FLEDGED

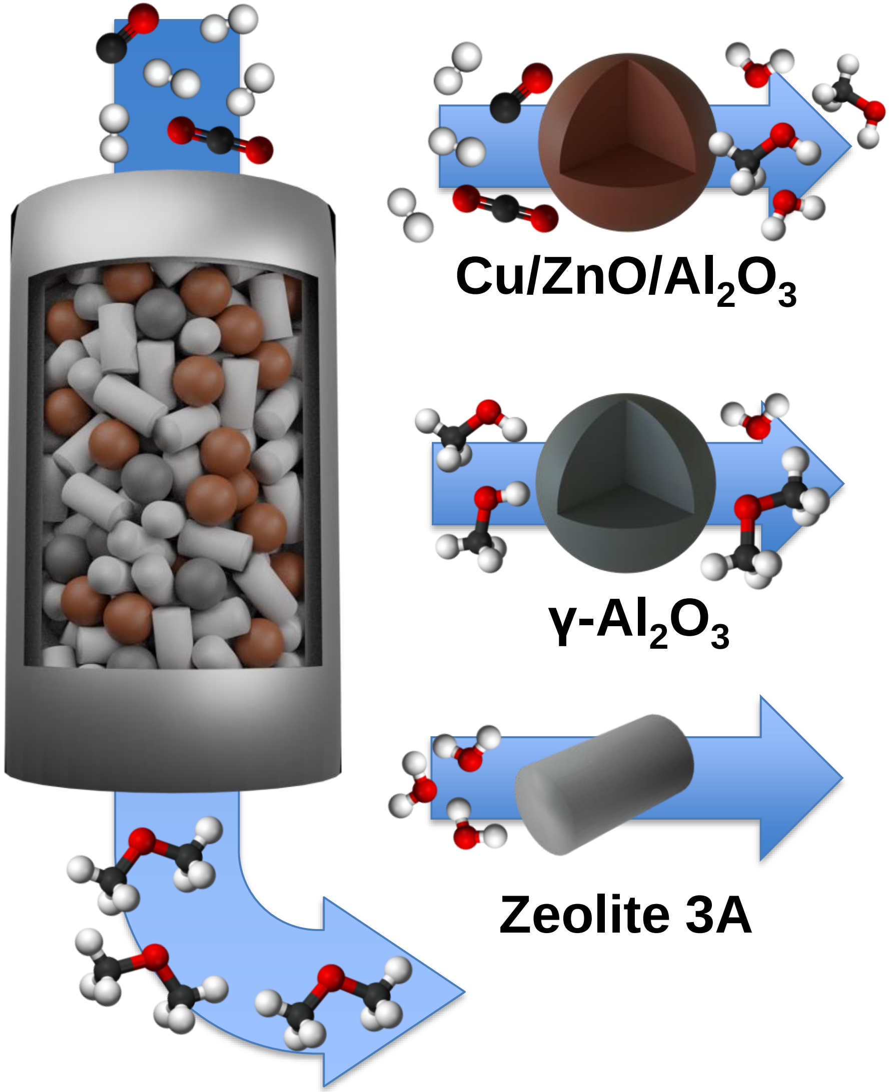
Modelling and design of fixed bed reactors for sorption enhanced dimethyl ether synthesis

Simone Guffanti, Carlo Giorgio Visconti, Gianpiero Groppi

POLITECNICO MILANO 1863

Laboratory of Catalysis and Catalytic Processes LCCP

Introduction



$$CO + 2\,H_2 \leftrightarrow CH_3OH$$

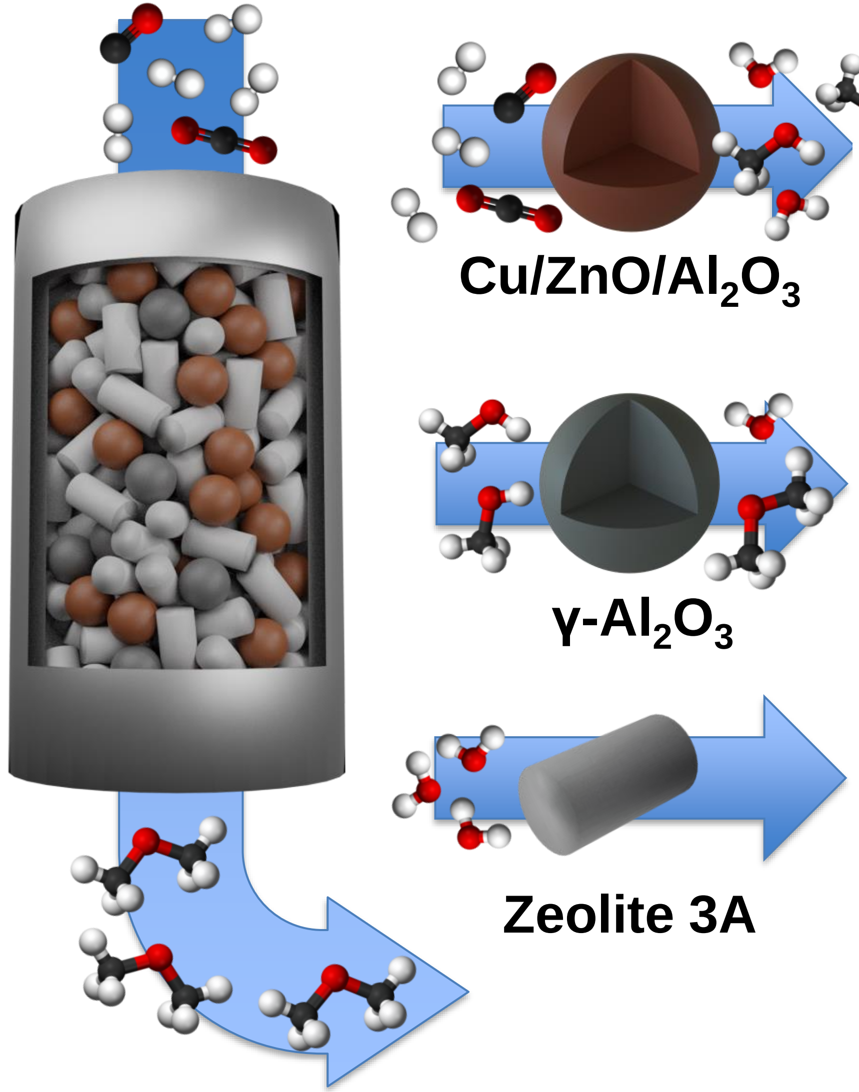
$$CO_2 + H_2 \leftrightarrow CO + H_2O$$

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

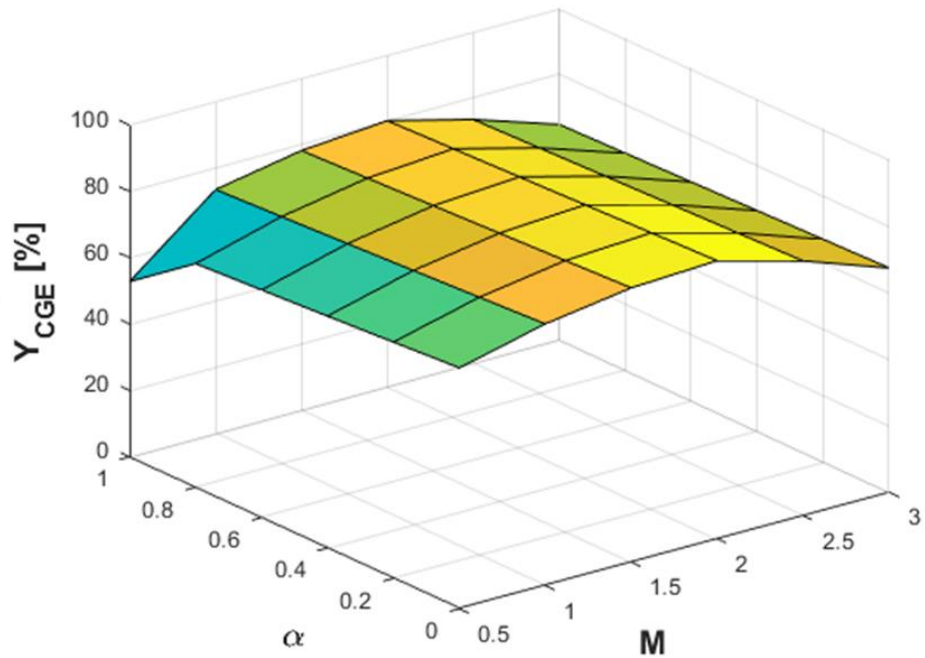
$$2\,CH_3OH \leftrightarrow CH_3OCH_3 + H_2O$$

