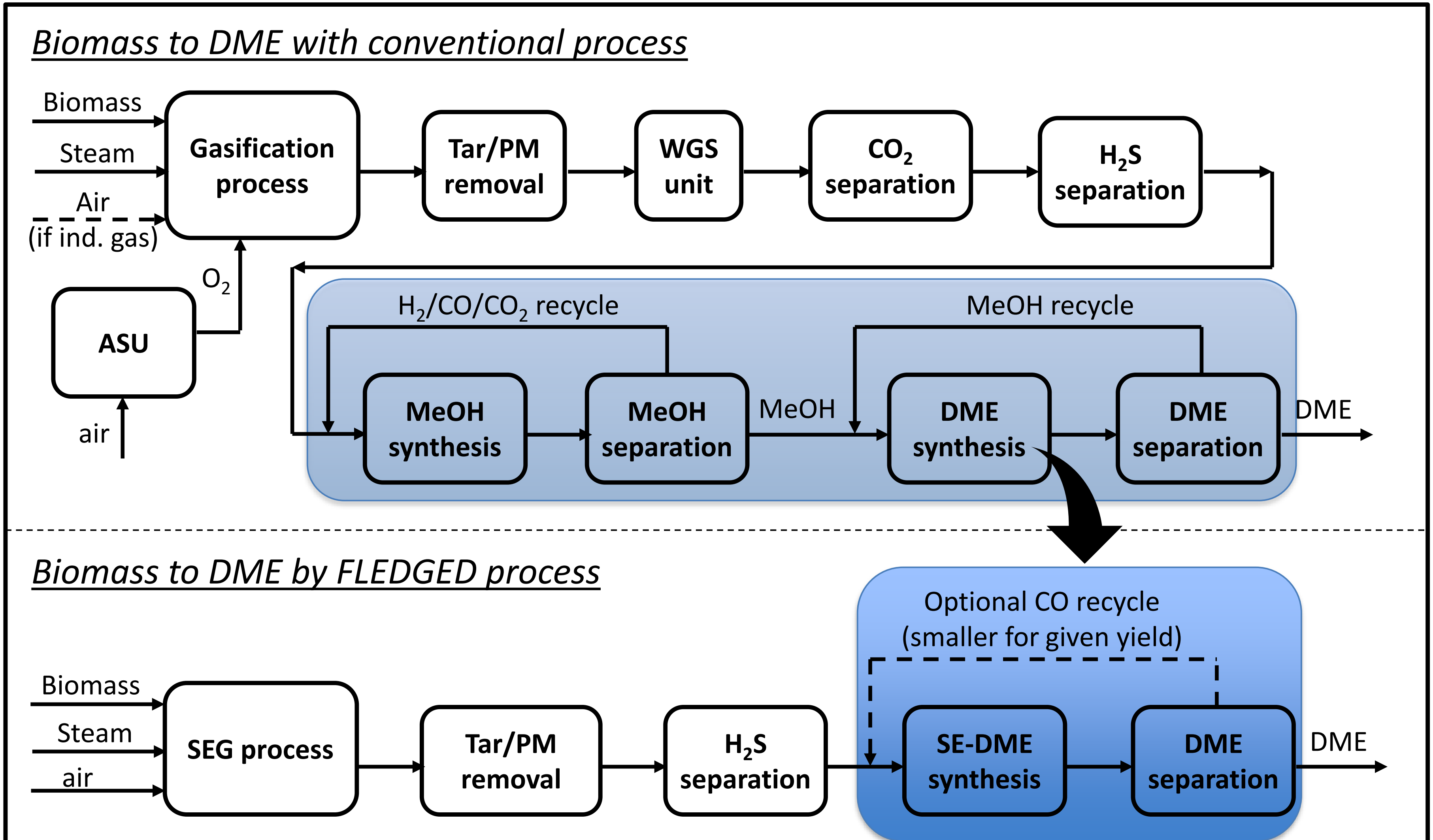
Sorption-Enhanced Dimethyl Ether Synthesis (SEDMES)

Process intensification: Sorption-Enhanced DME Synthesis



Process intensification: Direct DME Synthesis

Feed gas

CO and CO_2 with stoichiometric H_2 ($M = \frac{[H_2]-[CO_2]}{[CO]+[CO_2]} = 2$)

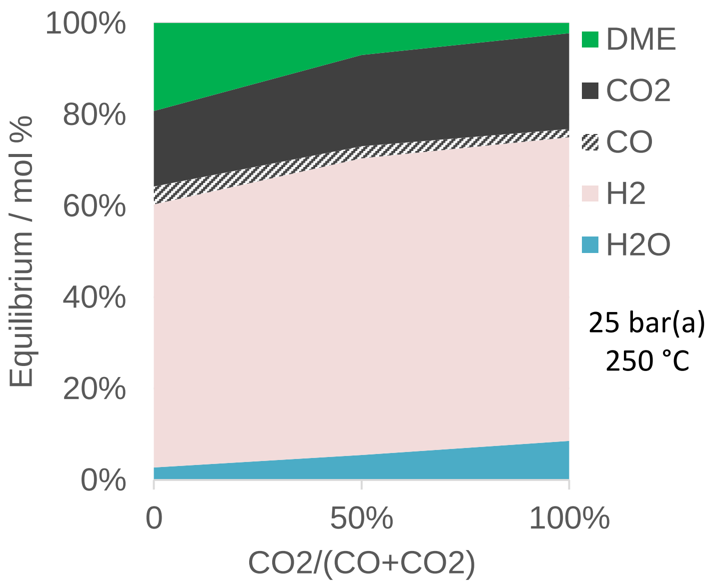
Direct DME synthesis equilibrium

$$2CO + 4H_2 \rightleftharpoons CH_3OCH_3 + H_2O \quad (1)$$

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

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \quad (3)$$

- Poor conversion per pass
- High CO_2 concentration product ($CO + H_2O \rightarrow CO_2 + H_2$)



Process intensification: Sorption-Enhanced DME Synthesis

Feed gas

CO and CO_2 with stoichiometric H_2 ($M = \frac{[H_2]-[CO_2]}{[CO]+[CO_2]} = 2$)

Sorption-enhanced DME synthesis

$2CO + 4H_2 \rightarrow CH_3OCH_3 + H_2O$ (1)

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

$CO_2 + H_2 \rightarrow CO + H_2O$ (3)

- High conversion per pass
- High CO concentration product ($CO_2 + H_2 \rightarrow CO + H_2O$)

Henry Louis Le Chatelier (1850 – 1936)

Process intensification: Sorption-Enhanced DME Synthesis

Feed gas

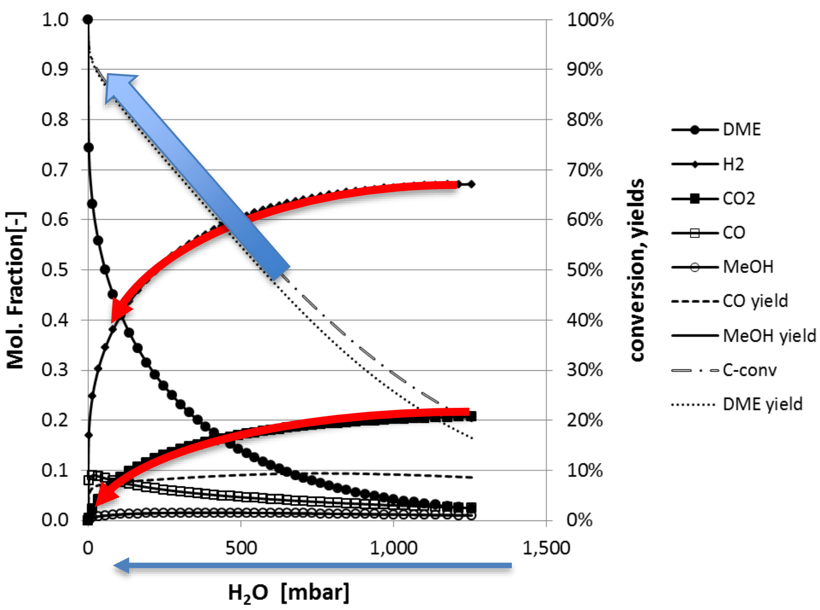
CO and CO_2 with stoichiometric H_2 ($M = \frac{[H_2]-[CO_2]}{[CO]+[CO_2]} = 2$)

