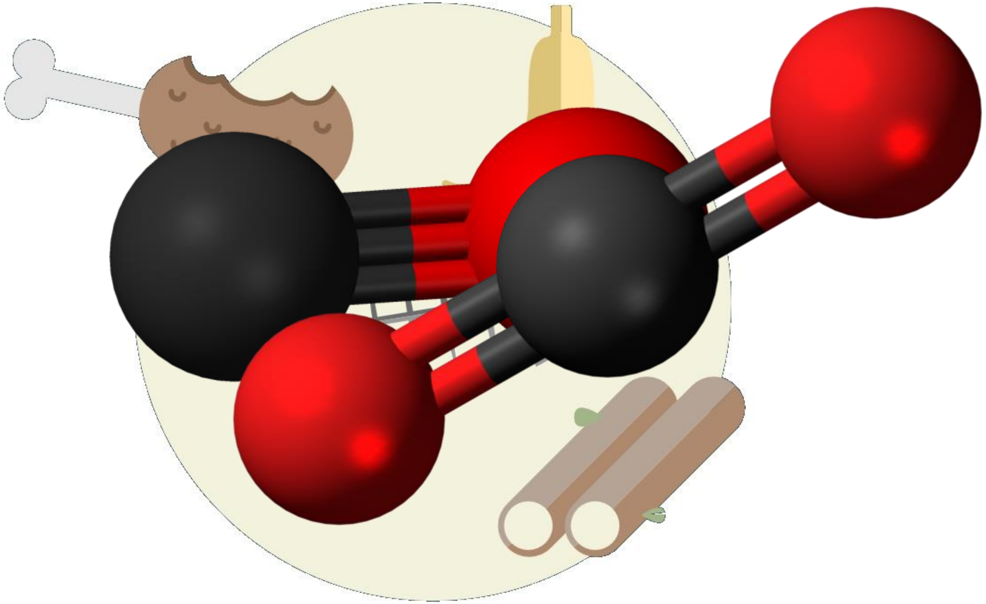
SORPTION ENHANCED DME SYNTHESIS (SEDMES)

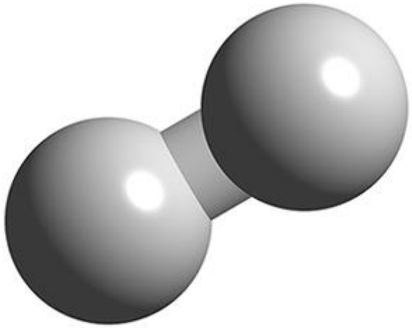
- Direct DME: $2\,CO_2 + 6\,H_2 \rightarrow CH_3OCH_3 + 3\,H_2O$
- Direct DME: $2\,CO + 4\,H_2 \rightarrow CH_3OCH_3 + H_2O$
- Adsorption: $H_2O\ (g) \rightarrow H_2O\ (ads)$