$$H_2O \rightarrow H_2O_{ads}$$

Introduction

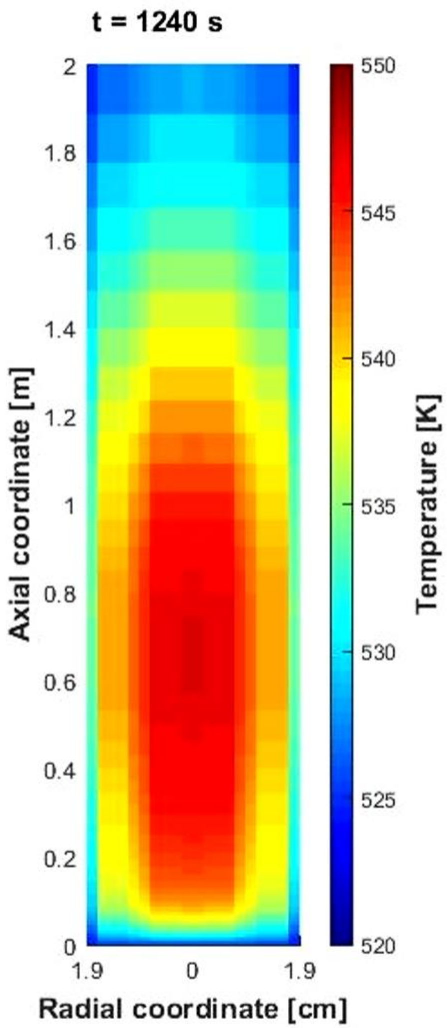


$$Y_{CGE} = \frac{LHV_{DME_{out}}}{LHV_{syngas_{in}}}$$

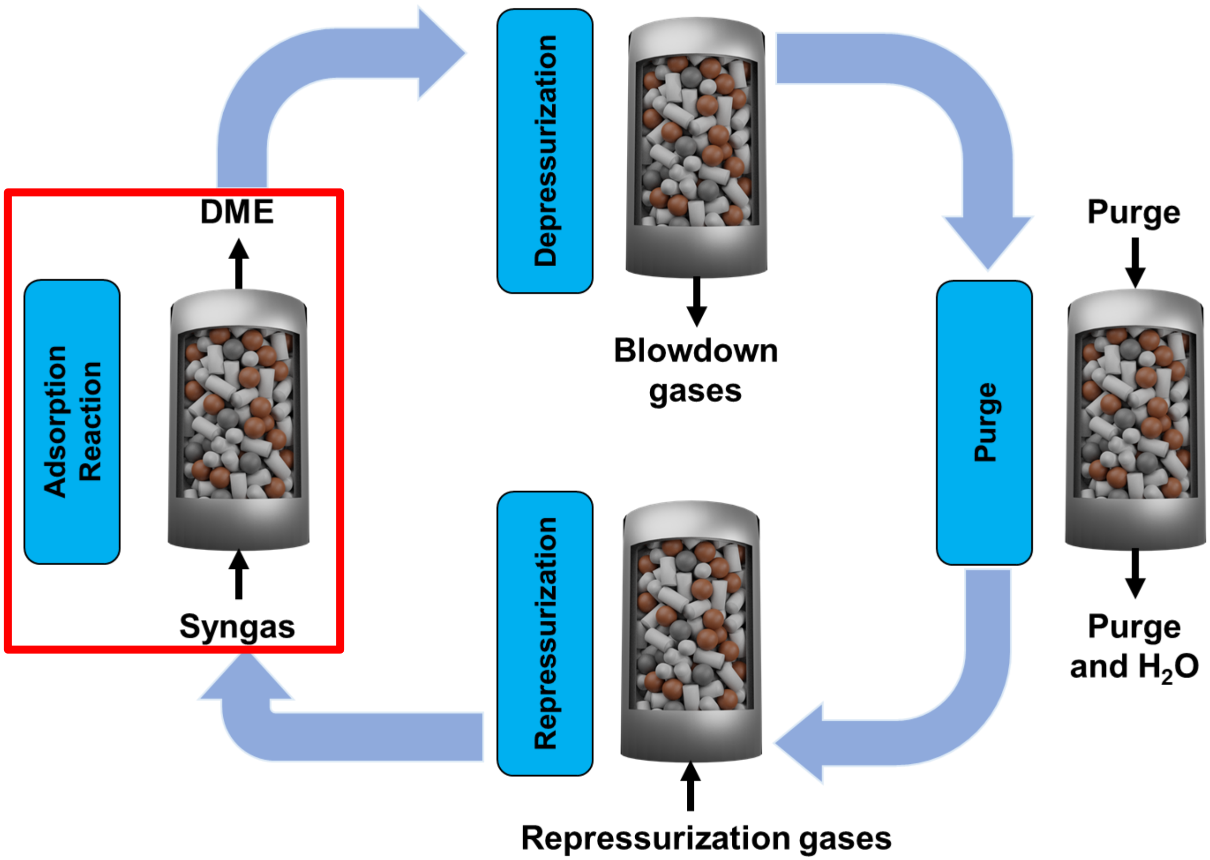


$$\alpha = \frac{CO}{CO + CO_2} \qquad M = \frac{H_2 - CO_2}{CO + CO_2}$$

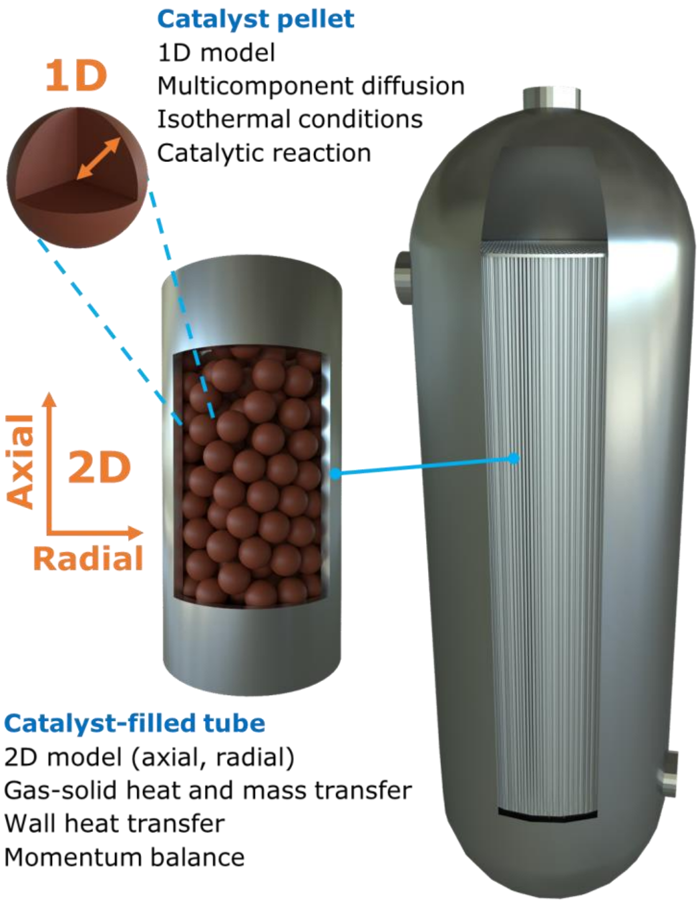
Scope of the work



Pressure Swing Adsorption (PSA) cycle

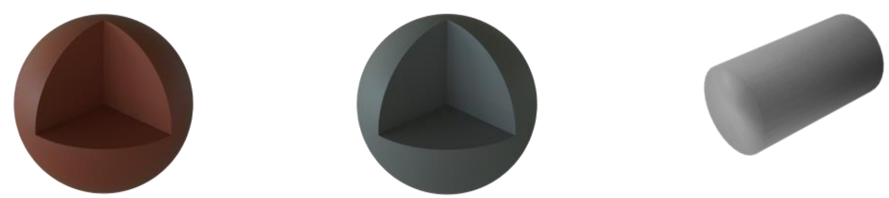


Reactor model



SEDMES reactor:

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



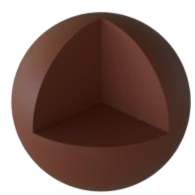
$Cu/ZnO/Al_2O_3$ γ-Al_2O_3 Zeolite 3A

Model validation: experimental set up (TRL4)