Sorption-enhanced DME synthesis

$2CO + 4H_2 \rightarrow CH_3OCH_3 + H_2O$

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

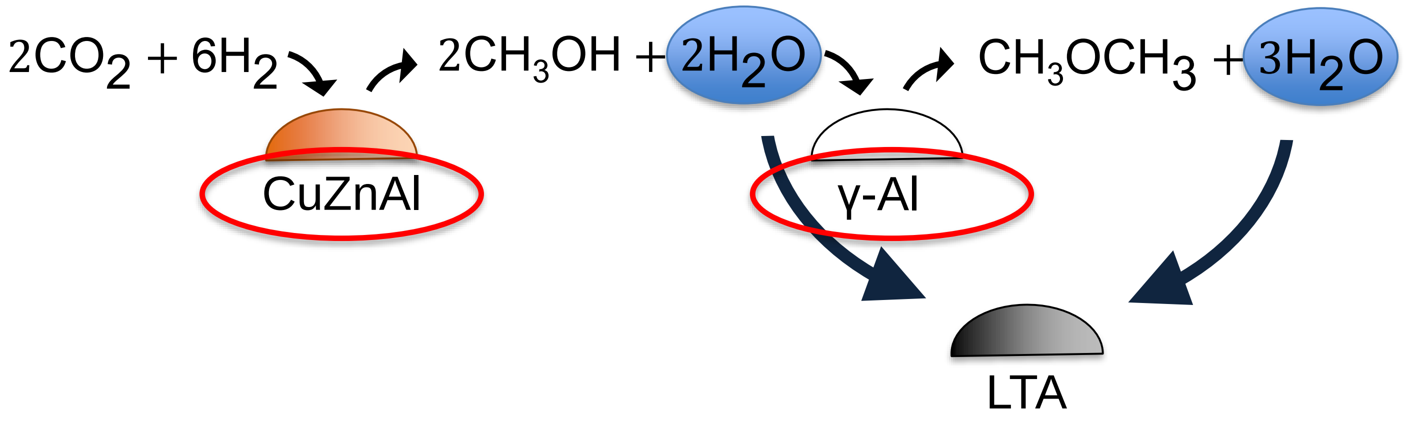
$CO_2 + H_2 \rightarrow CO + H_2O$



- High conversion per pass
- High CO concentration product ($CO_2 + H_2 \rightarrow CO + H_2O$)

SEDMES

In sorption-enhanced DME synthesis, SEDMES, the equilibrium of direct DME synthesis is shifted by using a physical adsorbent



Catalyst development

- **Syngas → Methanol (CSIC made $Cu/ZnO/Al_2O_3$, *CZA*)**
  - *Effect of CuO loading: > X_{CO+CO_2} at higher CuO loading (62 – 58 – 52 – 46 – 39 – 33 wt.%)*
  - *Effect of the syngas composition: > X_{CO+CO_2} at lower CO_2 content (CO_2/CO= 1.9 and 1)*
  - *Effect of promoters: no promotion effect of Zr, Ga or Pd*
  - *Comparison with commercial catalyst Katalco™51-8: novel catalyst 62 wt.% CuO loading reached similar TOF*

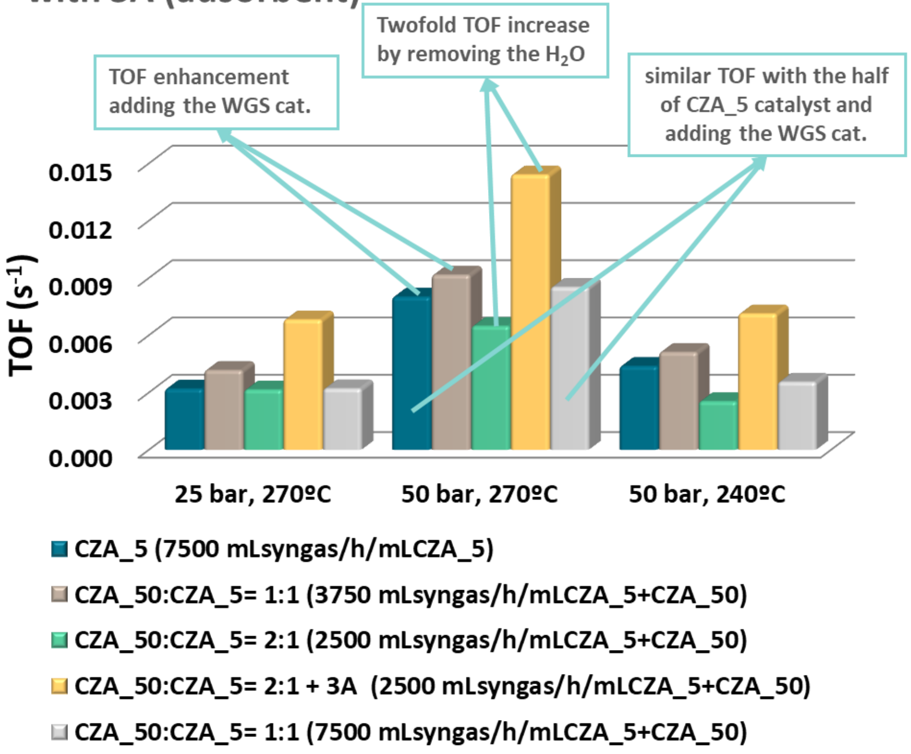
- **Methanol → DME (supported heteropolyacids, $H_4SiW_{12}O_{40}$ or $H_3PW_{12}O_{40}$)**
  - Effect of reaction conditions : *> X_{MeOH} favoured at 180<T<240 ºC and P> 24 bar*
  - Effect of HPA nature: : *> X_{MeOH} with HSiW*
  - Effect of the support: *X_{MeOH}: SiO_2>TiO_2>ZrO_2*
  - Comparison with commercial catalysts: γ-Al_2O_3 and HZSM-5
    - HZSM-5: *not selective for DME*
    - γ-Al_2O_3: : *X_{MeOH} with HSiW/SiO_2 or HSiW/TiO_2 thrice that with γ-Al_2O_3*