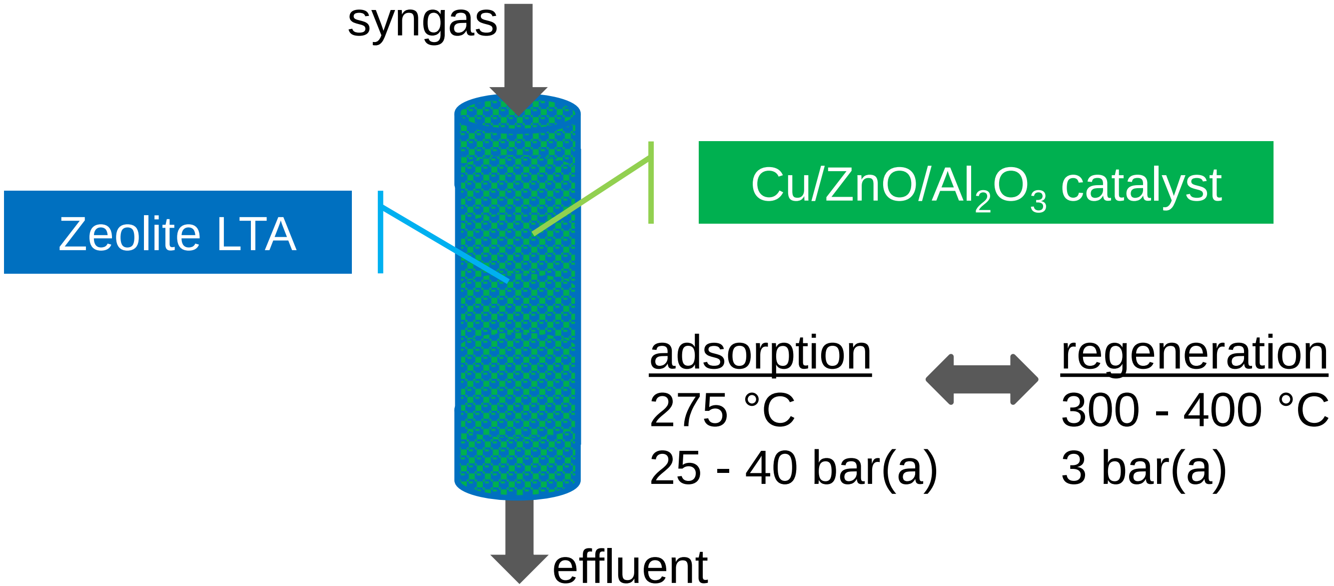


FEED FLEXIBILITY





EXPERIMENTAL: SEDMES

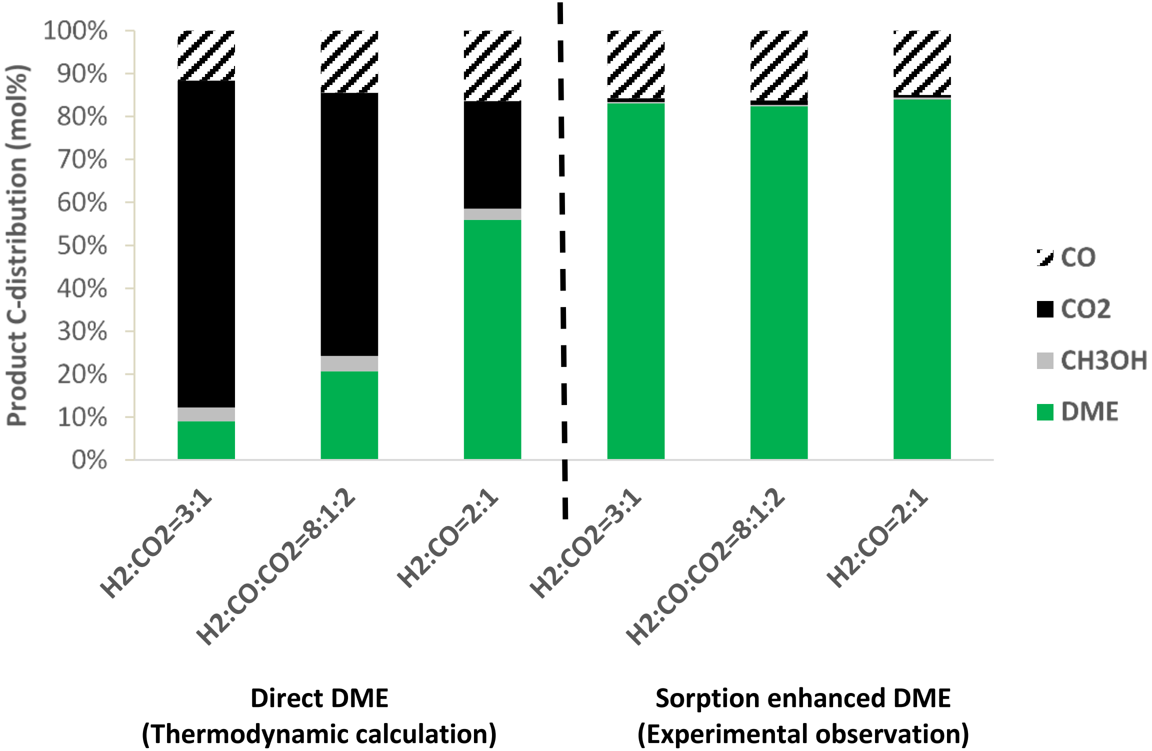


SEDMES FEED FLEXIBILITY

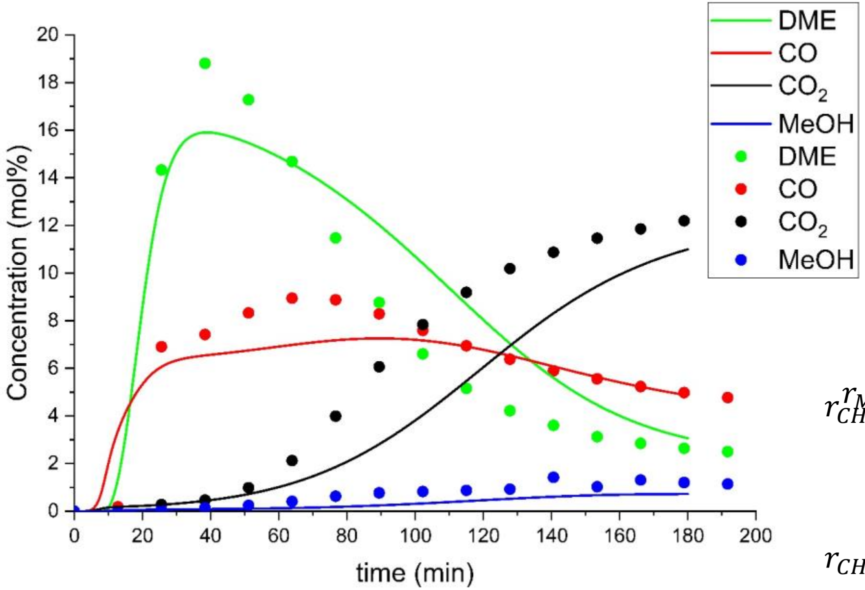
van Kampen et al., Chemical Engineering Journal 374 (2019) 1286–1303.

- 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, Journal of Catalysis 161 (1996) 1-10.

