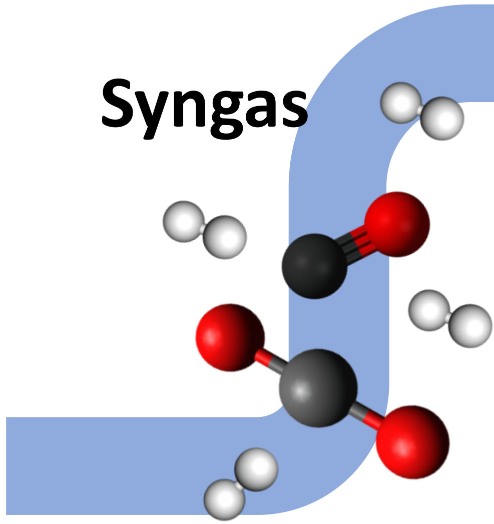
THE EFFECTS OF INTRAPARTICLE DIFFUSION PHENOMENA ON DIMETHYL ETHER DIRECT SYNTHESIS

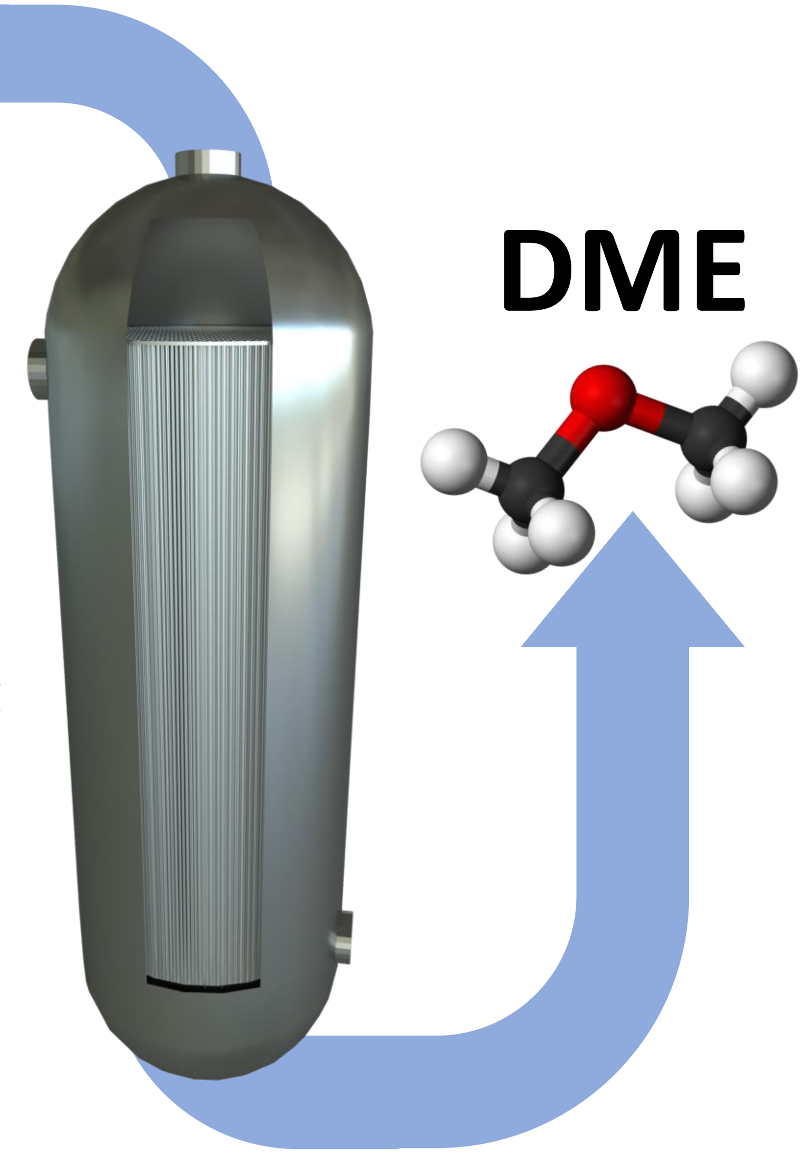
Guffanti S., Visconti C.G., Groppi G.