- **Characterization:**

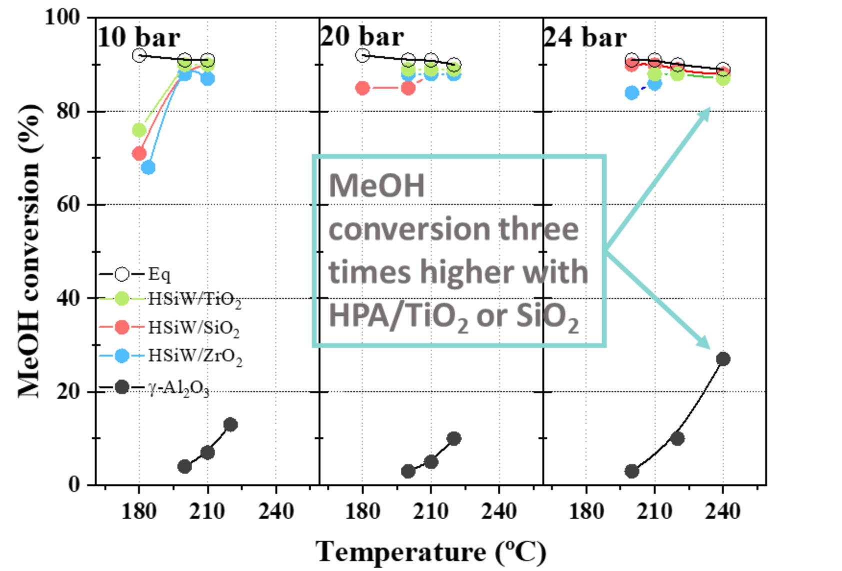
XRD, XPS, N_2 adsorption-desorption isotherms, H_2-TPR, H_2-N_2 and Air-TGA, SEM/EDX, TEM-STEM, NH_3-TPD, N_2O-Chemisorption, ICP-OES, NMR and Raman spectroscopy, at the ICP-CSIC. Some of the $Cu/ZnO/Al_2O_3$ catalysts were analysed by X-ray Absorption Spectroscopy at the ESFR synchrotron facilities in Grenoble (France)

Methanol synthesis & dehydration catalysis

- **Methanol productivity enhancement: Double beds WGS (CZA_50) & Methanol (CZA_5) catalysts with 3A (adsorbent)**



- **Low Temperature DME production from MeOH with novel catalysts**



Stable methanol conversions (maintained at least for 6 h) for the HSiW/X catalysts and γ-Al_2O_3 at different conditions of P and T

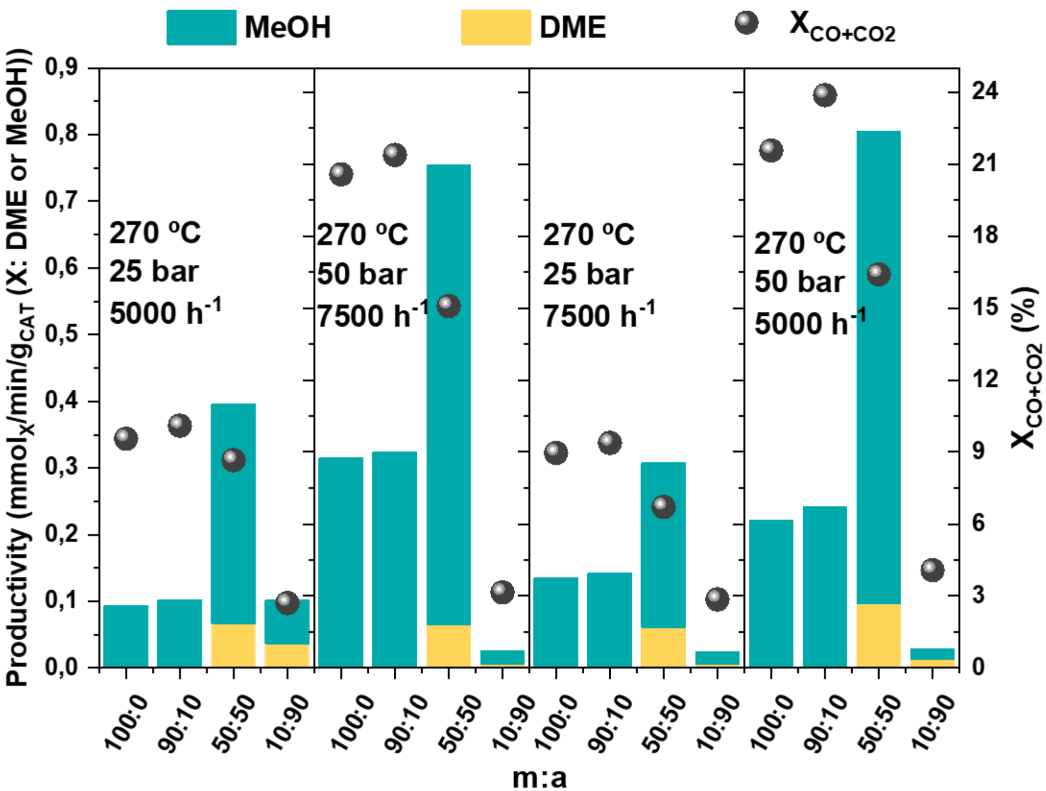
Direct DME synthesis catalysis

- **Direct synthesis of DME from syngas:**

catalytic bed optimization CZA:γ-Al_2O_3

CZA_comm	γ-Al_2O_3	*m:a (CZA_comm:γ-Al_2O_3)*
90 %	10 %	*90:10*
50 %	50 %	*50:50*
10 %	90 %	*10:90*

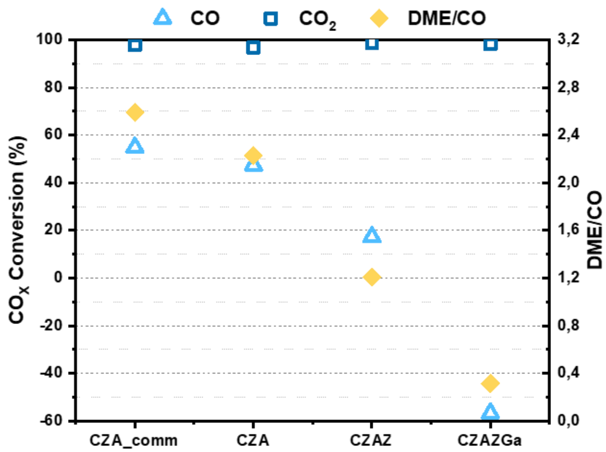
- *The highest DME productivity was obtained with the m:a= 50:50 at 270 ºC, 50 bar and 5000 h^{-1}*
- *Stability test during 270 h: the CO conversion decreased during the TOS, but the CO_2 conversion remains at 10%*
- *The highest DME selectivity obtained with the m:a = 10:90*

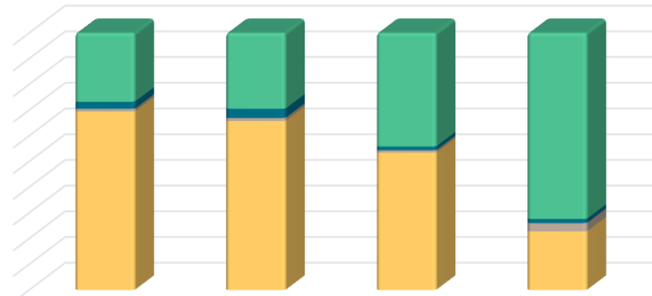


Sorption-enhanced DME synthesis catalysis

- Sorption enhanced DME synthesis from syngas:

Catalytic bed CZA:γ-Al_2O_3:3A





	CZA_comm	CZA_5	CZAZ	CZAZGa
% CO	26.8	29.5	44.2	72.4
% CO2	2.7	3.6	1.4	1.6
% MeOH	1.0	1.2	0.9	3.3
% DME	69.5	65.7	53.5	22.8

$(1)\ CO + 2H_2 \leftrightarrow CH_3OH$

$(2)\ CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O$

$(3)\ CO + H_2O \leftrightarrow CO_2 + H_2$

$(4)\ 2CH_3OH \leftrightarrow CH_3OCH_3 + H_2O$

Removing H_2O results in high CO_2 conversion and DME production

Very high DME production

Low CO_2 in products

↓

Easier separation DME/CO_2 downstream

Reverse Water Gas Shift Catalyst

$(-3)\ CO_2 + H_2 \leftrightarrow CO + H_2O$

Highest CO production

Highest non converted CH_3OH

Lowest DME production

275 ºC; 25 bar; 1080 h^{-1}; CO_2/CO=2; CO/CO_2/H_2= 9/18/73 (v/v)