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

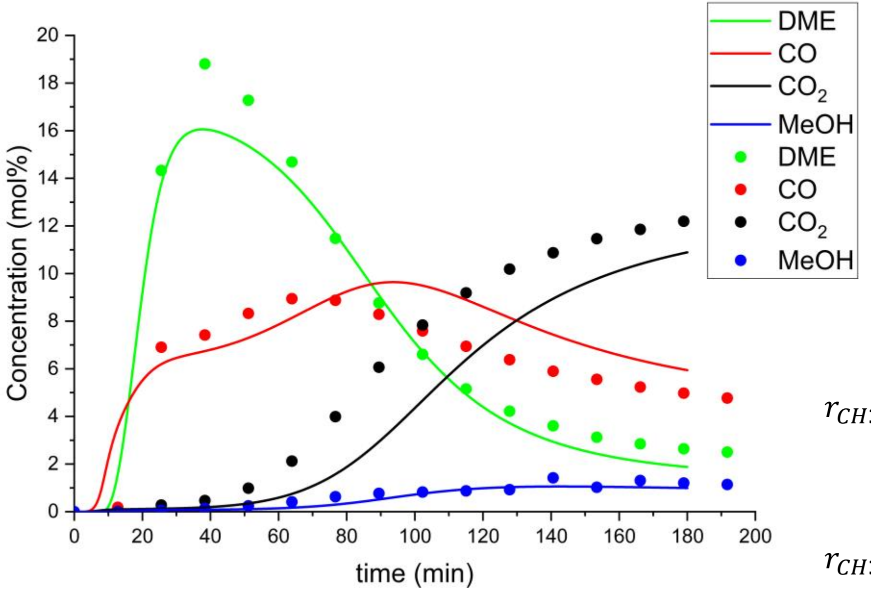
$$r_{RWGS} = \frac{k'_2\varphi_{CO2}\left[1 - K_{p2}\left(\varphi_{H2O}\varphi_{CO}/\varphi_{CO2}\varphi_{H2}\right)\right]}{1 + K_3\left(\varphi_{H2O}/\varphi_{H2}\right) + \sqrt{K_1\varphi_{H2}} + K_4\varphi_{H2O}}$$

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

$$r_{MeOH} = \frac{k'_3\varphi_{H2}\varphi_{CO2}\left[1 - \left(1/K_{p1}\right)\left(\varphi_{CH3OH}\varphi_{H2O}/\varphi_{H2}^{3}\varphi_{CO2}\right)\right]}{\left(1 + K_3\left(\varphi_{H2O}/\varphi_{H2}\right) + \sqrt{K_1\varphi_{H2}} + K_4\varphi_{H2O}\right)^3}$$

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

SEDMES BREAKTHROUGH MODEL



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

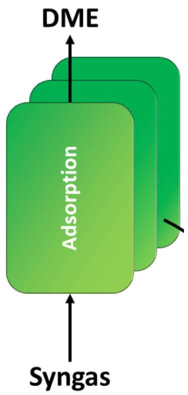
$$r_{CO} = \frac{k_2 K_{CO2}\left[\varphi_{CO2}\varphi_{H2} - \varphi_{H2O}\,\varphi_{CO}/K_{p2}\right]}{\left(1 + K_{CO}\varphi_{CO} + K_{CO2}\varphi_{CO2}\right)\left[\varphi_{H2}^{1/2} + \left(K_{H2O}/K_{H2}^{1/2}\right)\varphi_{H2O}\right]}$$