Laboratory of Catalysis and Catalytic Processes LCCP

Introduction: direct dimethyl ether synthesis

Biomass gasification





METHANOL SYNTHESIS

$$CO_2 + 3\,H_2 \leftrightarrow CH_3OH + H_2O \quad \Delta H_r = -49.4\ kJ/mol$$

WATER GAS SHIFT

$$CO + H_2O \leftrightarrow H_2 + CO_2 \quad \Delta H_r = -41.1\ kJ/mol$$

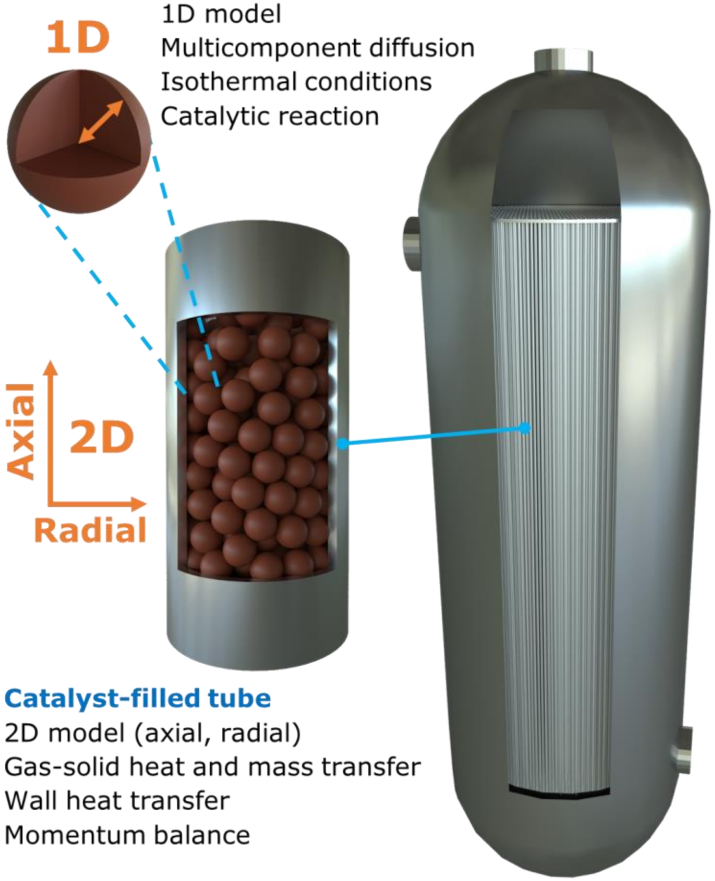
METHANOL DEHYDRATION TO DIMETHYL ETHER

$$2\,CH_3OH \leftrightarrow CH_3OCH_3 + H_2O \quad \Delta H_r = -23.0\ kJ/mol$$

Z. Azizi et al., Chem. Eng. Process., 82 (2014) 150-172

Reactor model

Catalyst pellet
1D model
Multicomponent diffusion
Isothermal conditions
Catalytic reaction



Catalyst-filled tube
2D model (axial, radial)
Gas-solid heat and mass transfer
Wall heat transfer
Momentum balance

gPROMS PSE

2D gas mass balances

$$-W_t \frac{\partial \omega_{g,i}}{\partial z} + \rho_g D_{er,i} \left(\frac{\partial^2 \omega_{g,i}}{\partial r^2} + \frac{1}{r} \frac{\partial \omega_{g,i}}{\partial r} \right) + \rho_g K_{m,i} a_v (\omega_{s,i} - \omega_{g,i}) = 0$$

Interphase mass continuity equations

$$\rho_g K_{m,i} a_v (\omega_{g,i} - \omega_{s,i}) + \rho_s \xi \sum_{j=1}^{NR} \nu_{ij} R_j^{eff} MW_i = 0$$

2D energy balance

$$-W_t C_{p,g} \frac{\partial T_g}{\partial z} + \lambda_{er}^{g} \left(\frac{\partial^2 T_g}{\partial r^2} + \frac{1}{r} \frac{\partial T_g}{\partial r} \right) + h a_v (T_s - T_g) = 0$$

Interphase energy continuity equation

$$h a_v (T_g - T_s) + \rho_s \xi \sum_{j=1}^{NR} R_j^{eff} (-\Delta H_{R,j}^0) = 0$$

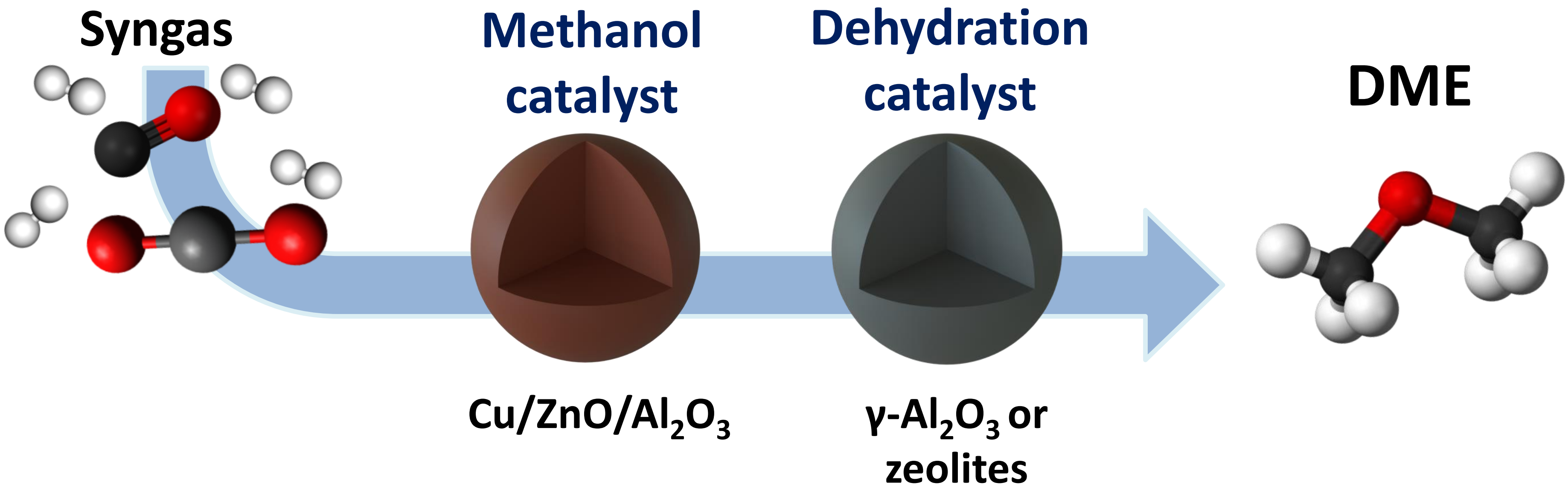
Momentum balance

$$\left(\frac{\rho_g}{W_t^2} - \frac{1}{P} \right) \frac{\partial P}{\partial z} + \frac{1}{T_g} \frac{\partial T_g}{\partial z} + MW_g \sum_{i=1}^{NC} \frac{1}{MW_i} \frac{\partial \omega_{i,g}}{\partial z} + 2 f_m a_v = 0$$