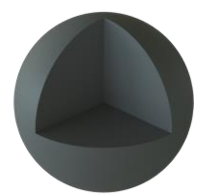
innovation
for life

Input parameters

T_{inlet}	525 K
T_{cool}	525 K
P_{inlet}	25 bar
GHSV	100 h^{-1}
Ads:Cat.	4 : 1 w/w
CZA:γ-Al_2O_3	1 : 1 w/w
L_t	2 m
D_t	38.0 mm



$Cu/ZnO/Al_2O_3$

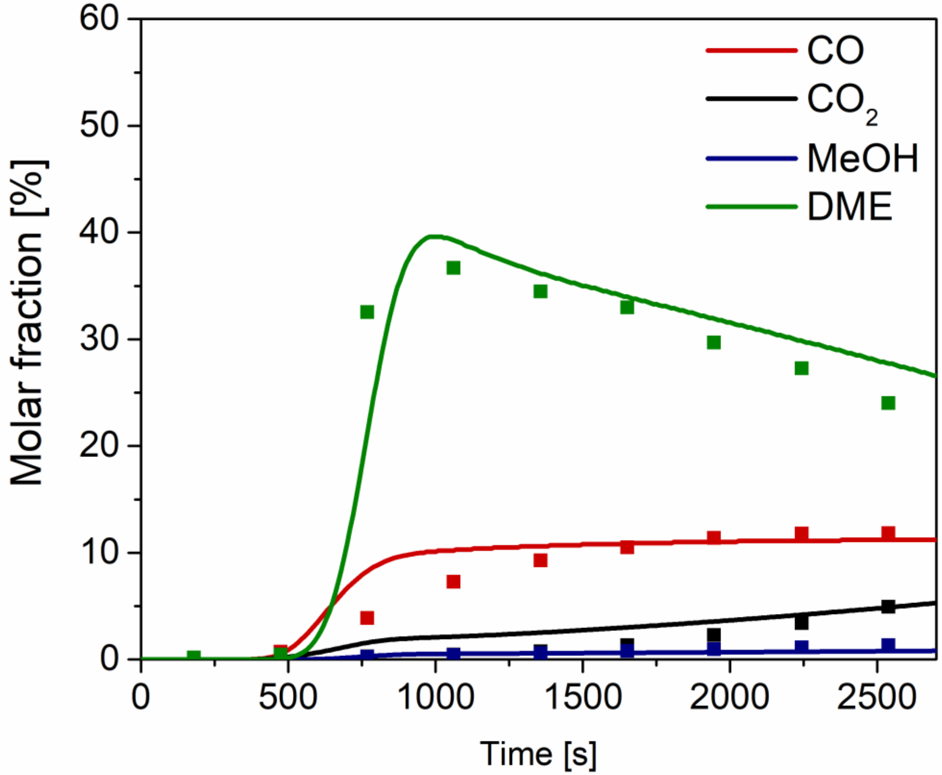


γ-Al_2O_3

Zeolite 3A

Model validation: outlet composition experimental vs. model

S. Guffanti et al., Chem. Eng. J., 404 (2021) 126573



$$CO + 2\,H_2 \leftrightarrow CH_3OH$$ **↑ x5**

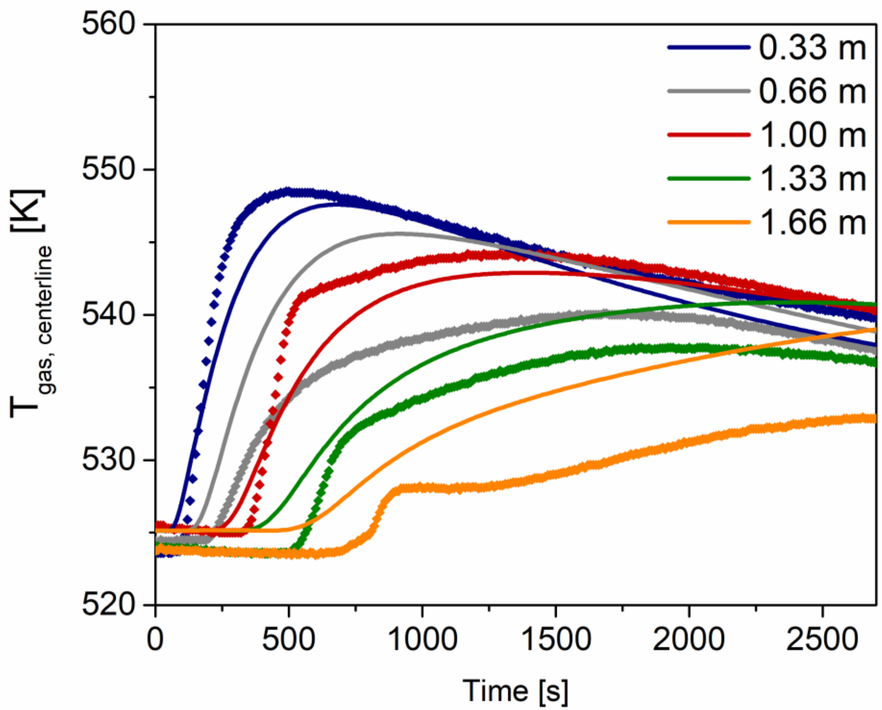
$$CO_2 + H_2 \leftrightarrow CO + H_2O$$ **↑ x7.5**

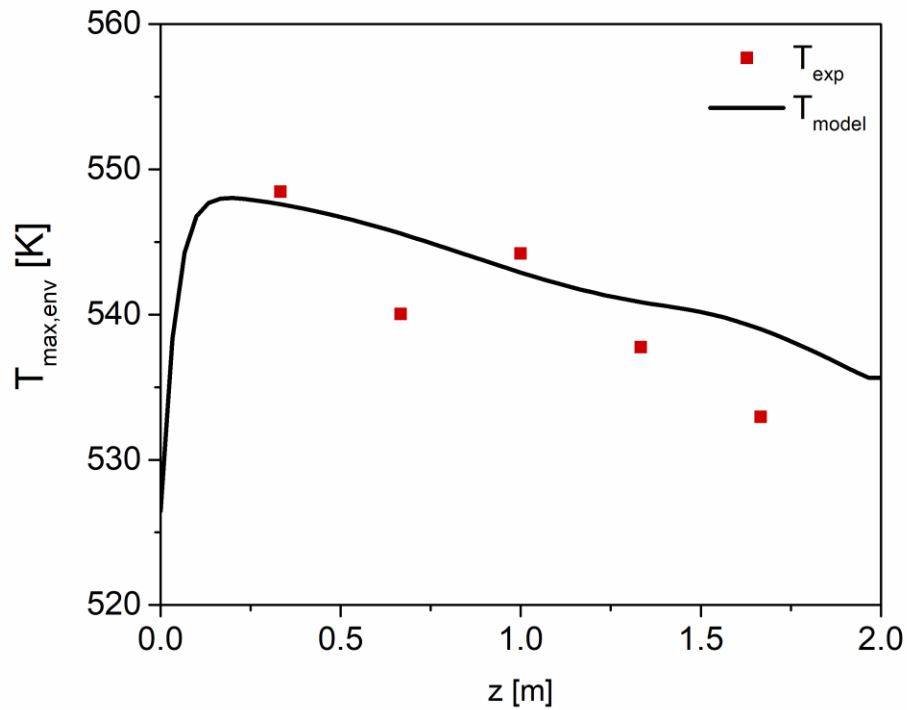
$$CO_2 + 3\,H_2 \leftrightarrow CH_3OH + H_2O$$ **↑ x5**

G.H. Graaf et al., Chem. Eng. Sci. 43 (1988) 3185–3195
A. Montebelli et al., Catal. Today. 215 (2013) 176–185
M.B. Fichtl et al., Appl. Catal. A Gen. 502 (2015) 262–270