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

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

CYCLE DESIGN

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

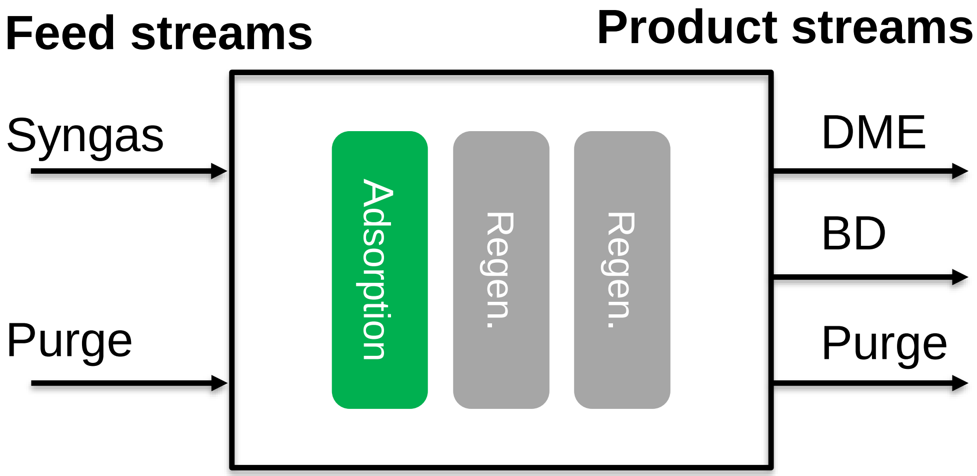


CYCLE DESIGN

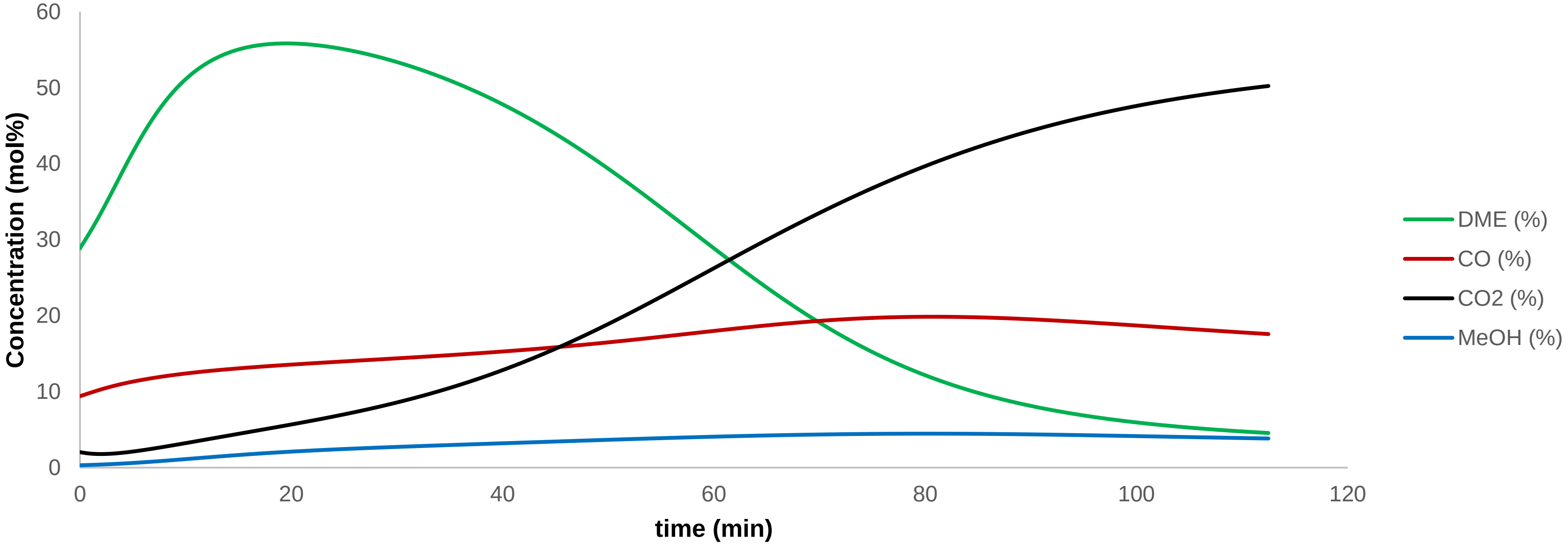
- **3 column** design for continuous operation