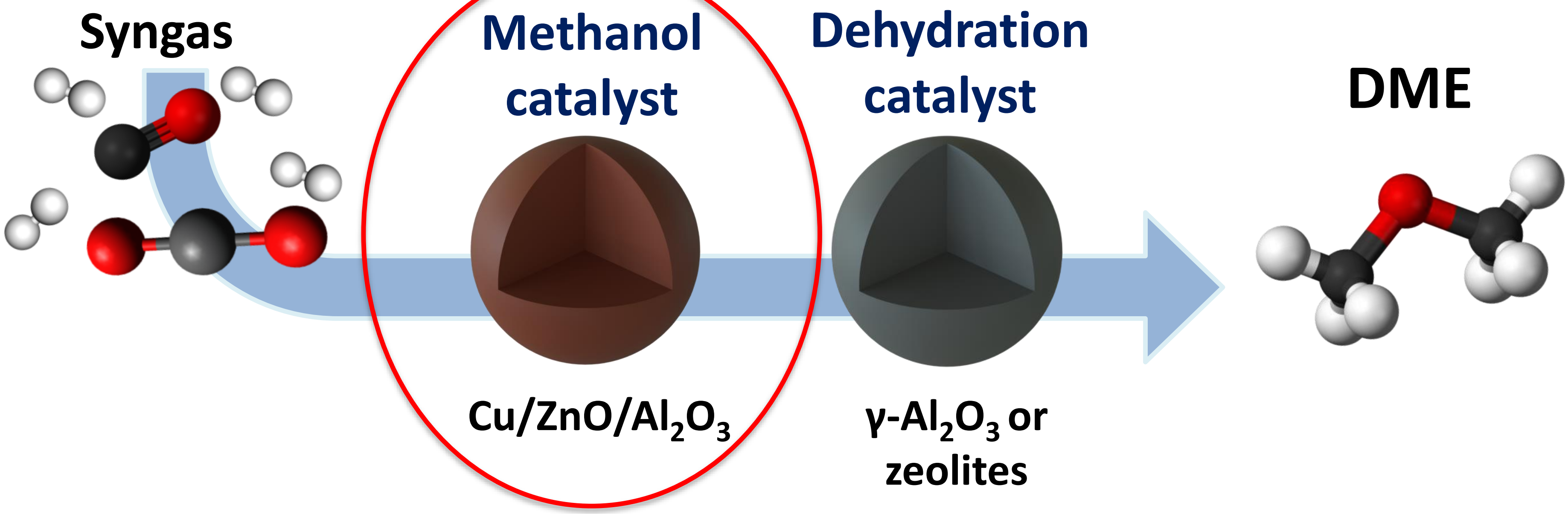
1D solid mass balances

$$\frac{1}{x^2} \frac{\partial}{\partial x} \left(D_{eff,i}\, x^2 \frac{\partial \omega_i^s}{\partial x} \right) + \frac{\rho_s}{\rho_g} MW_i \sum_{j=1}^{NR} \nu_{ij} R_j = 0$$

Catalyst configuration



Catalyst configuration



$$R_1 = K_1 \frac{f_{CO_2} f_{H_2}\left(1-(1/K_{eq,1})(f_{H_2O} f_{CH_3OH}/f_{CO_2} f_{H_2}^3)\right)}{\left(1+K_{\frac{H_2O}{H_2}}\frac{f_{H_2O}}{f_{H_2}}+\sqrt{K_{H_2} f_{H_2}}+K_{H_2O} f_{H_2O}\right)^3}$$