Model validation: temperature experimental vs. model

S. Guffanti et al., Chem. Eng. J., 404 (2021) 126573





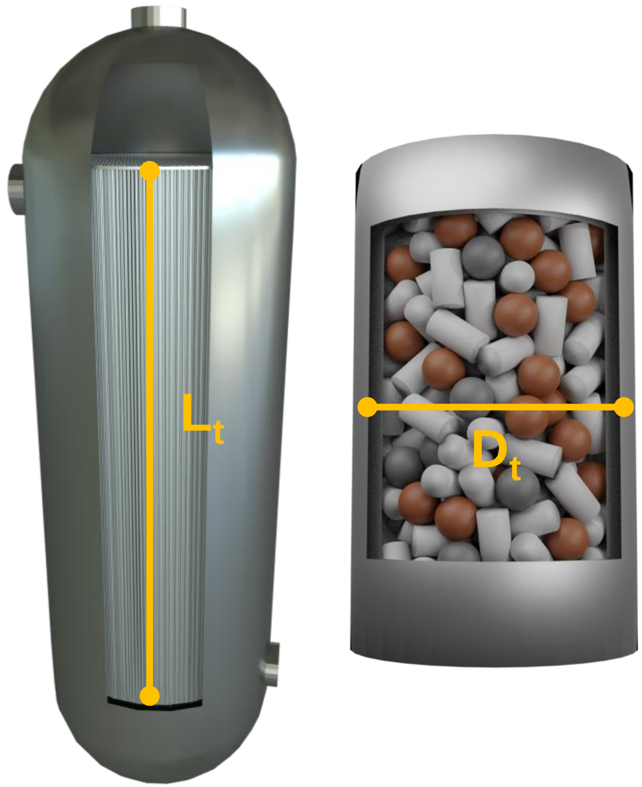
$$CO + 2\,H_2 \leftrightarrow CH_3OH$$ ↑ x5

$$CO_2 + H_2 \leftrightarrow CO + H_2O$$ ↑ x7.5

$$CO_2 + 3\,H_2 \leftrightarrow CH_3OH + H_2O$$ ↑ x5

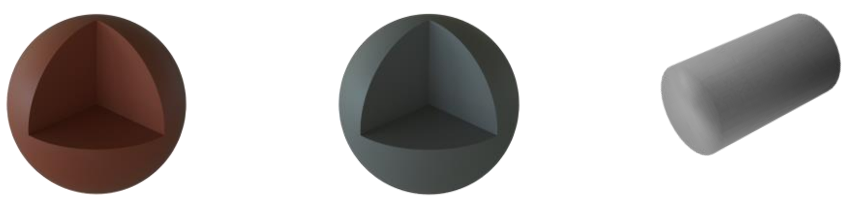
G.H. Graaf et al., Chem. Eng. Sci. 43 (1988) 3185–3195
A. Montebelli et al., Catal. Today. 215 (2013) 176–185
M.B. Fichtl et al., Appl. Catal. A Gen. 502 (2015) 262–270

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 Zeolite 3A

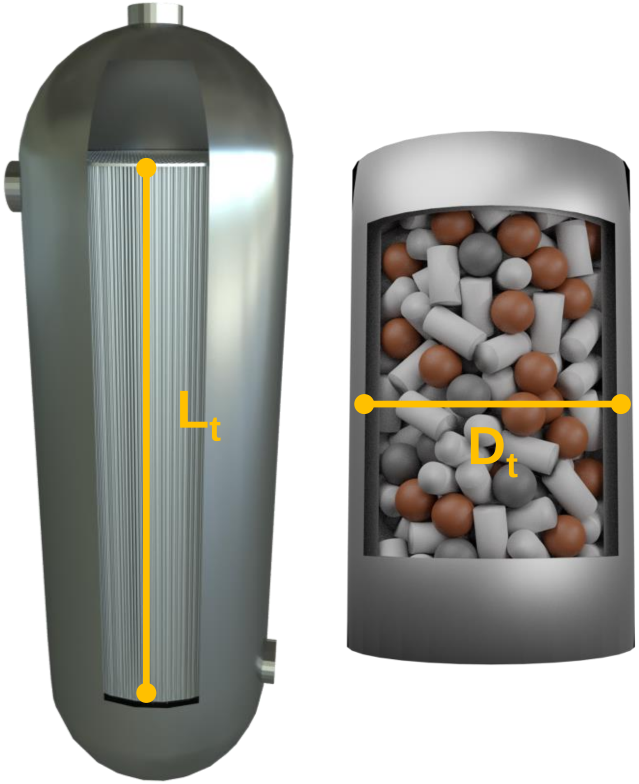
Input parameters

T_{inlet}	523 K
T_{cool}	523 K
Ads:Cat.	4 : 1 w/w
CZA:γ-Al_2O_3	1 : 1 w/w
L_t	6 m
M	2

Analyzed parameters

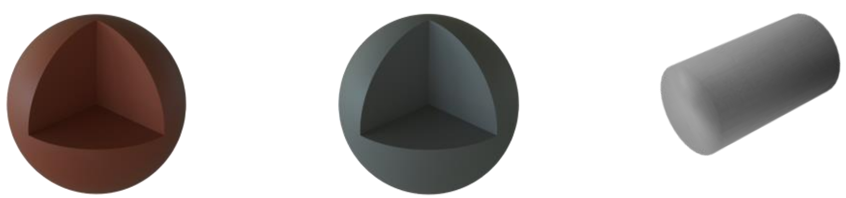
α	0.5
D_t	38.0 mm
P_{inlet}	25 bar
GHSV	140 h^{-1}

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 Zeolite 3A

Input parameters

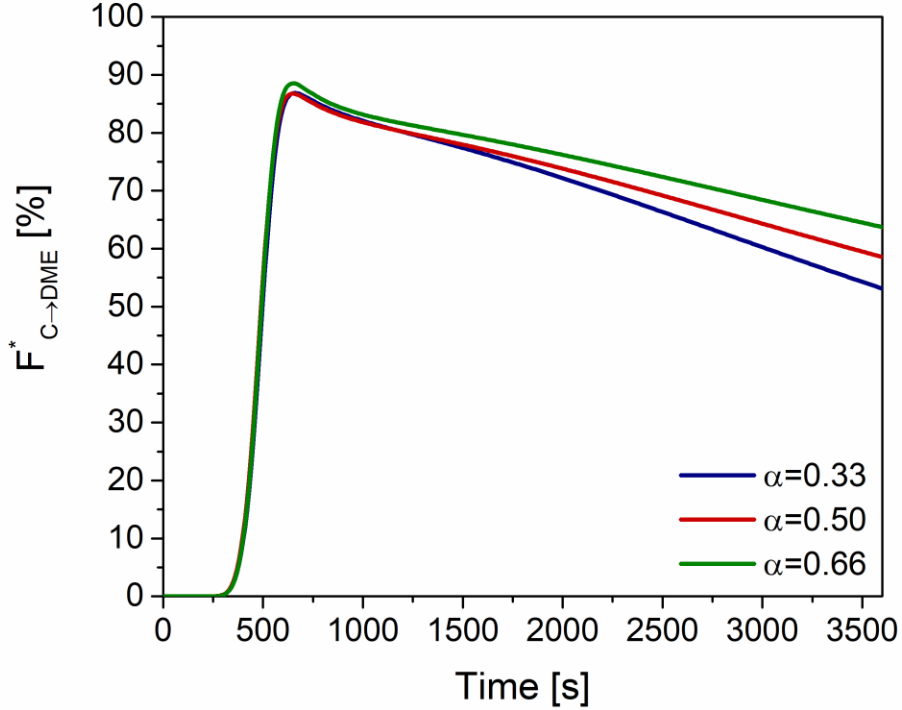
T_{inlet}	523 K
T_{cool}	523 K
Ads:Cat.	4 : 1 w/w
CZA:γ-Al_2O_3	1 : 1 w/w
L_t	6 m
M	2