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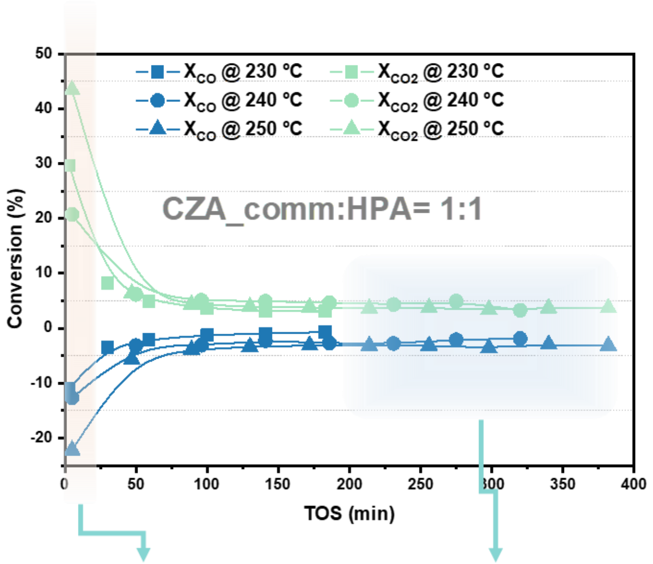
Sorption-enhanced DME synthesis catalysis

- **Sorption enhanced DME synthesis from syngas:**

catalytic bed CZA:γ-HWSi/TiO_2:3A

230-240-250 ºC; 25 bar; 5000 h^{-1}; CO_2/CO=1.9; CO/CO_2/H_2= 9/18/73 (v/v)



250 ºC

% DME: 40

% CH_3OH: 49

250 ºC

% DME: 26

% CH_3OH: 71

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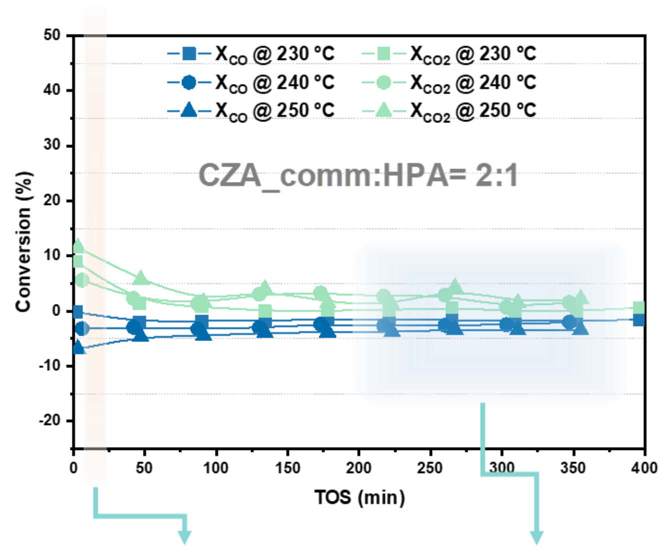