METHANOL SYNTHESIS FROM CO_2

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

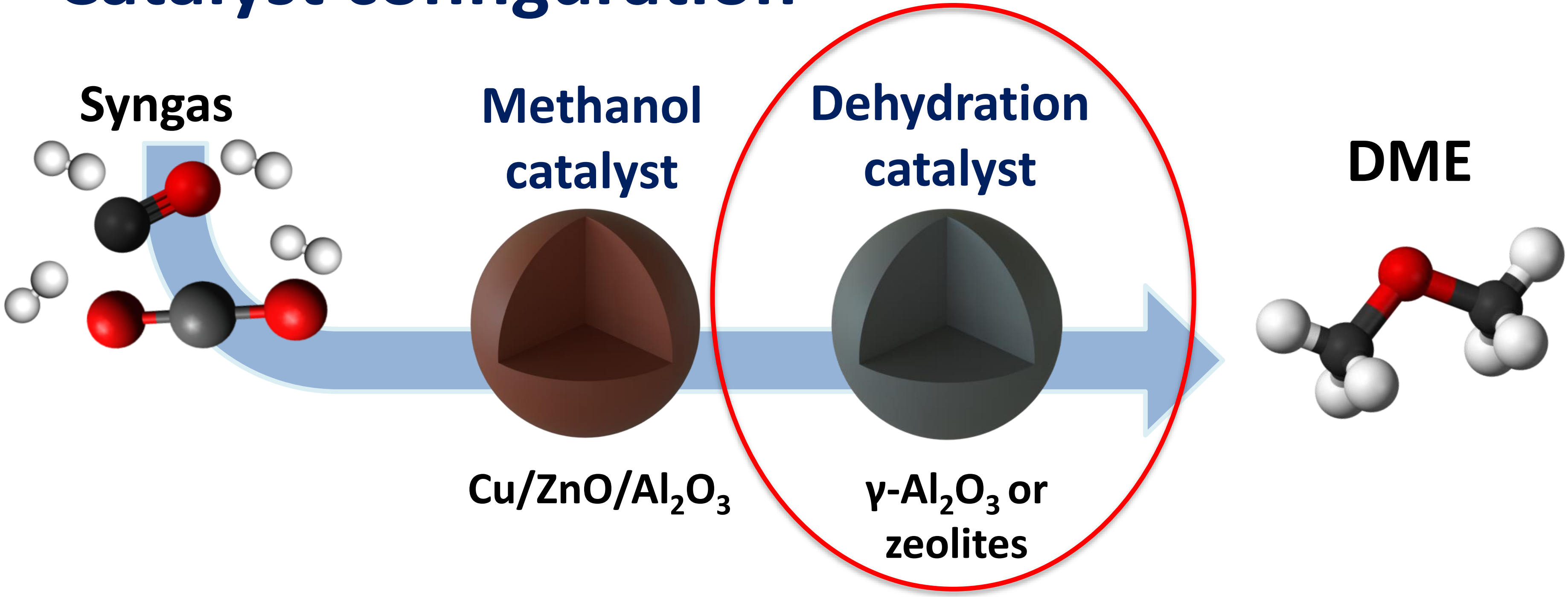
$$R_2 = K_2 \frac{f_{CO_2}\left(1-(1/K_{eq,2})(f_{H_2O} f_{CO}/f_{CO_2} f_{H_2})\right)}{\left(1+K_{\frac{H_2O}{H_2}}\frac{f_{H_2O}}{f_{H_2}}+\sqrt{K_{H_2} f_{H_2}}+K_{H_2O} f_{H_2O}\right)}$$

REVERSE WATER GAS SHIFT

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

K.L. Ng et al., Chem. Eng. Sci. 54 (1999), 3587-3592
K. M. Vanden Bussche et al., J. Catal., 161 (1996), 1-10

Catalyst configuration



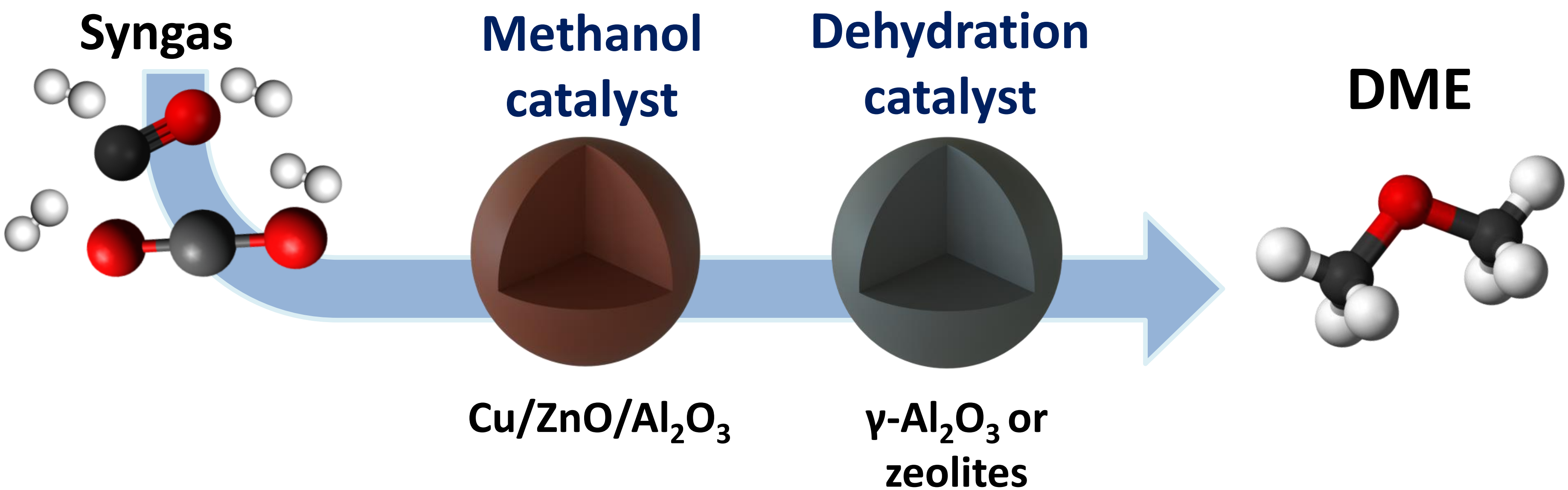
$$R_3 = K_3 \frac{K^2_{CH_3OH}\left(C^2_{CH_3OH} - \left(C_{H_2O}C_{CH_3OCH_3}/K_{eq,3}\right)\right)}{\left(1 + 2\sqrt{K_{CH_3OH}C_{CH_3OH}} + K_{H_2O}C_{H_2O}\right)^4}$$