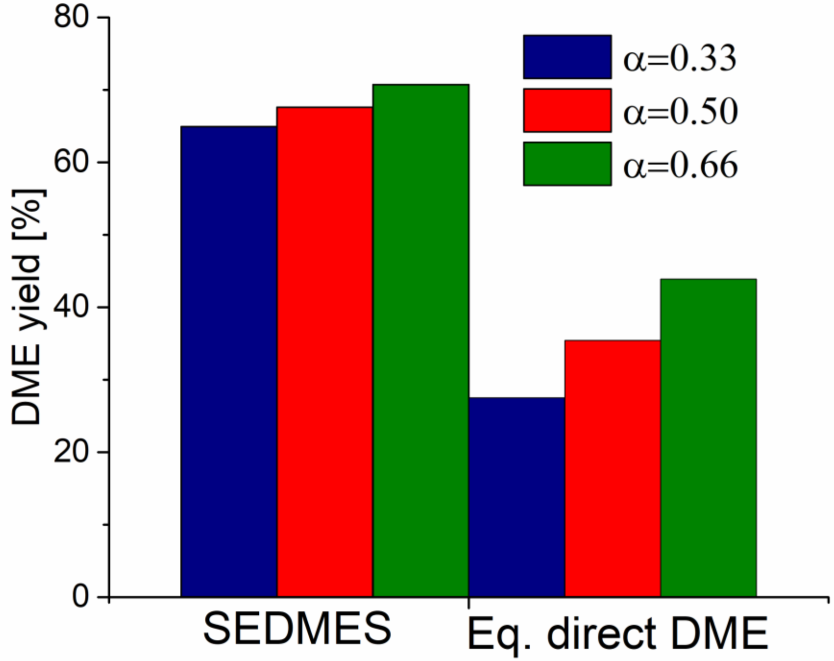
Analyzed parameters

α	0.33-0.66
D_t	25.6-46.6 mm
P_{inlet}	12.5-50 bar
GHSV	140-280 h^{-1}

SEDMES reactor: effect of α=CO/CO_x on DME yield

S. Guffanti et al., Chem. Eng. J., 404 (2021) 126573





$$F^*_{C\to DME} = \frac{2F_{DME_{out}}}{F_{CO_{in}} + F_{CO_{2_{in}}}}$$

$$Y_{DME} = \frac{2\left(\int_0^{t_{end}} F_{DME_{out}} dt + \int_0^{V_t} C_{gas,DME}(t_{end}) dV_t\right)}{\int_0^{t_{end}} \left(F_{CO_{in}} + F_{CO_{2_{in}}}\right) dt}$$

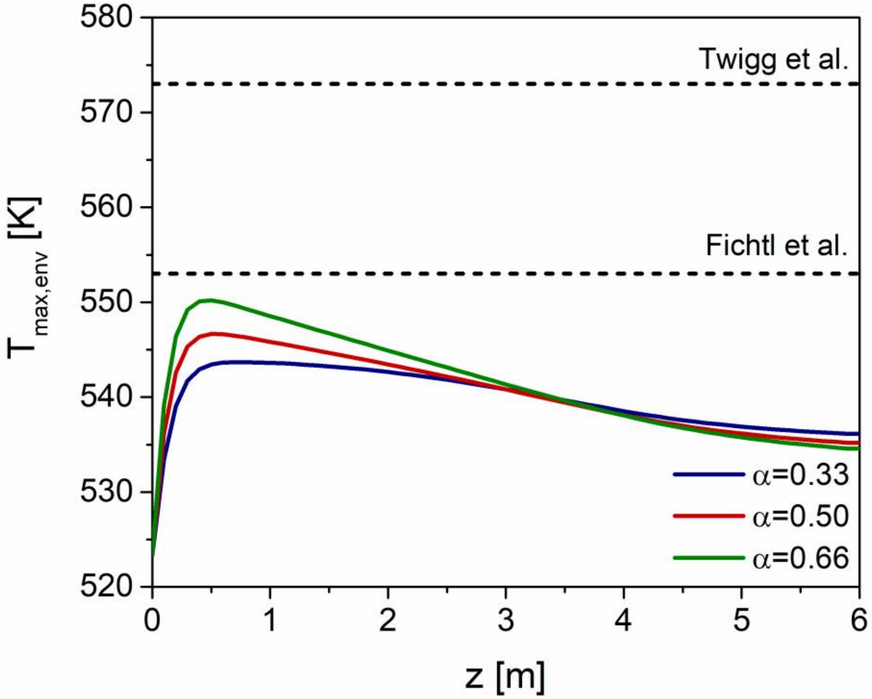
J. van Kampen et al., J. CO_2 Util. 37 (2020) 295–308.

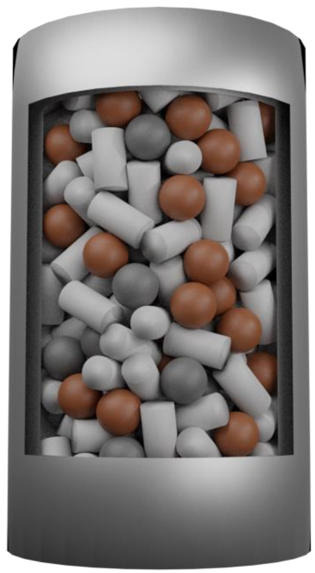
SEDMES reactor: effect of $\alpha = CO/CO_x$ on thermal stresses

S. Guffanti et al., Chem. Eng. J., 404 (2021) 126573

$$2\,CO + 4\,H_2 \leftrightarrow CH_3OCH_3 + H_2O \qquad \Delta H_r^0 = -204.0\ \mathrm{kJ/mol}_{DME}$$

$$2\,CO_2 + 6\,H_2 \leftrightarrow CH_3OCH_3 + 3\,H_2O \qquad \Delta H_r^0 = -121.8\ \mathrm{kJ/mol}_{DME}$$





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

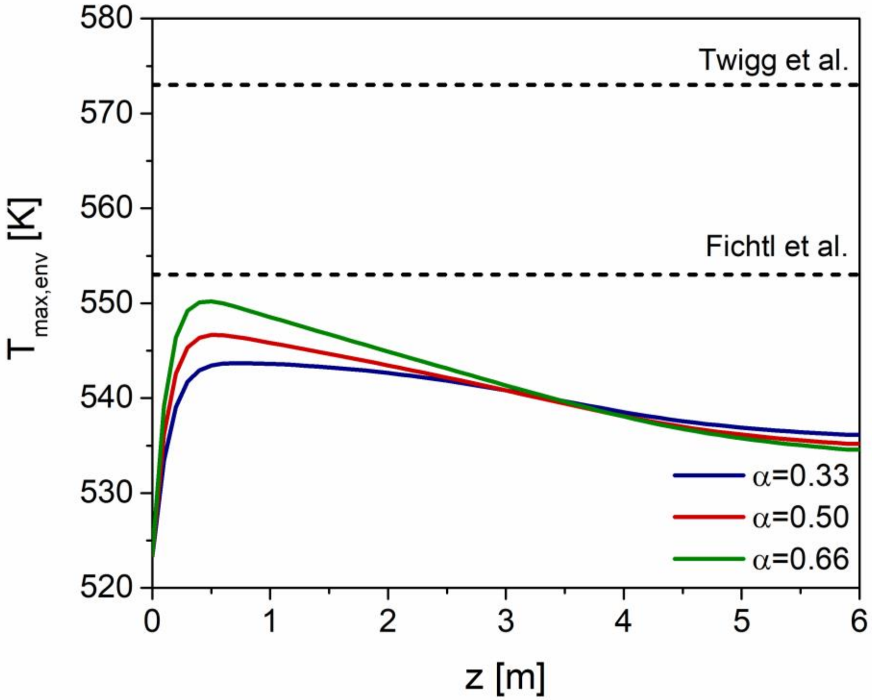
M. V. Twigg et al., Appl. Catal. A Gen. 212 (2001) 161–174
M.B. Fichtl et al, Appl. Catal. A Gen. 502 (2015) 262–270

SEDMES reactor: effect of α=CO/CO_x on thermal stresses

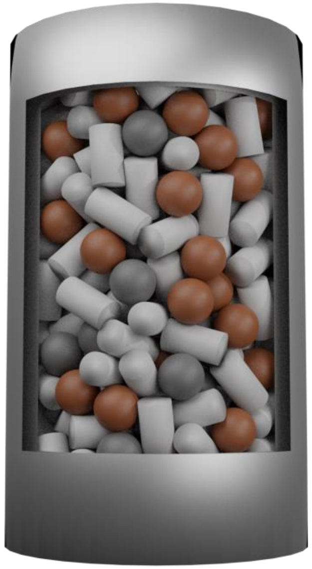
S. Guffanti et al., Chem. Eng. J., 404 (2021) 126573