- 2 feed streams
  - Syngas
  - Purge gas

- 3 product streams
  - DME product
  - Blowdown product
  - Purge product

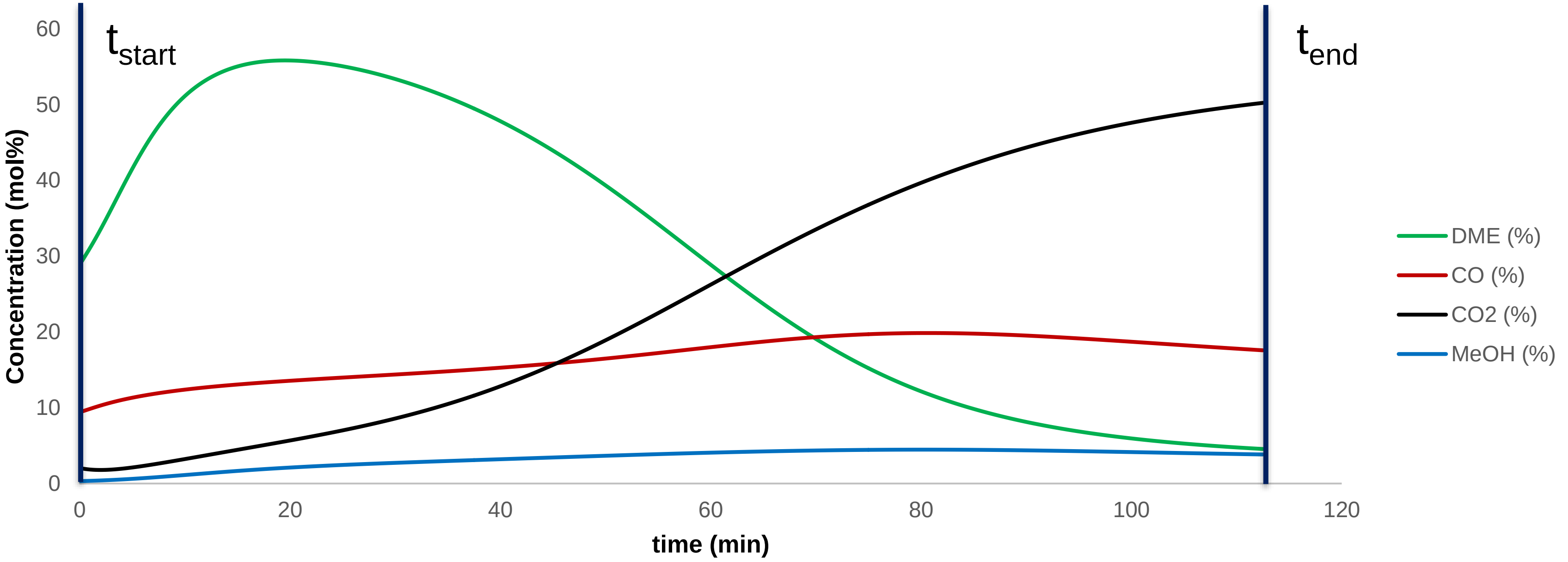


BASE CASE



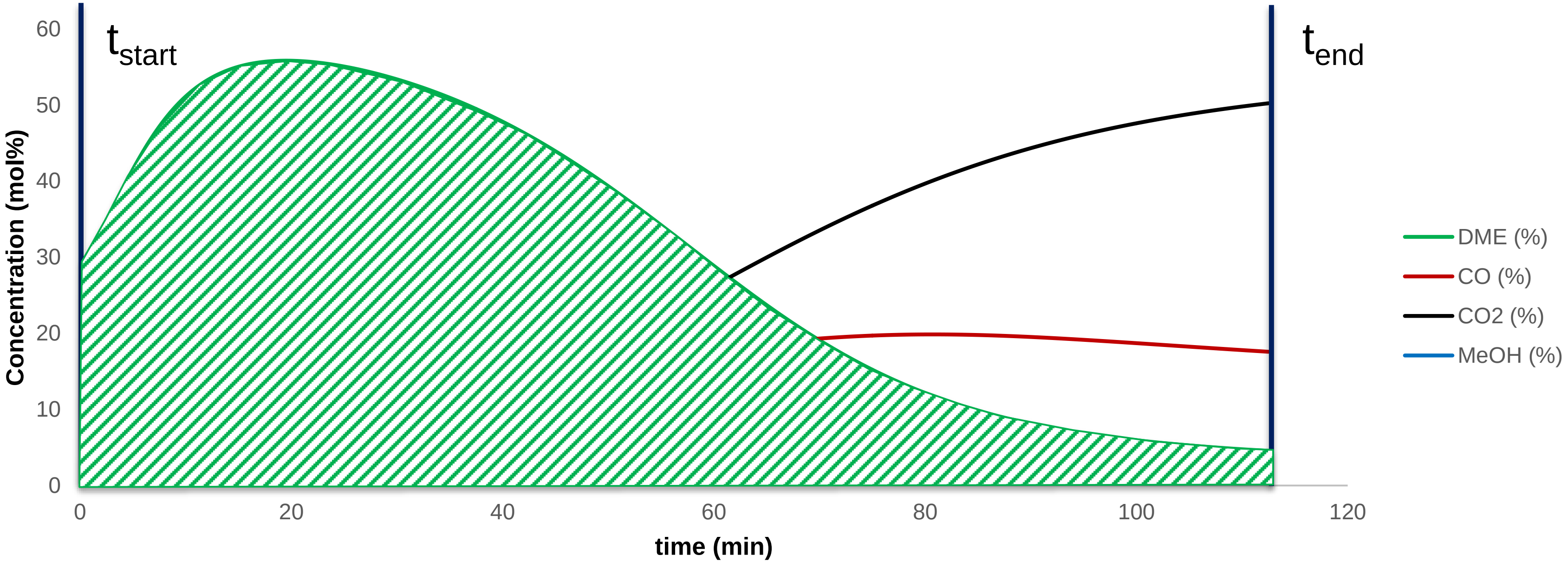
60
50
40
30
20
10
0
Concentration (mol%)
0
20
40
60
80
100
120
time (min)
DME (%)
CO (%)
CO2 (%)
MeOH (%)

BASE CASE



t_{start}
t_{end}
Concentration (mol%)
60
50
40
30
20
10
0
0
20
40
60
80
100
120
time (min)
DME (%)
CO (%)
CO2 (%)
MeOH (%)

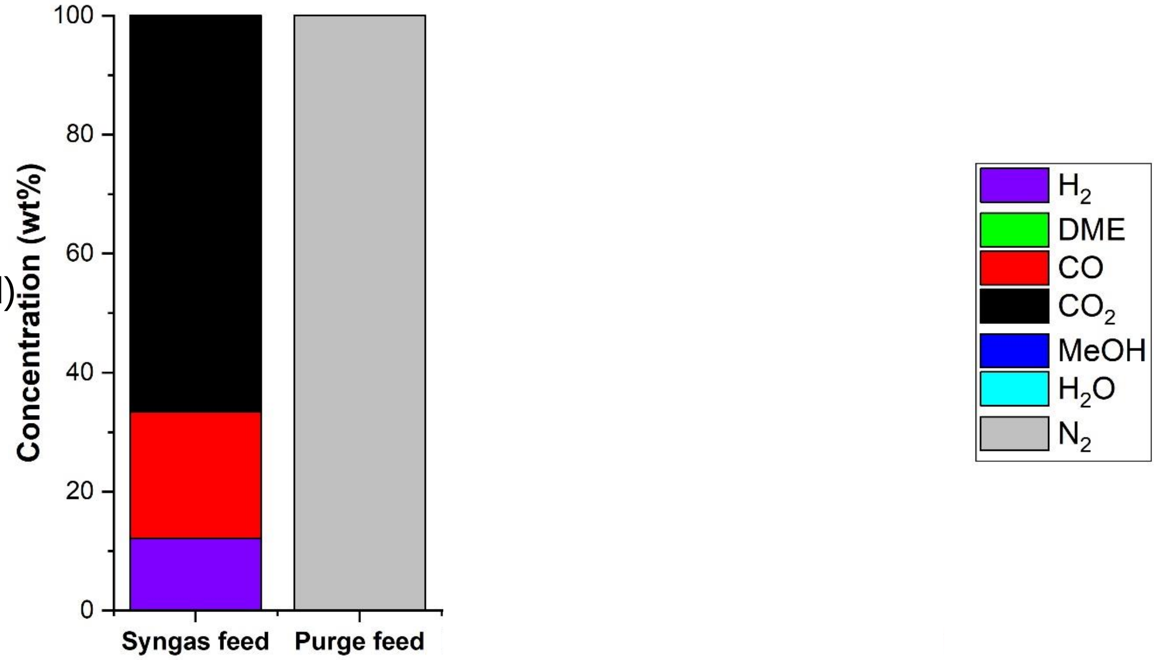
BASE CASE



t start
t end
Concentration (mol%)
60
50
40
30
20
10
0
0
20
40
60
80
100
120
time (min)
DME (%)
CO (%)
CO2 (%)
MeOH (%)