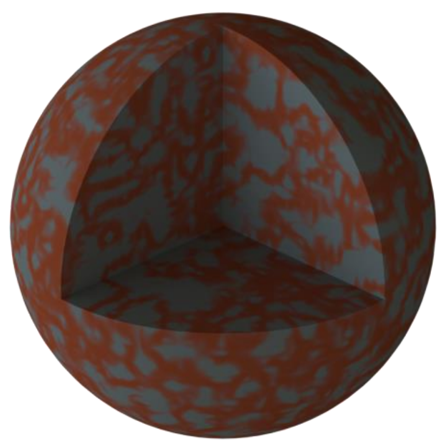
DIMETHYL ETHER SYNTHESIS

$$2CH_3OH \leftrightarrow CH_3OCH_3 + H_2O$$

K.L. Ng et al., Chem. Eng. Sci. 54 (1999), 3587-3592
G. Bercic et al., Ind. Eng. Chem. Res., 31 (4) (1992), 1035–1040

Catalyst configuration

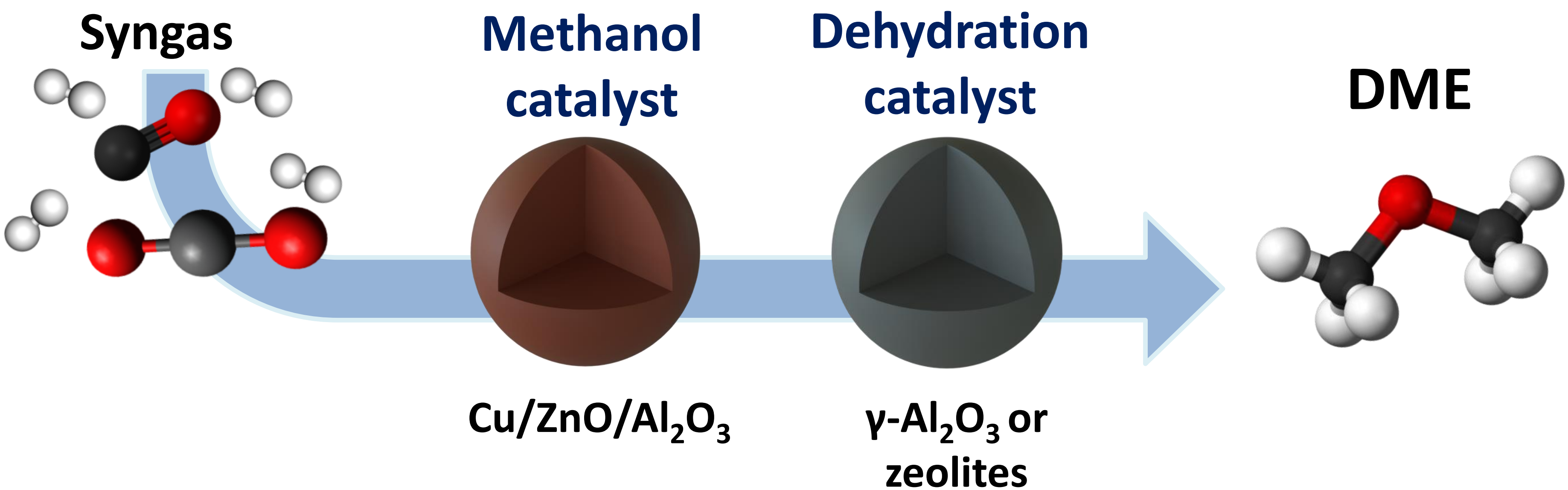


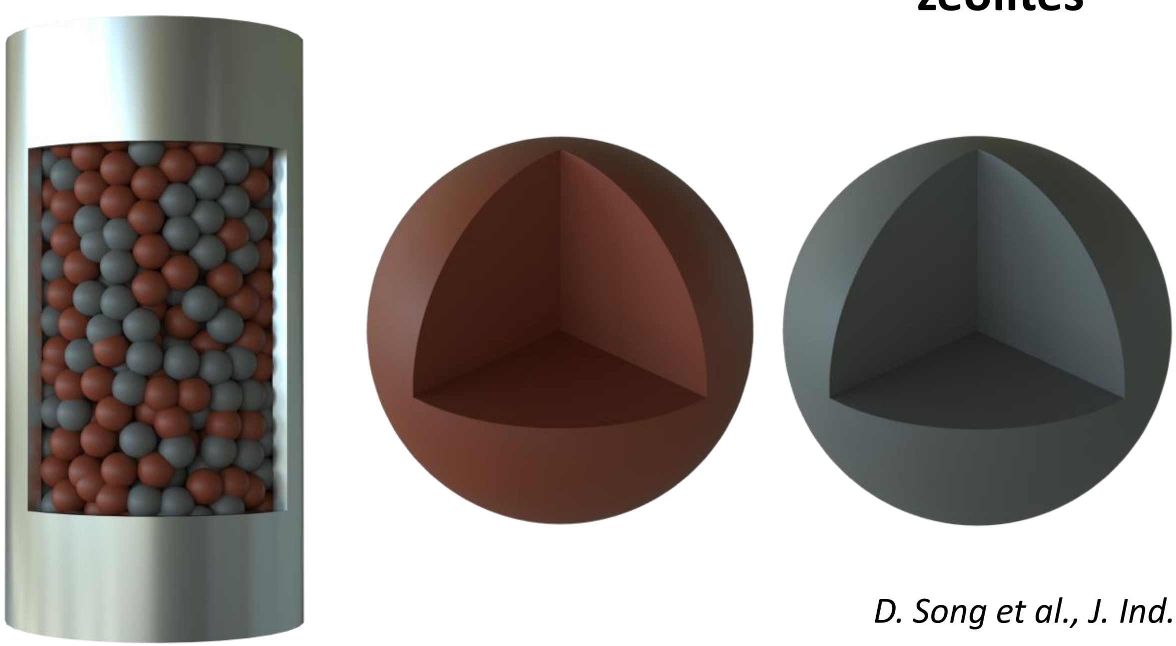


Hybrid pellet

D. Song et al., J. Ind. Eng. Chem., 13 (5) (2007) 815-826
A. Garcia-Trenco et al., Cat. Today, 227 (2014) 144-153
B. Voss et al., Book of abstracts ISCRE25, (2018)