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

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



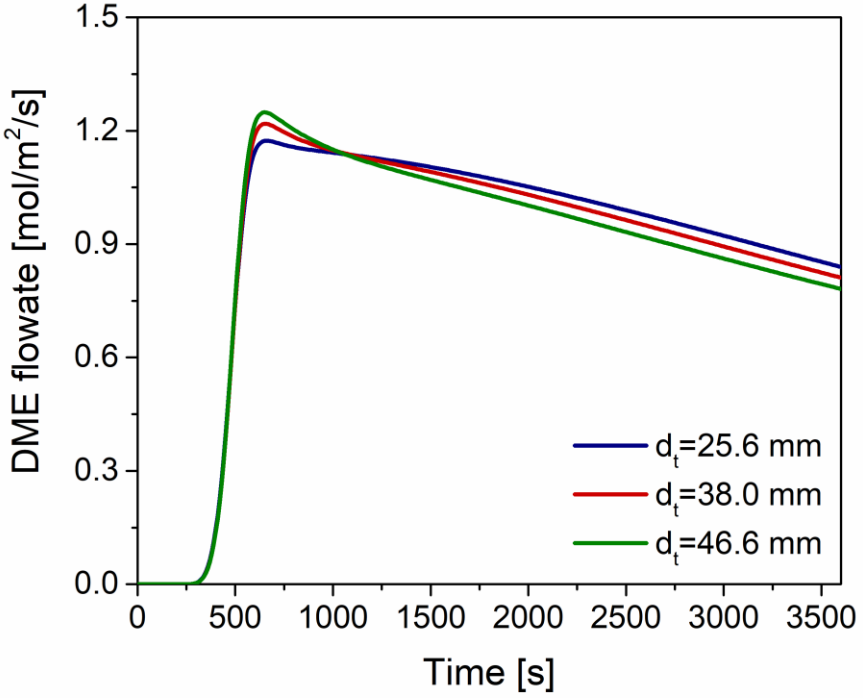
M. V. Twigg et al., Appl. Catal. A Gen. 212 (2001) 161–174
M.B. Fichtl et al, Appl. Catal. A Gen. 502 (2015) 262–270

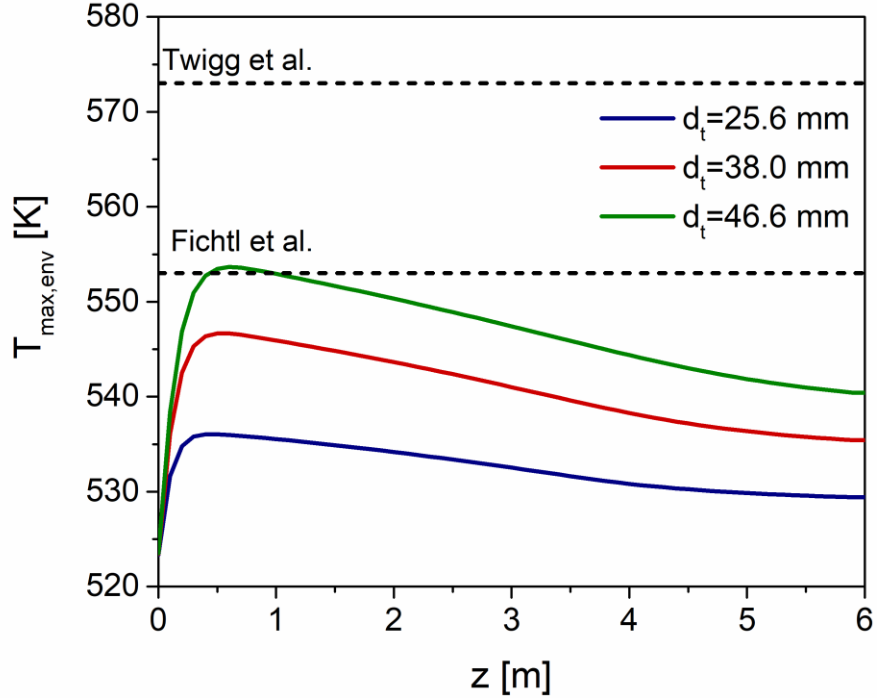


Ads./Cat. = 4/1 w/w

SEDMES reactor: effect of the tube diameter

S. Guffanti et al., Chem. Eng. J., 404 (2021) 126573

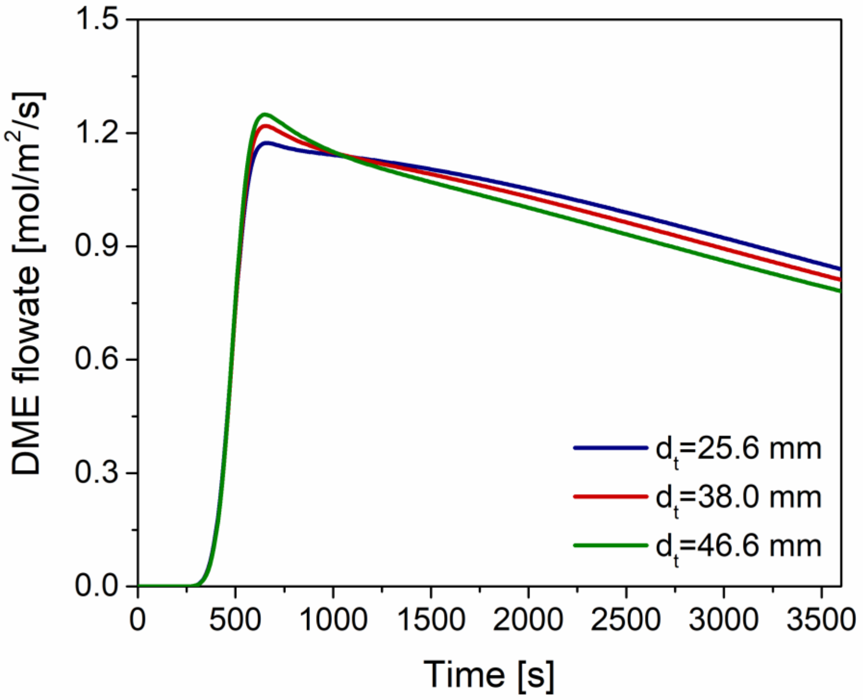


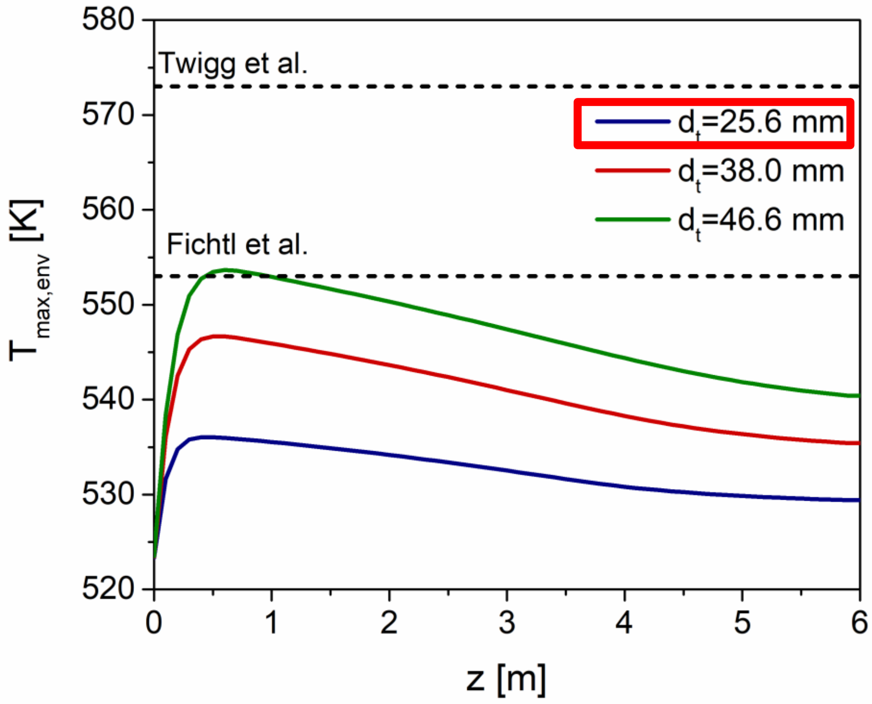


- **Dilution of catalyst in the adsorbent: moderate maximum thermal stresses**
- **Possible to use tube diameters up to 46.6 mm**
- **Neglible effect of tube diameter on DME yield**