FEED & PRODUCT

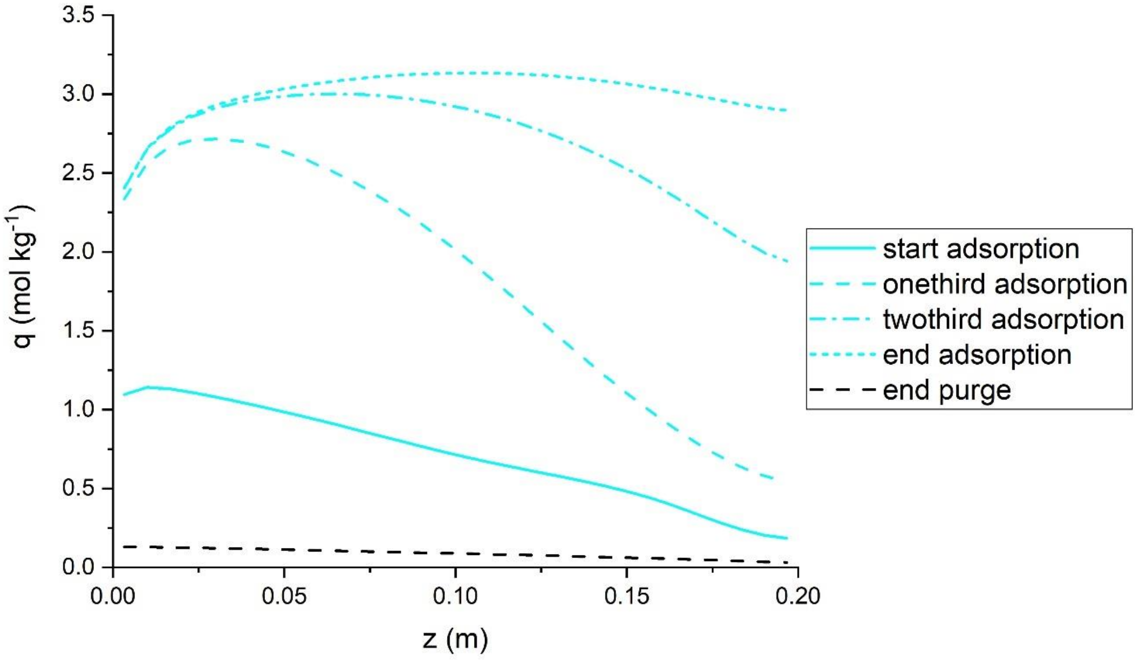
- Feed
  - CO_2:CO=2:1
  - M=2
- Product
  - 64% conversion (unoptimized)
  - Thermodynamically only 26%
- Purge product: N_2+H_2O
  - recycle



WORKING CAPACITY

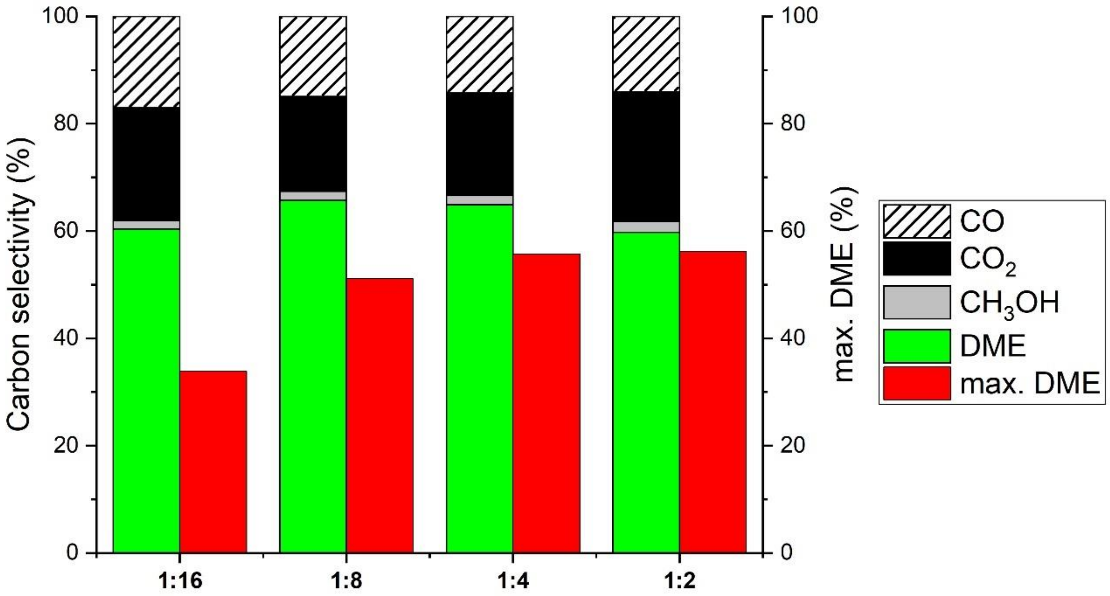
- Working capacity
  - adsorption
  - regeneration
- Determines conversion & yield
  - Limitation