Catalyst configuration



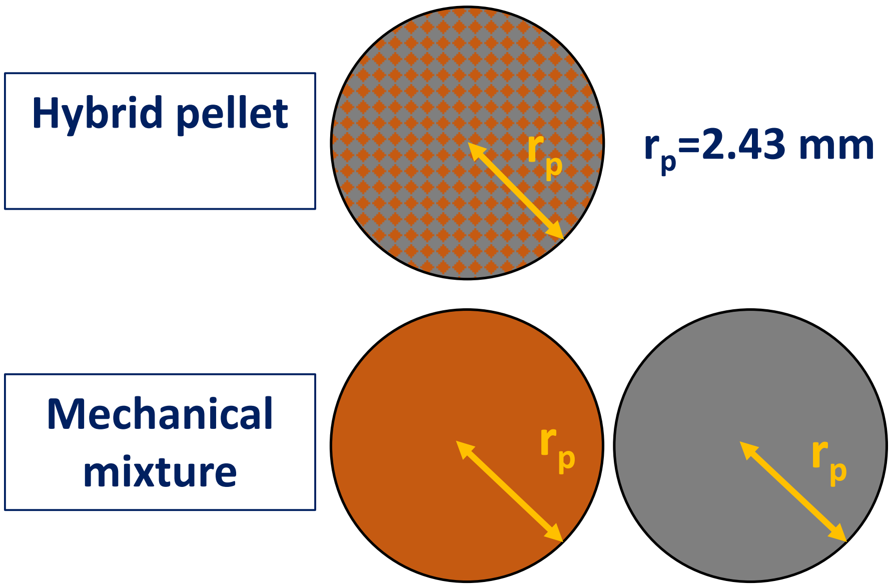


Mechanical mixture

D. Song et al., J. Ind. Eng. Chem., 13 (5) (2007) 815-826

Catalyst configuration analysis

Cat_{MeOH}/Cat_{DME} **= 2 w/w***



- **DME carbon yield**

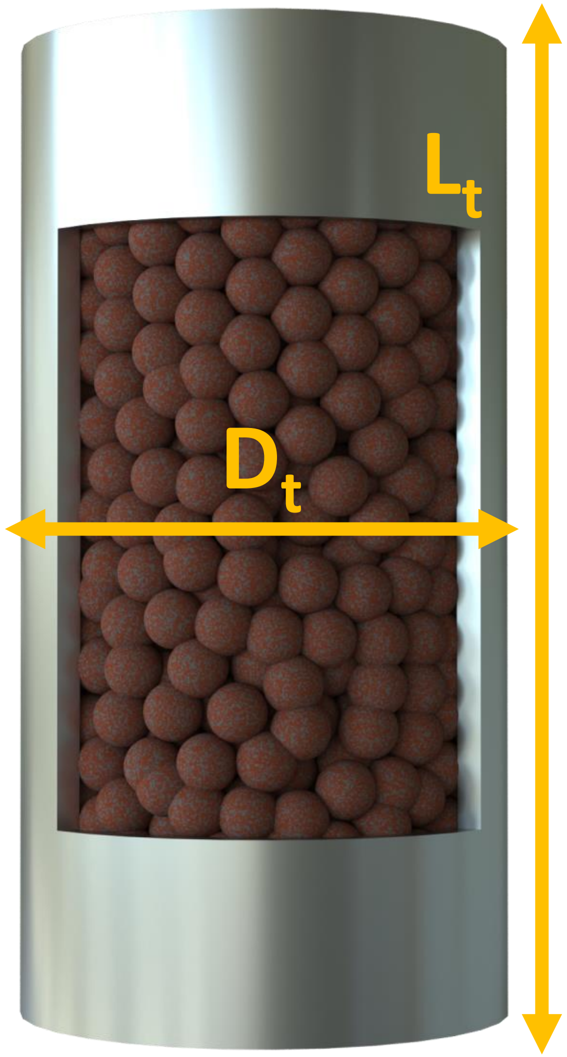
$$Y_{DME} = \frac{2F_{DME}}{\left(F_{CO} + F_{CO_2}\right)_{in}}$$