250 ºC

% DME: 7

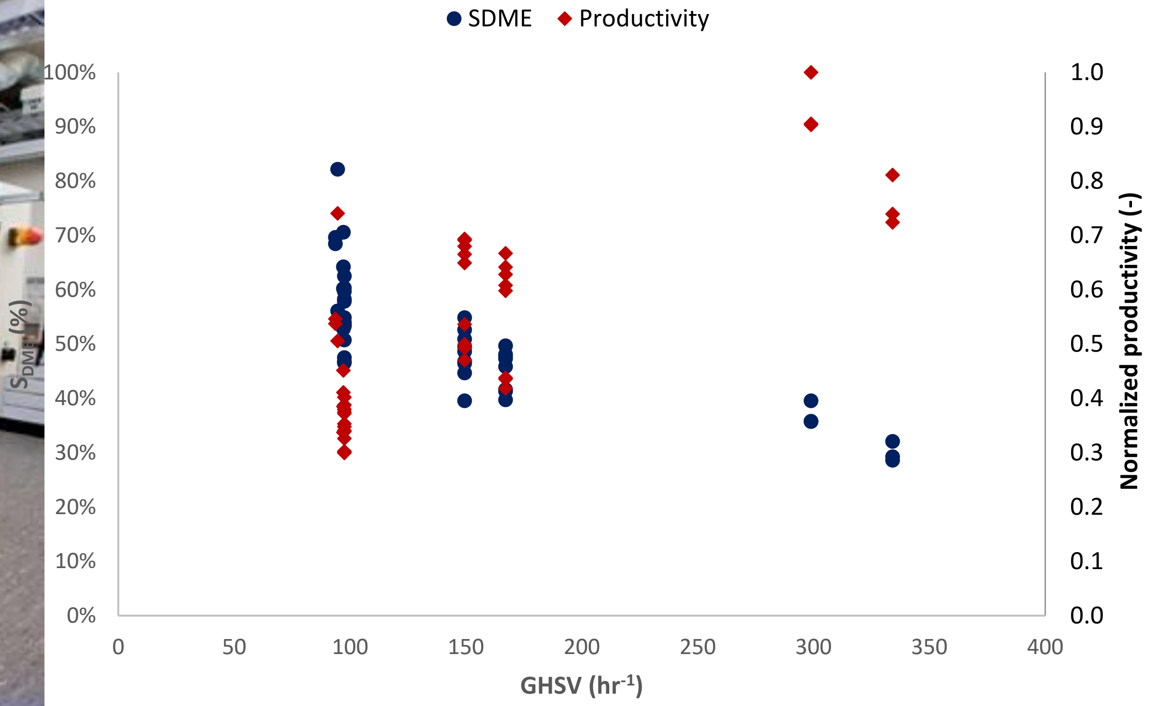
% CH_3OH: 30

250 ºC

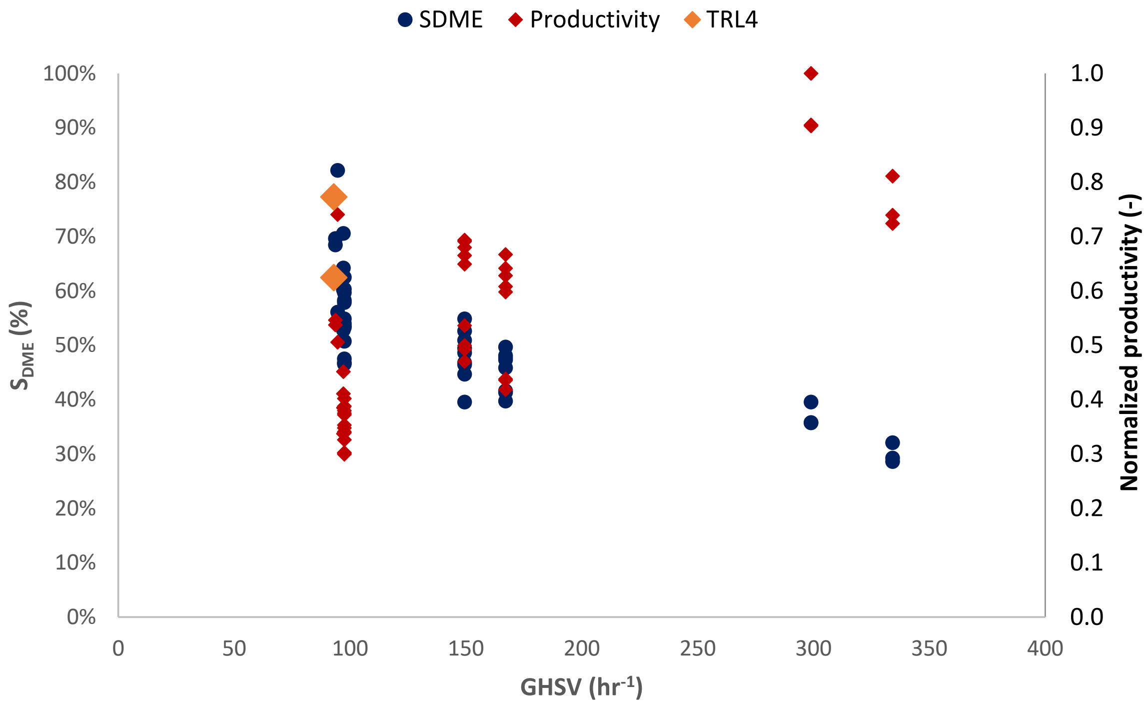
% DME: 7

% CH_3OH: 86

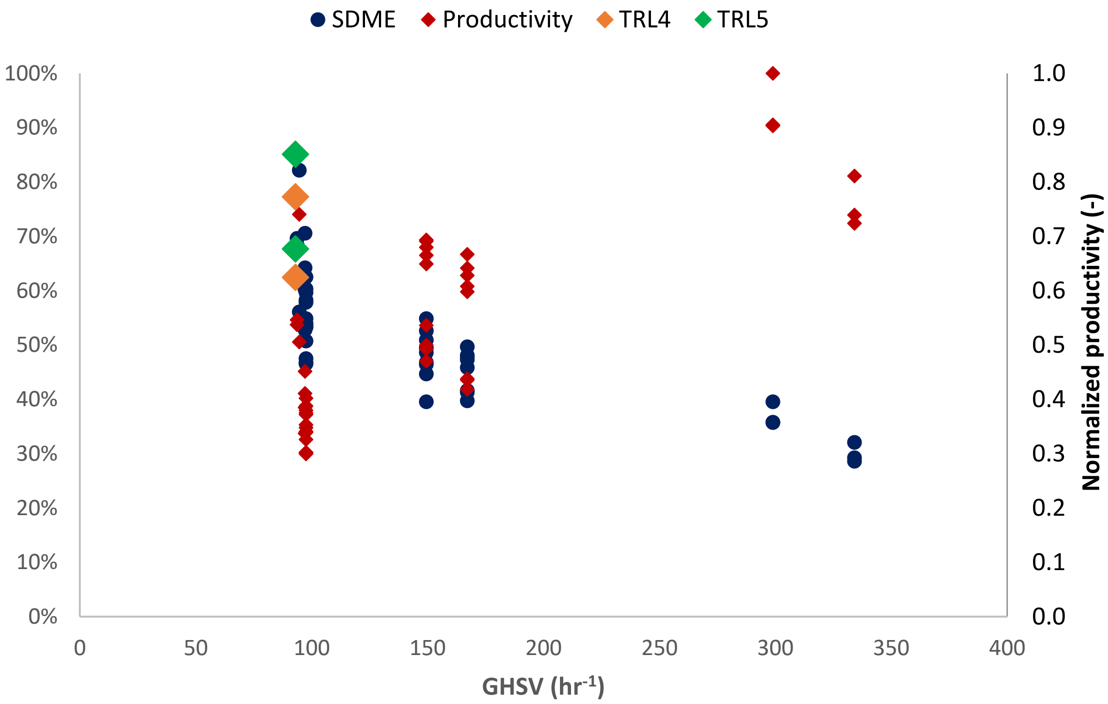
SEDMES: Experimental validation



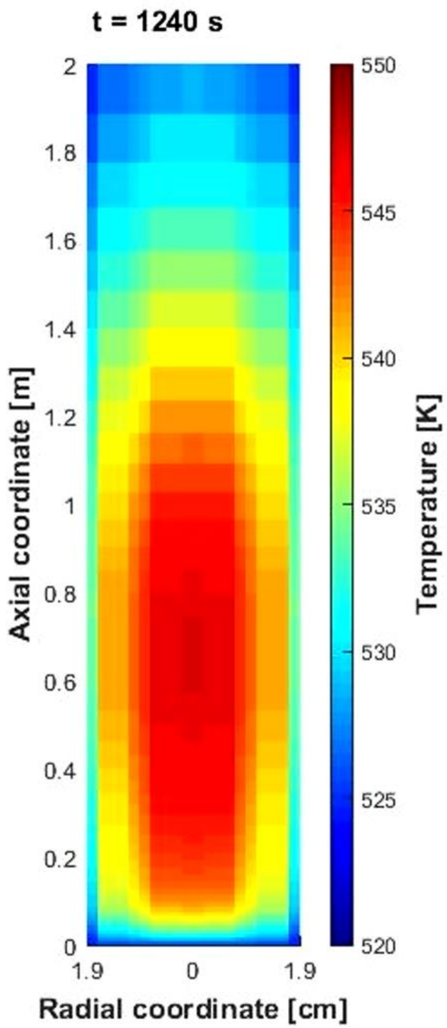
SEDMES: Experimental validation



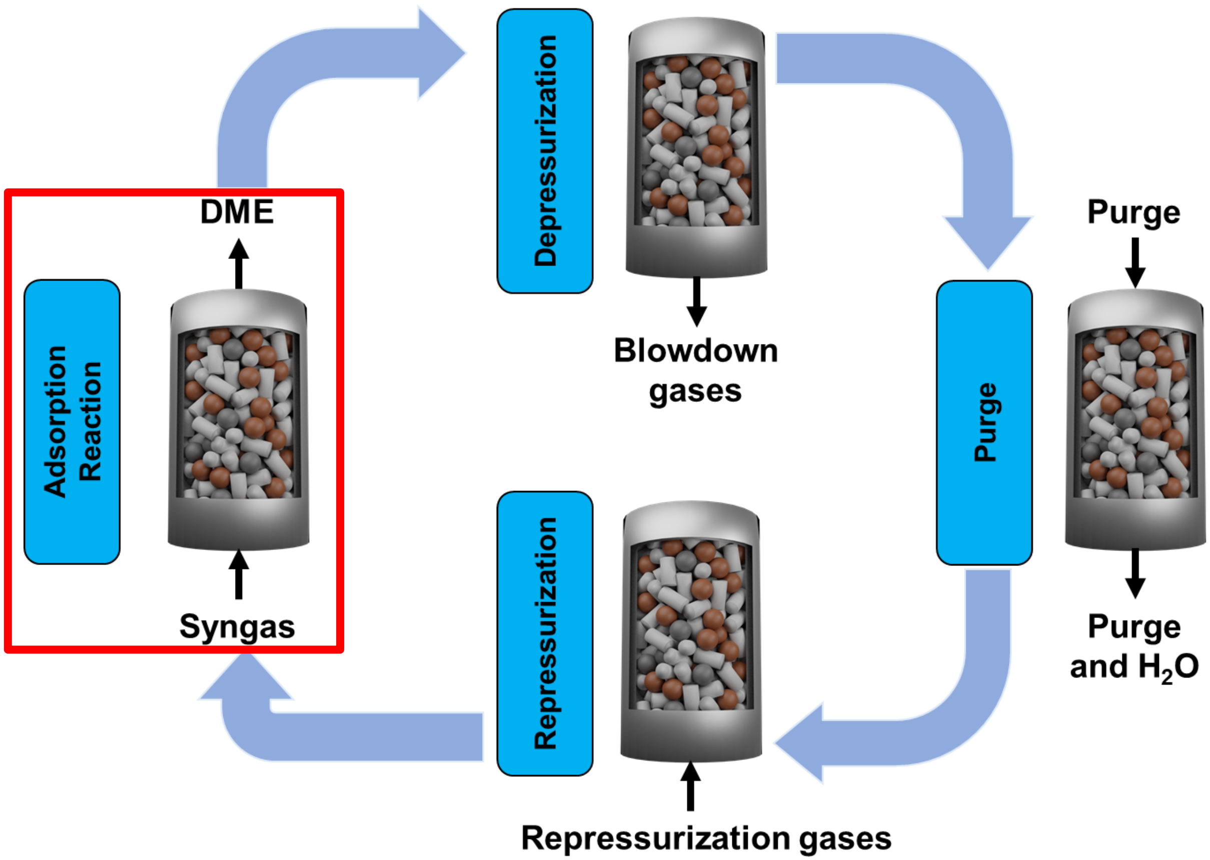
SEDMES: Experimental validation



SEDMES: 2D reactor modelling



Pressure Swing Adsorption (PSA) cycle