SEDMES reactor: effect of the tube diameter

S. Guffanti et al., Chem. Eng. J., 404 (2021) 126573

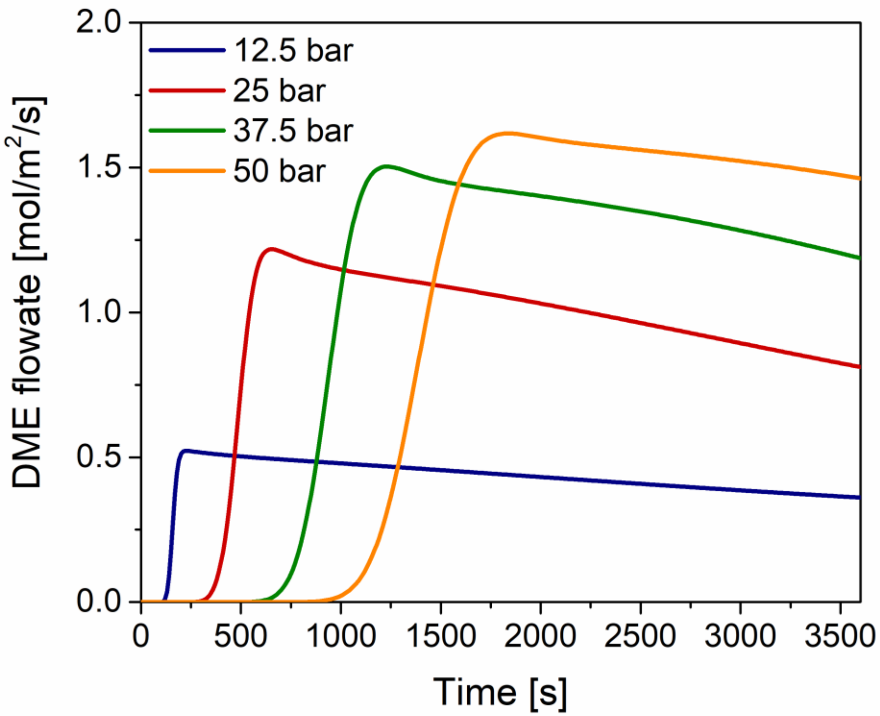


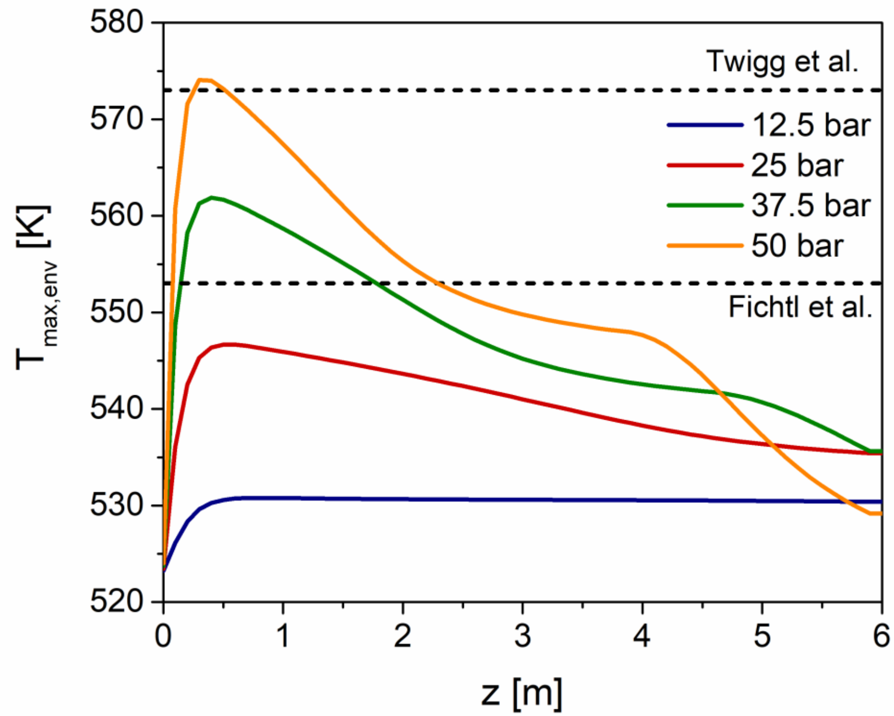


S. Guffanti, Ind. Eng. Chem. Res. 59 (2020) 14252–14266

- **Dilution of catalyst in the adsorbent: moderate maximum thermal stresses**
- **Possible to use tube diameters up to 46.6 mm**
- **Neglible effect of tube diameter on DME yield**

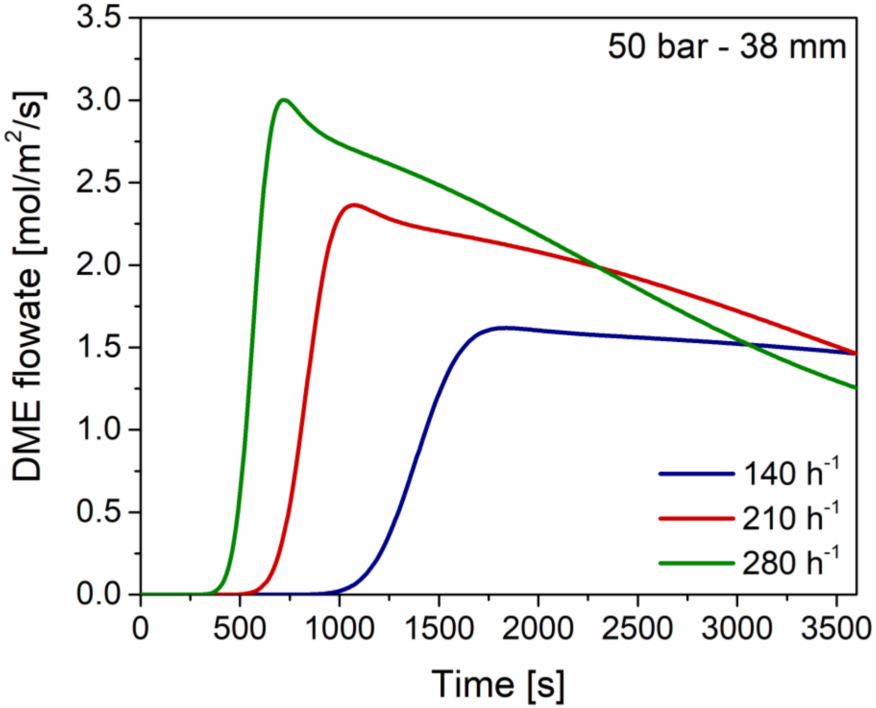
SEDMES reactor: effect of the pressure

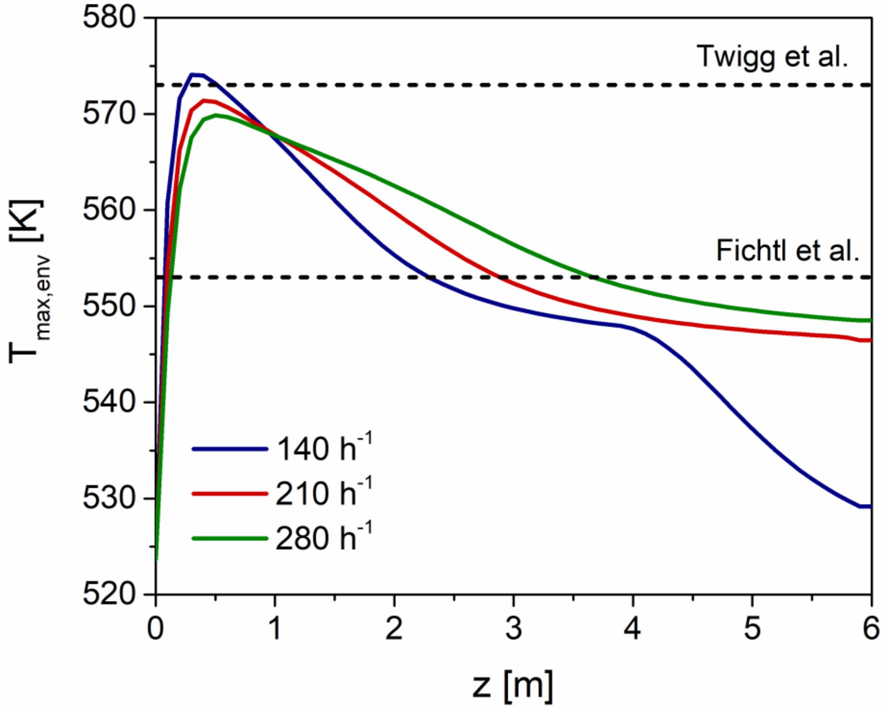




- **Increase in DME yield with pressure increase**
- **Breakthrough delay increases with the pressure**
- **Temperature profiles are strongly affected by the increase of pressure**