- ***Reactor centerline temperature***
- ***Catalyst efficiency factor***

$$\eta_j = \frac{R_j^{cat,av}}{R_j^{cat,surf}}$$

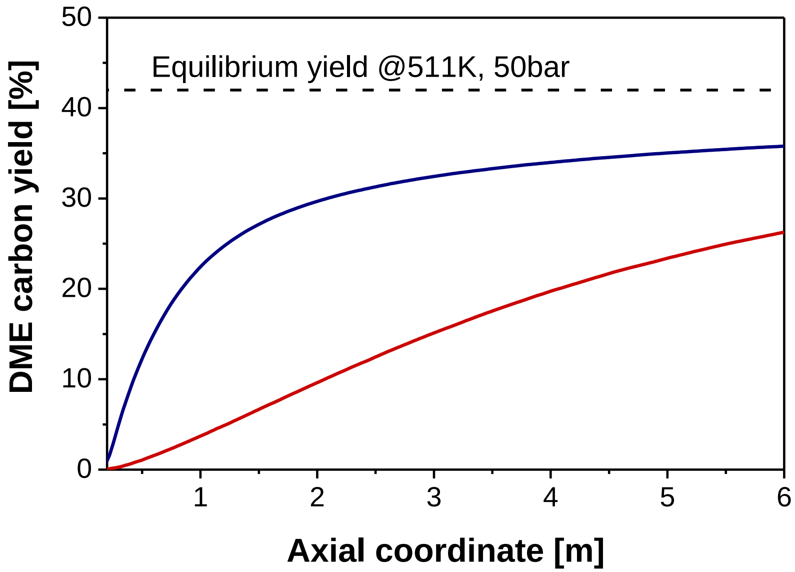
*K.L. Ng et al., Chem. Eng. Sci. 54 (1999), 3587-3592

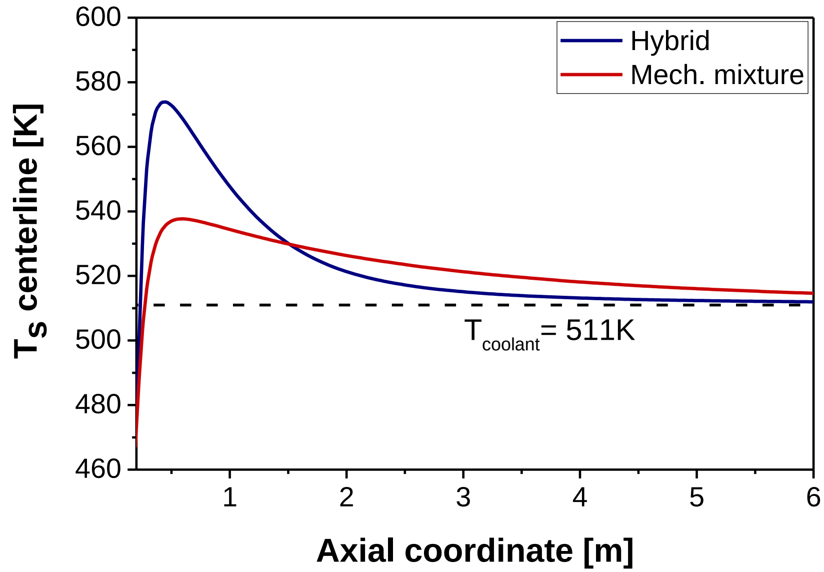
Operating conditions



D_t	25.65 mm
L_t	6 m
GHSV	1407 h^{-1}
$T_{coolant}$	511 K
T_{inlet}	323 K
P_{inlet}	50 bar
Inlet CO/CO_2	1.3
$M=(H_2-CO_2)/CO_x$	1
Inlet inert	8%
d_{pellet}	4.86 mm