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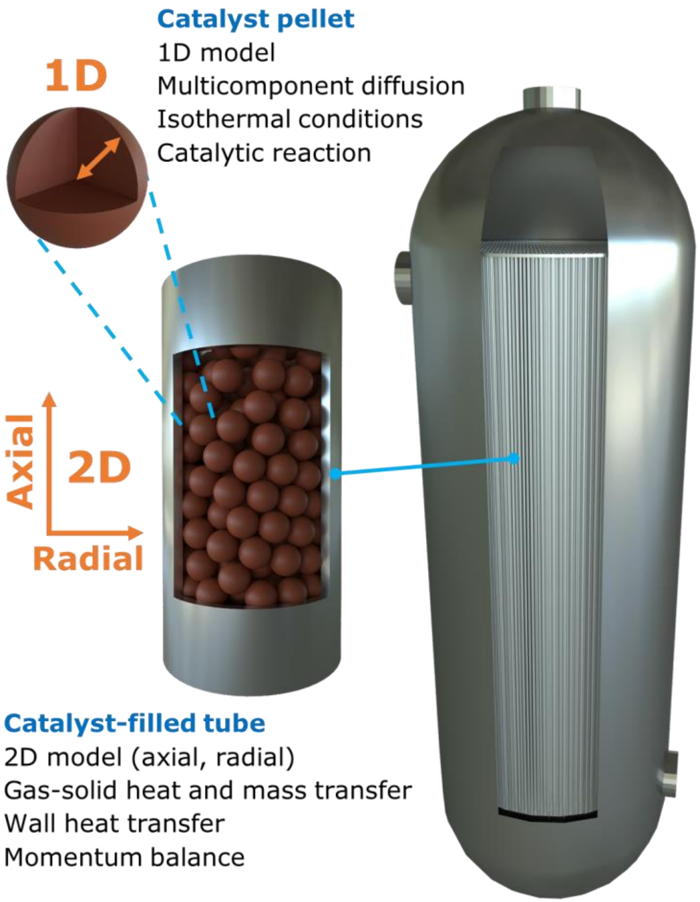
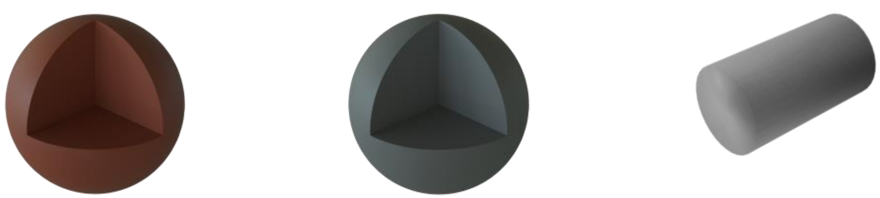
Reactor model



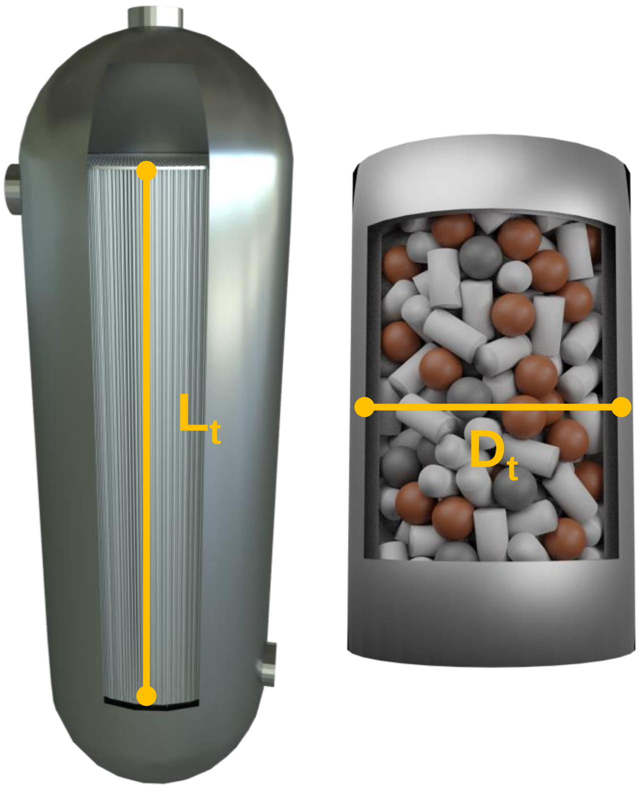
SEDMES reactor:

- **Multitubular fixed bed reactor externally cooled**
- **Dynamic conditions**
- **2D single tube heterogeneous model**
- **1D catalyst pellet model**
- **Linear Driving Force for adsorbent pellet**



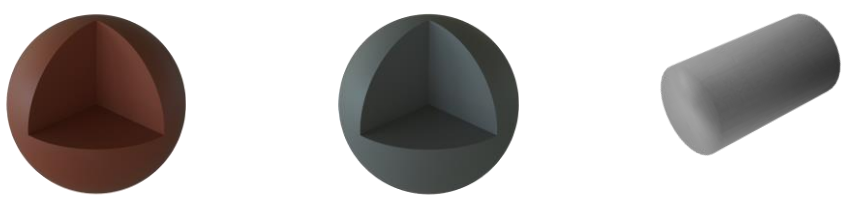
$Cu/ZnO/Al_2O_3$ **γ-Al_2O_3** **LTA zeolite**

