Catalyst activation in Sorption-Enhanced DME Synthesis

www.ecn.nl
P.O. Box 1
1755 ZG Petten
The Netherlands

Authors

S. Booneveld[1], J. van Kampen[1],
R. Hoogendoorn[1,2], S. Grecea[2], J. Boon[1]

Corresponding author: boon@ecn.nl

Introduction

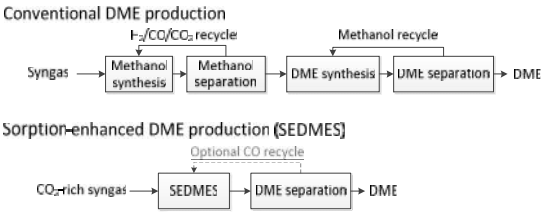
EU Horizon 2020 project FLEDGED combines flexible sorption-enhanced processes to produce dimethyl ether from biomass with an efficient and low cost process.

- DME: one of the most promising alternative fuels under consideration worldwide.
- Sorption-enhanced DME synthesis (SEDMES) is a novel process for the direct production of DME from synthesis gas.
- CO_2 could be utilised directly or via biomass conversion.
- Sustainable hydrogen production from renewable energy sources could be included, supporting Power-to-Product conversion.

Sorption-enhanced DME synthesis (SEDMES)

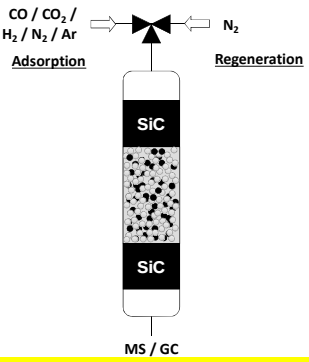
Methanol synthesis:	$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O$
Water-gas shift:	$CO + H_2O \rightleftharpoons H_2 + CO_2$
Methanol dehydration:	$2CH_3OH \rightleftharpoons CH_3OCH_3 + H_2O$

SEDMES: In situ H_2O removal by a solid adsorbent



SEDMES test

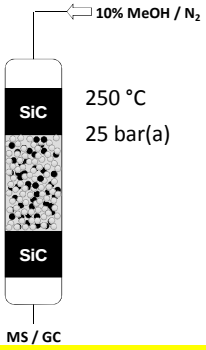
- Adsorption 275 °C & 25 bar(a)
- Regeneration 300 °C or 400 °C and 3 bar(a)
- 5 g $CuO/ZnO/Al_2O_3$ (CZA) catalyst & 21 gram zeolite LTA adsorbent, well mixed as sieve fractions (212-425 µm)
- Feed mix CO_2, CO, H_2 in N_2/Ar 90 ml_n min^{-1}
- M = $([H_2]-[CO_2])/([CO]+[CO_2])$ = 2



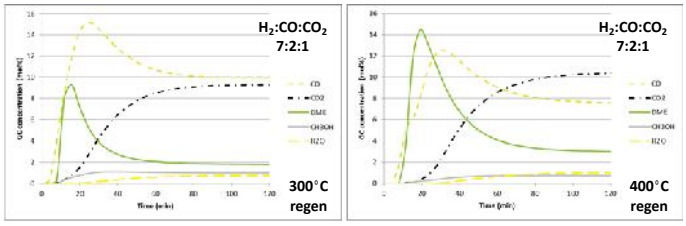
Methanol dehydration test

- 889 ml_n min^{-1} methanol/N_2 feed
- 5.26 g γ-Al_2O_3 catalyst sieve fraction (212-425 µm) in SiC

1. Methanol dehydration 250 °C
2. Exposure to 250 °C, 14 bar steam
3. Methanol dehydration 250-350-250 °C

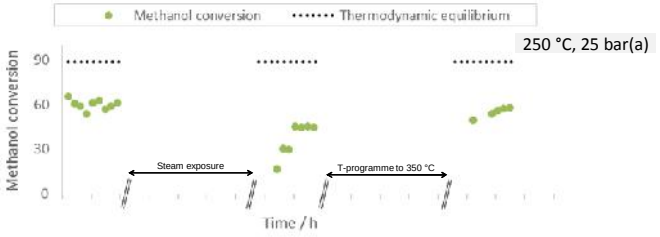


SEDMES and direct DME synthesis

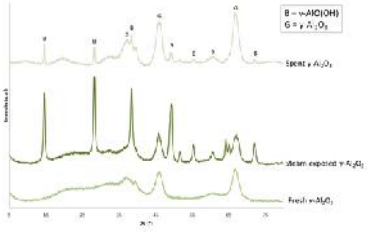


- CZA active for water-gas shift, methanol synthesis, dehydration
- Pre water breakthrough: high DME and CO, low CO_2 and methanol
- Post water breakthrough: low DME, high CO_2
- 400 °C regeneration temperature enhances water adsorption: increased breakthrough time and DME yield pre water breakthrough
- 400 °C also increases steady state DME yield: does the alumina dehydration catalyst activity increase by H_2O desorption at 400 °C?

Activation of alumina methanol dehydration catalyst



- Exposure to 14 bar steam converts γ-Al_2O_3 to γ-AlO(OH), reducing activity for methanol dehydration
- Activity for methanol dehydration largely restored in situ at 250 °C
- γ-AlO(OH) remains after testing at 350 °C without affecting activity



Conclusions

- CZA catalyst active for sorption-enhanced DME synthesis (SEDMES)
- SEDMES able to reach high DME yield pre water breakthrough
- Regeneration by temperature swing to 400 °C improves DME yield pre and post water breakthrough
- Adsorbent capacity increases with temperature swing to 400 °C
- After high steam exposure, γ-AlO(OH) remains yet catalyst activity is already largely restored for methanol dehydration at 250 °C

Acknowledgements

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

[1] Sustainable Process Technology, ECN, P.O. Box 1, 1755 ZG Petten, The Netherlands.

[2] Van 't Hoff Institute for Molecular Sciences, UvA, P.O. Box 94157, 1090GD Amsterdam, The Netherlands.