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



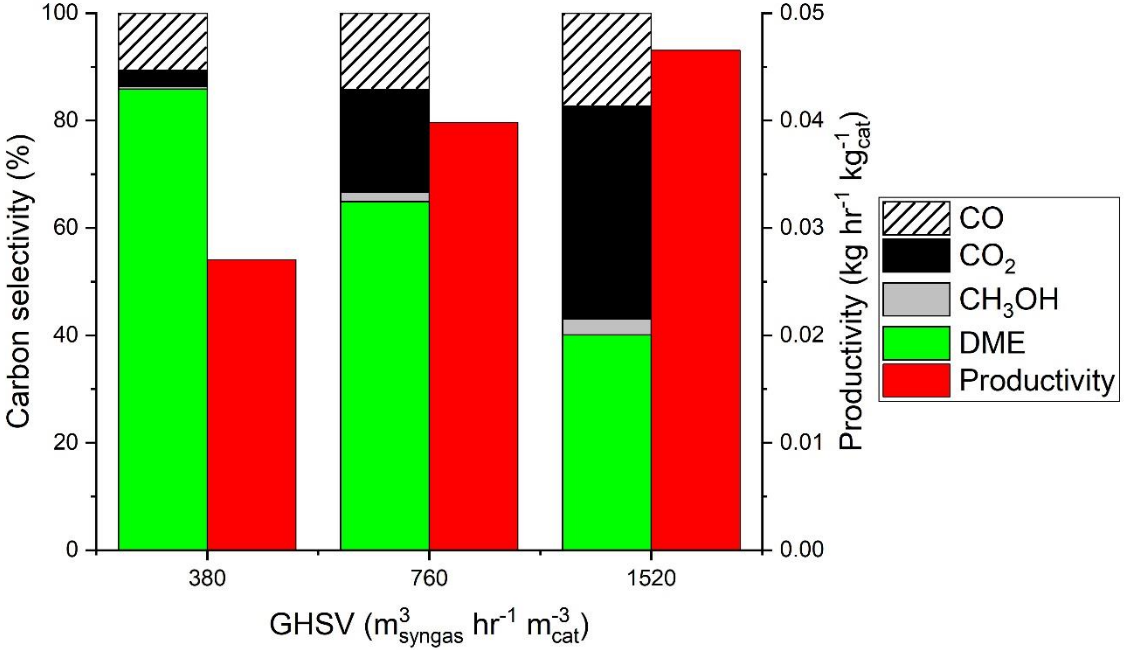
CATALYST VS. SORBENT

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



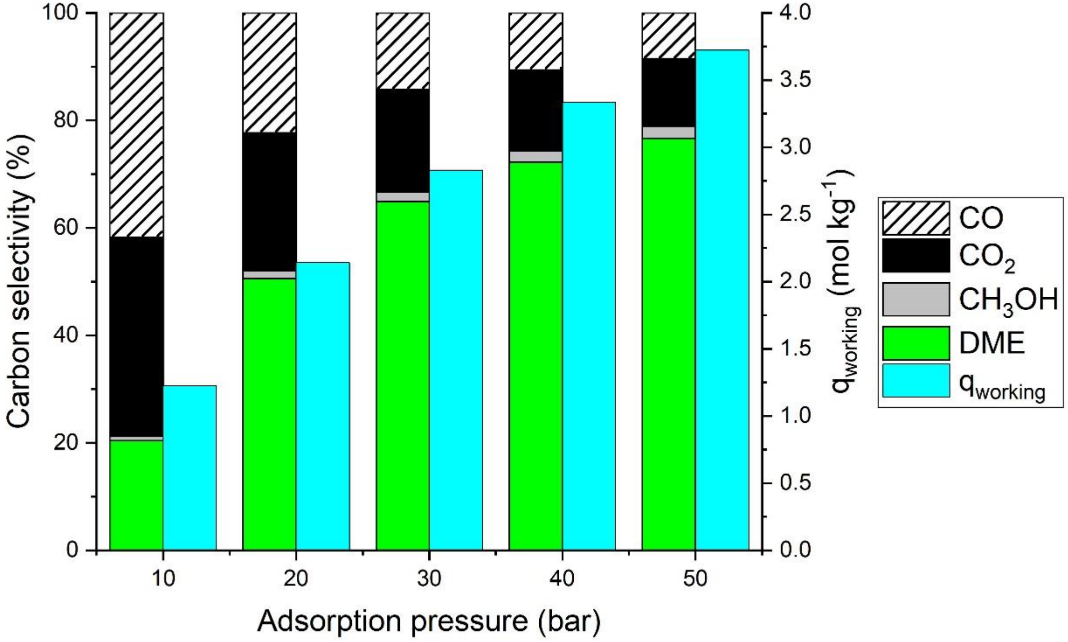
SELECTIVITY VS. PRODUCTIVITY

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



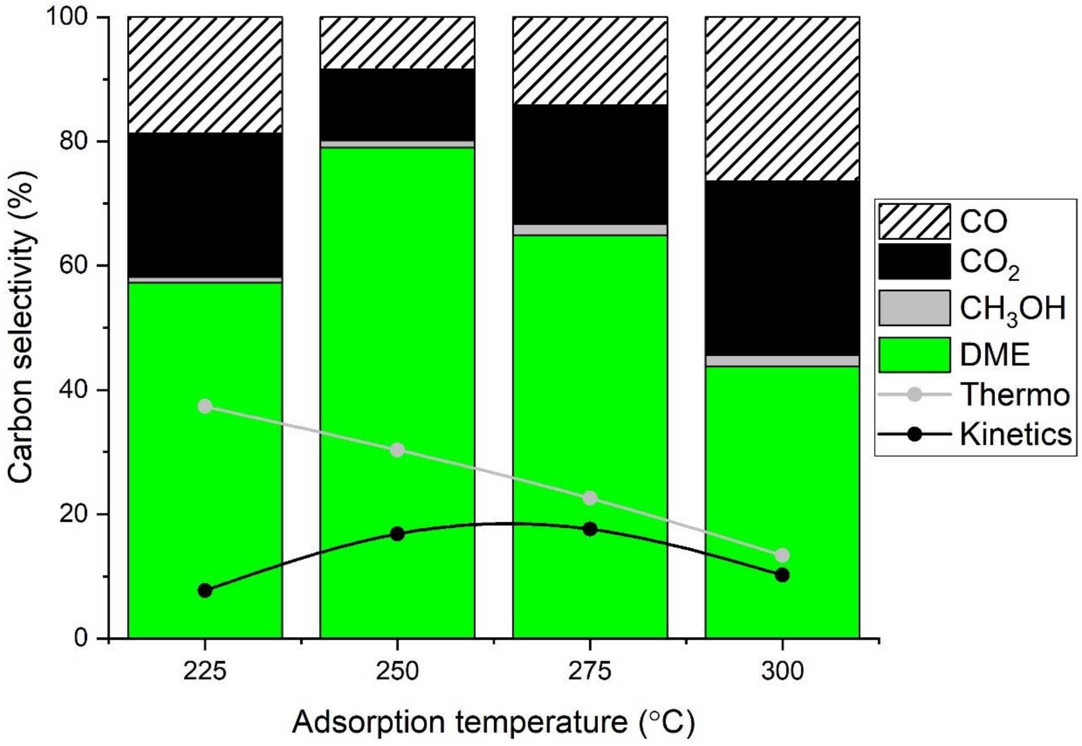
PRESSURE

- Pressure
  - Increased methanol synthesis
  - Increased working capacity
- Flowsheet optimisation



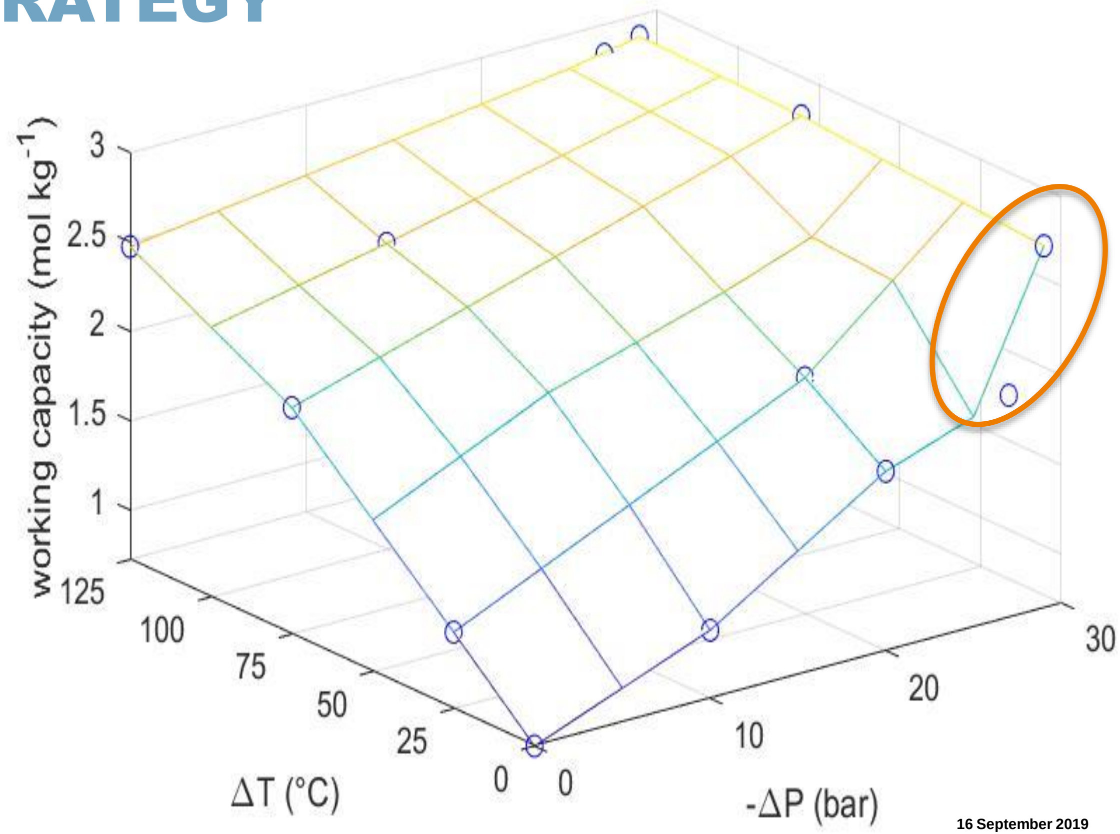
TEMPERATURE

- Temperature
  - Catalyst
    - Activity vs. Thermo
  - Adsorbent
    - Isotherm capacity



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 → direct CO_2 utilisation

  - 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

- Sorption enhanced DME synthesis (SEDMES):
  - Regeneration strategy
    - TSA vs PSA

  - Heat management
    - Adiabatic or non-adiabatic operation
    - Integration of temperature swing regeneration

  - Scale-up & system design

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THANK YOU FOR YOUR ATTENTION

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https://youtu.be/JEn39Zi_aCg

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