SEDMES reactor analysis and design



$$\alpha = \frac{CO}{CO + CO_2}$$

$$M = \frac{H_2 - CO_2}{CO + CO_2}$$



Cu/ZnO/Al_2O_3 γ-Al_2O_3 LTA zeolite

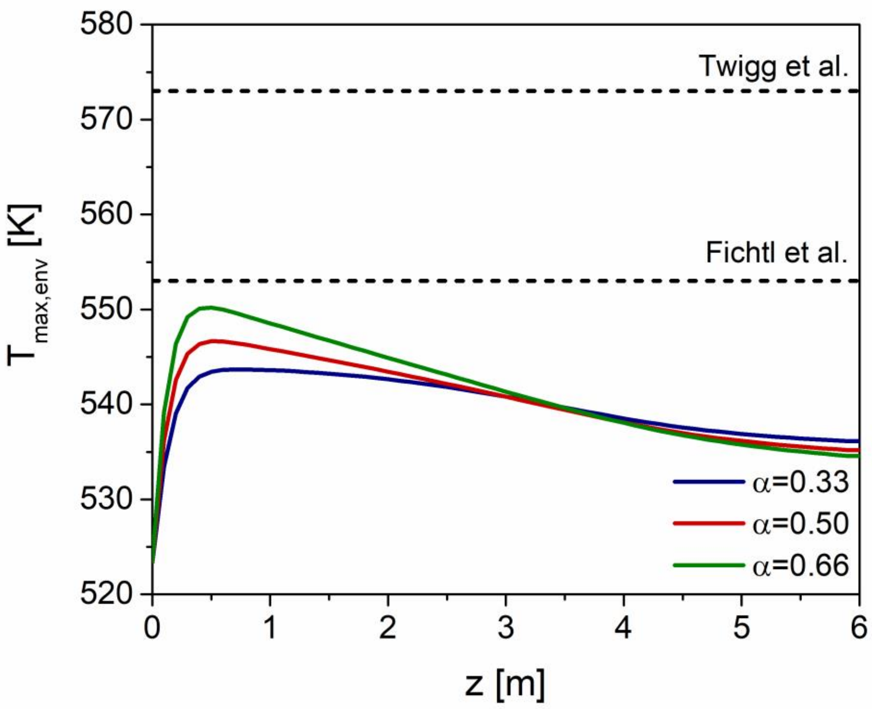
Input parameters

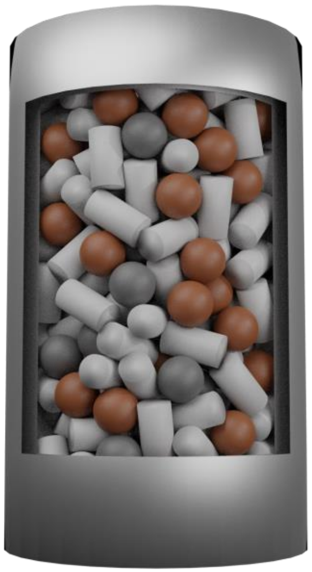
T_{inlet}	523 K
T_{cool}	523 K
P_{inlet}	25 bar
GHSV	140 h^{-1}
Ads:Cat.	4 : 1 w/w
CZA:γ-Al_2O_3	1 : 1 w/w
L_t	6 m
M	2

Analyzed parameters

α	0.33-0.66
D_t	25.6-46.6 mm

SEDMES reactor: effect of $\alpha=CO/CO_x$ on thermal stresses





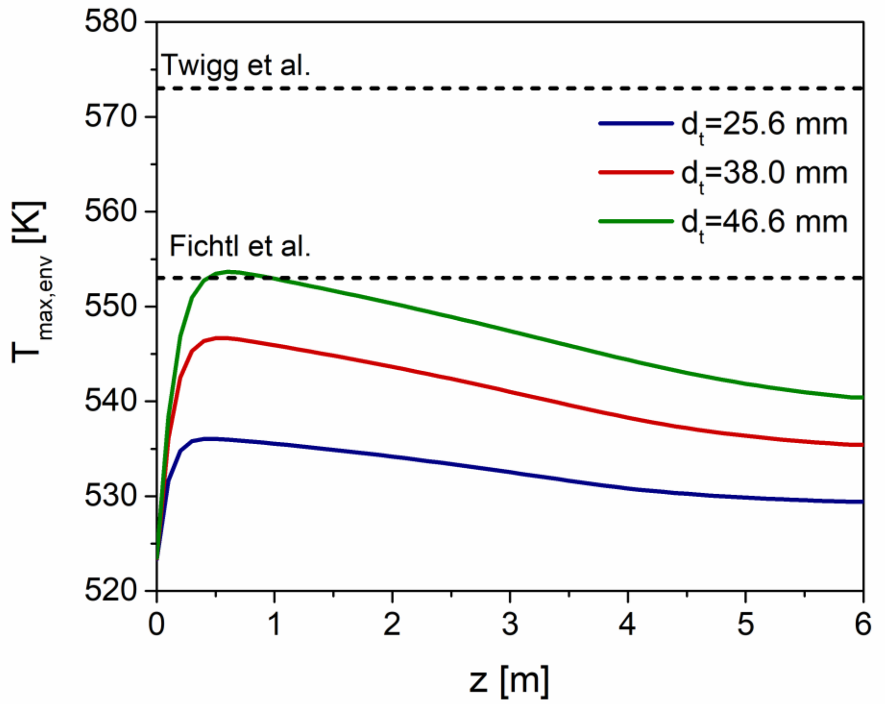
Ads./Cat. = 4/1 w/w

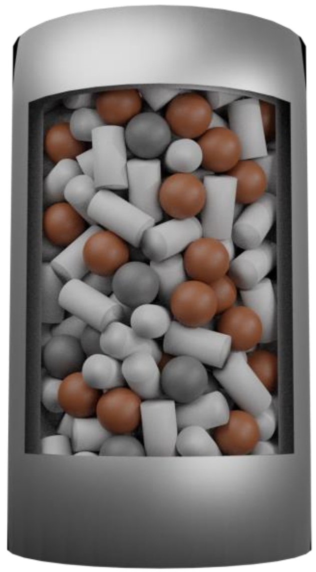
M. V. Twigg et al., Appl. Catal. A Gen. 212 (2001) 161–174.
M.B. Fichtl et al, Appl. Catal. A Gen. 502 (2015) 262–270.

$$2\ CO + 4\ H_2 \leftrightarrow CH_3OCH_3 + H_2O \downarrow_{ads} \qquad \Delta H_r^0 = -250.0\ \text{kJ/mol}_{DME}$$

$$2\ CO_2 + 6\ H_2 \leftrightarrow CH_3OCH_3 + 3\ H_2O \downarrow_{ads} \qquad \Delta H_r^0 = -259.7\ \text{kJ/mol}_{DME}$$

SEDMES reactor: effect of the tube diameter on thermal stresses





Ads./Cat. = 4/1 w/w

S. Guffanti et al., NGCS12, (2019), San Antonio (Texas – USA). → **25.6 mm**

$$2\ CO + 4\ H_2 \leftrightarrow\ CH_3OCH_3 + H_2O \downarrow_{ads} \qquad \Delta H_r^0 = -250.0\ kJ/mol_{DME}$$

$$2\ CO_2 + 6\ H_2 \leftrightarrow\ CH_3OCH_3 + 3\ H_2O \downarrow_{ads} \qquad \Delta H_r^0 = -259.7\ kJ/mol_{DME}$$

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Sub conclusions

- **A SEDMES 2D reactor model has been developed and validated against bench scale experimental data (TRL4).**

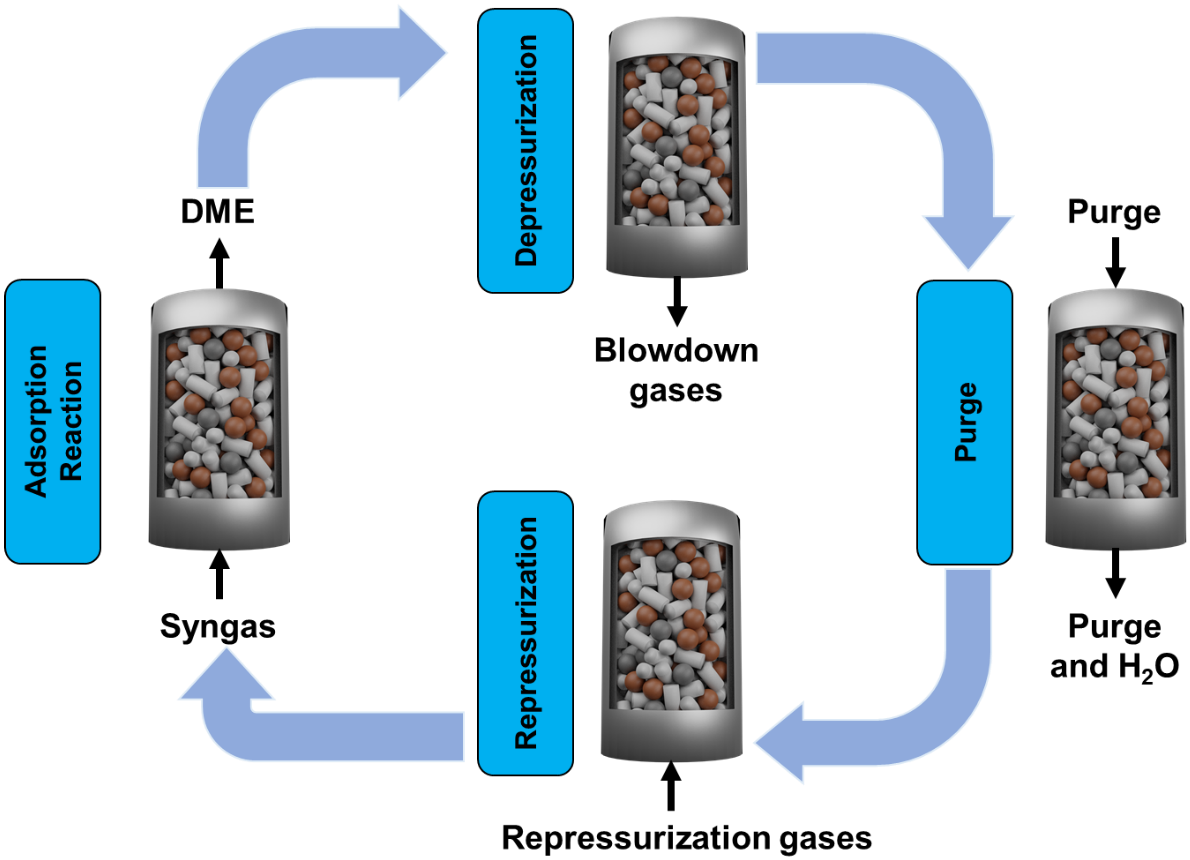
- **Model results confirm high DME yields for SEDMES, independently of syngas CO/CO_x ratio, which is particularly advantageous at high CO_2 content.**