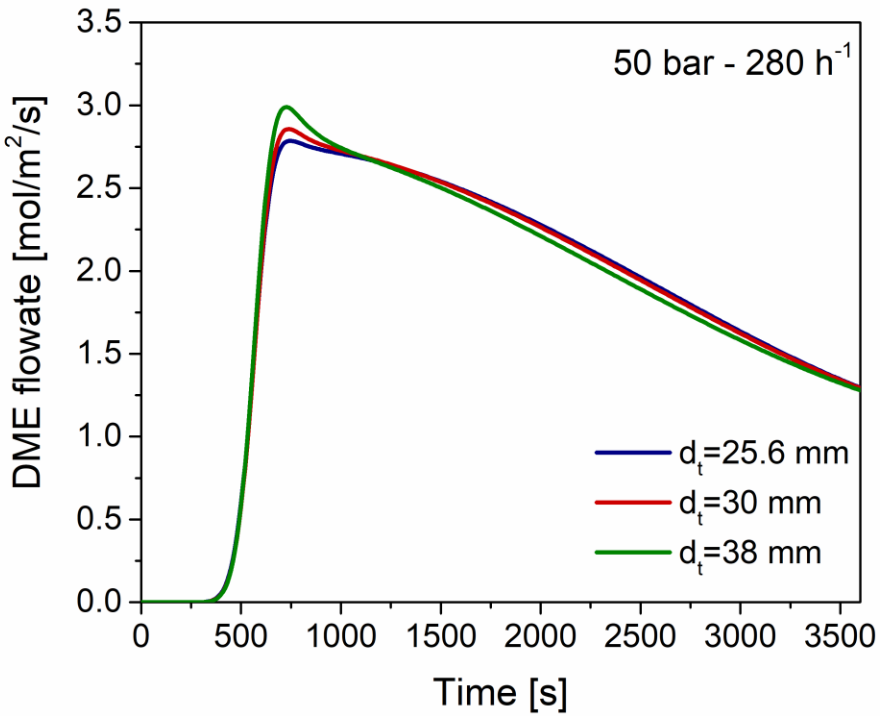
SEDMES reactor: effect of GHSV (50 bar)

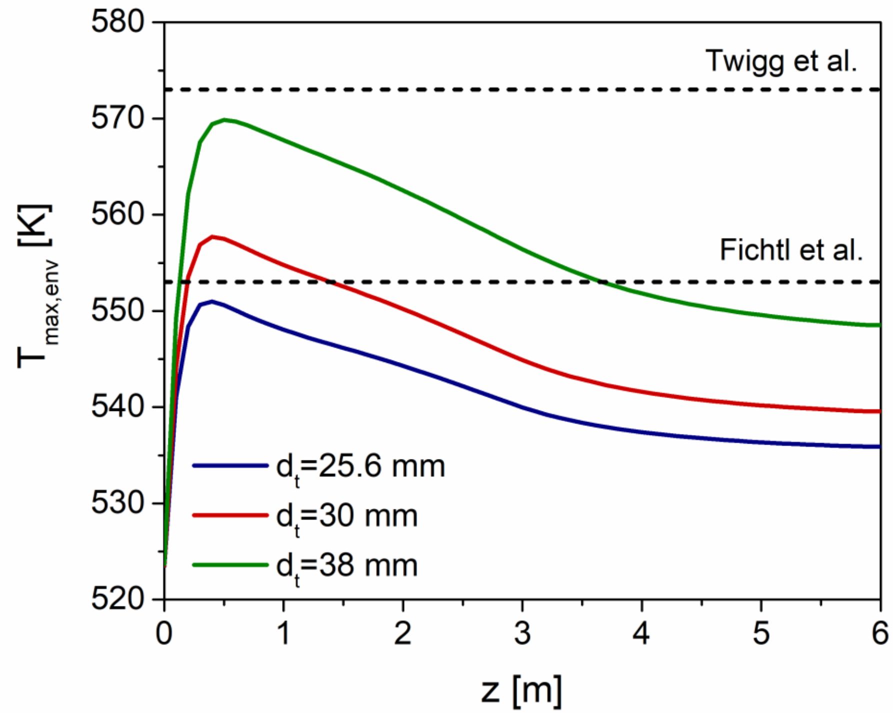




- **DME productivity increases with GHSV**
- **Minor effect of the GHSV on the maximum thermal stress**

SEDMES reactor: effect of tube diameter (50 bar)



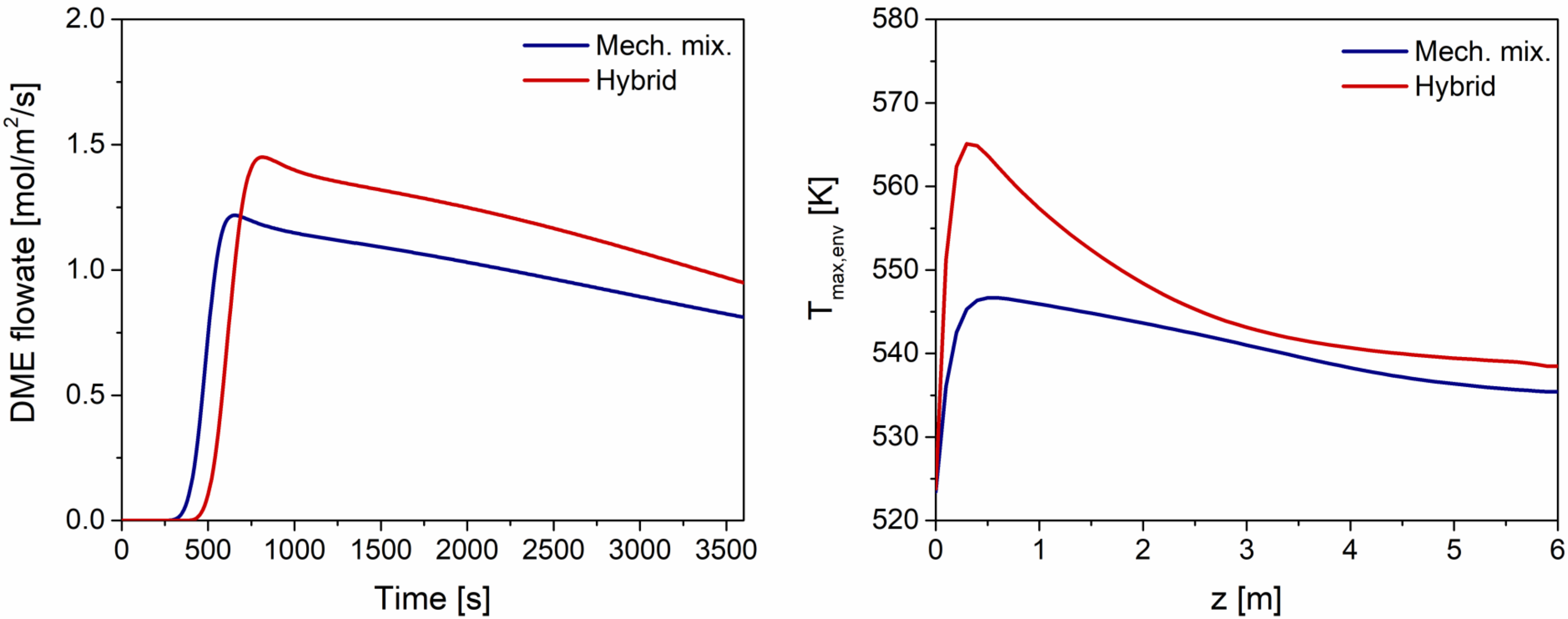


- **Neglible effect of tube diameter on DME yield**
- **Temperature stresses effectively moderated reducing the tube diameter**

SEDMES reactor: effect of catalyst configuration

S. Guffanti, Ind. Eng. Chem. Res. 59 (2020) 14252–14266

SEDMES reactor: effect of catalyst configuration



- **Intraparticle diffusion limitations are significative also in SEDMES**
- **Hybrid configuration has higher DME yield**
- **The thermal stresses are significantly higher with hybrid configuration**

Conclusions

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

- Model results confirm that with SEDMES, high DME yields, are obtained 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 (38-46.6 mm) with respect to the conventional direct DME synthesis (25.6 mm).

- The DME yield and productivity can be improved increasing the pressure, the GHSV and using hybrid catalyst pellets, however this leads to higher thermal stresses.

Thank you for your attention!

POLITECNICO MILANO 1863

Prof. Carlo Giorgio Visconti
Prof. Gianpiero Groppi

Laboratory of Catalysis and Catalytic Processes LCCP

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

FLEDGED