- **The thermal dilution of catalyst in adsorbent material (1/4 w/w) allows to operate with larger tube diameters with respect to the conventional synthesis.**

SEDMES: Cycle design

- SEDMES
- Cyclic reactor model
- Validated at TRL4

Pressure Swing Adsorption (PSA) cycle



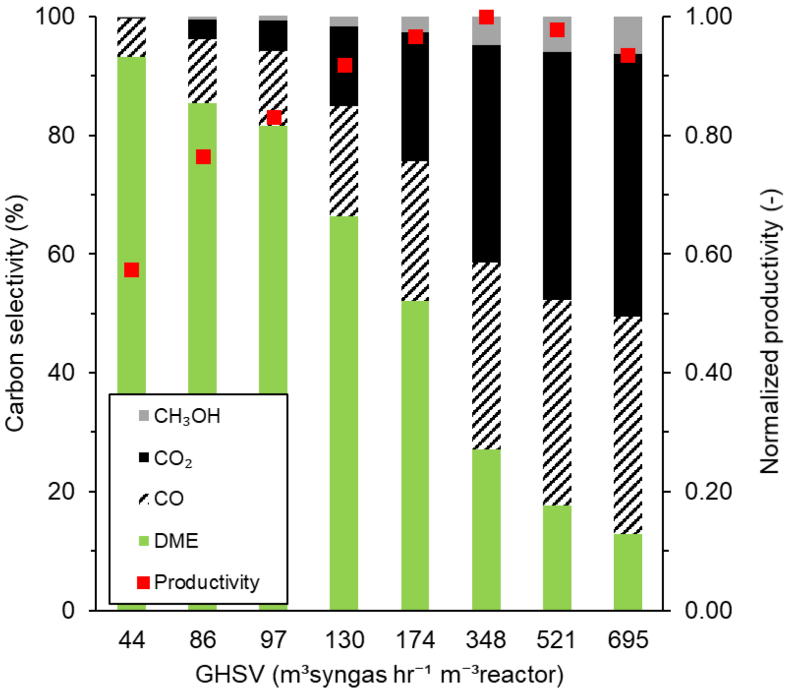
SEDMES: Cycle design

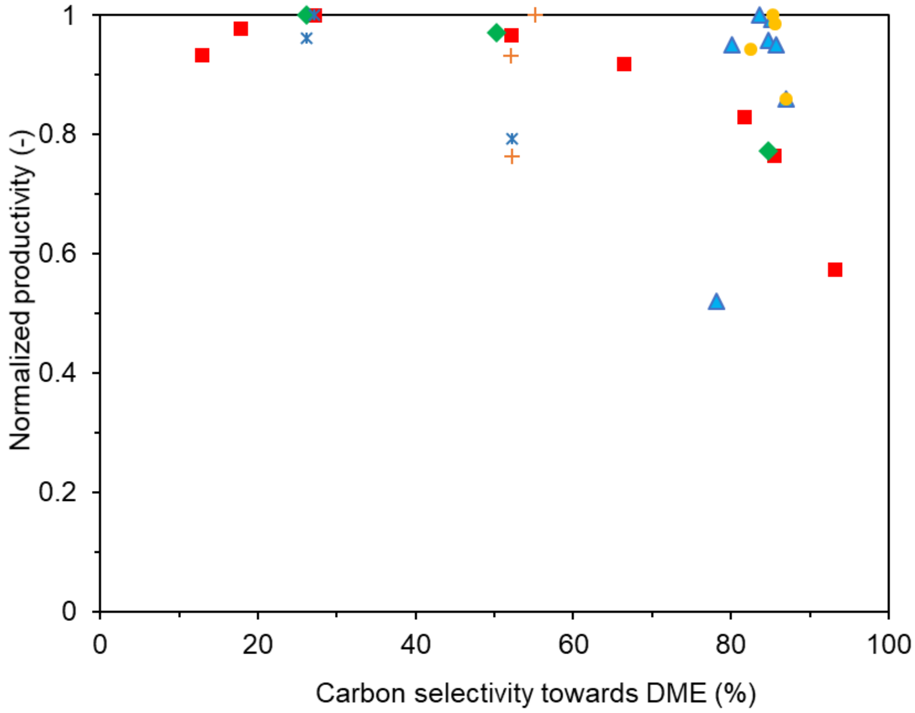
Column 1	ADS	PEQDN	BD	PURGE	PEQUP	REP
Column 2	REP	ADS	PEQDN	BD	PURGE	PEQUP
Column 3	PEQUP	REP	ADS	PEQDN	BD	PURGE
Column 4	PURGE	PEQUP	REP	ADS	PEQDN	BD
Column 5	BD	PURGE	PEQUP	REP	ADS	PEQDN
Column 6	PEQDN	BD	PURGE	PEQUP	REP	ADS

Optimization parameters:

- Gas hourly space velocity during adsorption, purge and repressurization step
- Cycle time
- Pressure equalization step(s)
- Gas recycling
- Operating conditions per step
- Adjusting boundary conditions

SEDMES: Cycle design

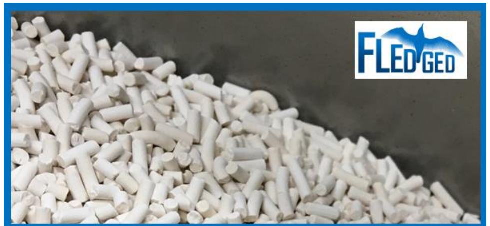




Typical for sorption-enhanced processes trade-off between carbon selectivity towards DME and productivity

SEDMES: Conclusions

- Separation-enhanced synthesis technology offers intensified processes for economic valorisation of CO_2-rich syngas
- Sorption-enhanced DME synthesis, SEDMES, has been developed using commercially available materials
- Novel catalysts show promising results: Especially HPA shows high activity for selective DME synthesis
- Validated modelling frameworks have allowed to design the SEDMES reactor and optimise the SEDMES process for Fledged case
- SEDMES technology validated in relevant multicolumn, environment (TRL5)



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