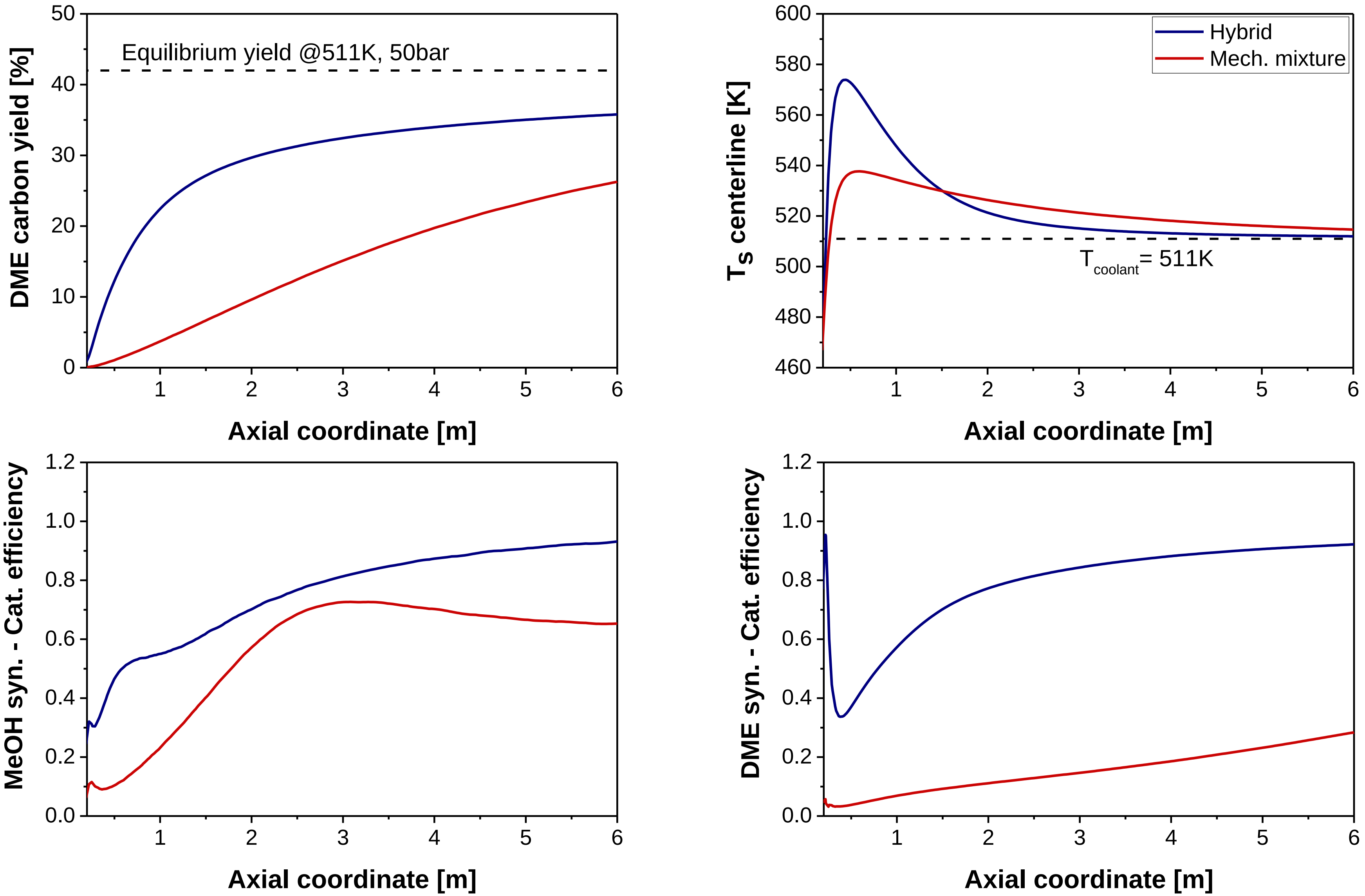
Hybrid pellet vs. mechanical mixture





T_{inlet} = 323 K; P_{inlet} = 50 bar; GHSV = 1407 h^{-1}; $M=(H_2-CO_2)/CO_x=1$; $CO/CO_2=1.3$; D_{tube} = 25.65 mm; L_{tube} = 6 m; d_{pellet} = 4.85 mm; Cat_{MeOH}/Cat_{DME} = 2 w/w.

Hybrid pellet vs. mechanical mixture



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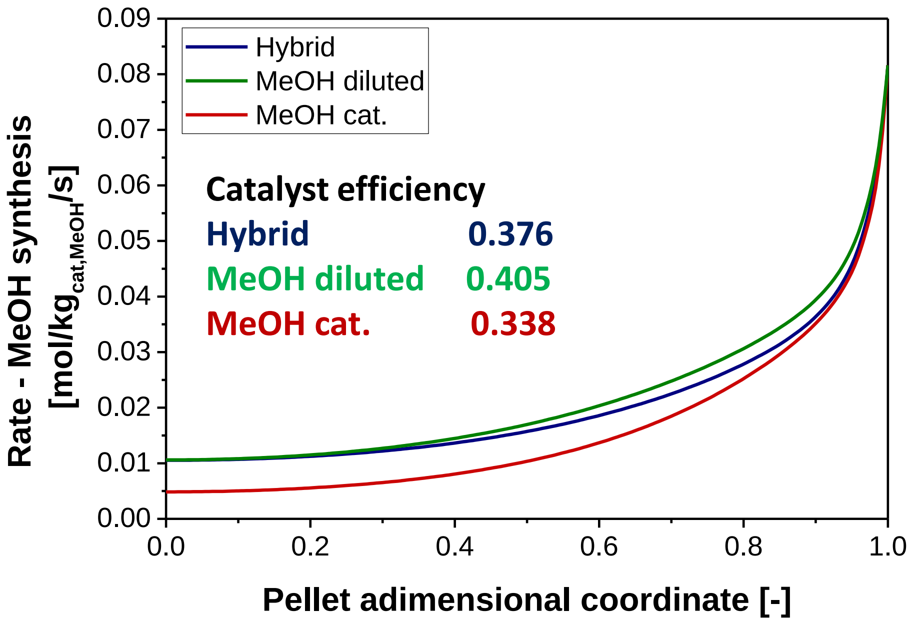
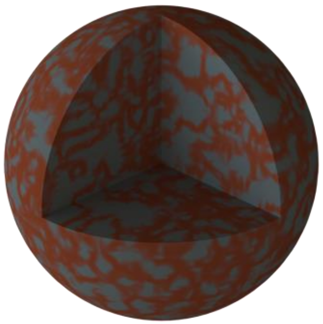
Dilution effects

$Cat_{MeOH}/Cat_{DME} = 2\ w/w$

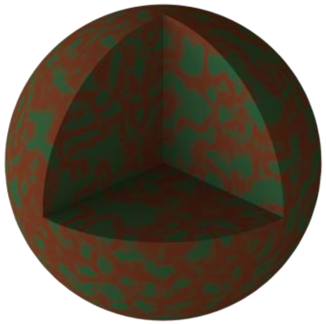
$$CO_2 + 3\ H_2 \rightarrow CH_3OH + H_2O$$



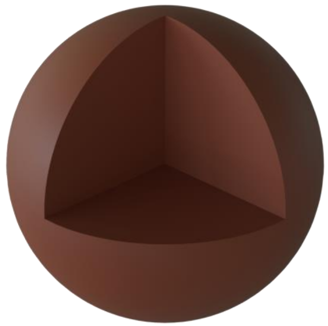
Hybrid pellet



MeOH diluted catalyst



MeOH catalyst

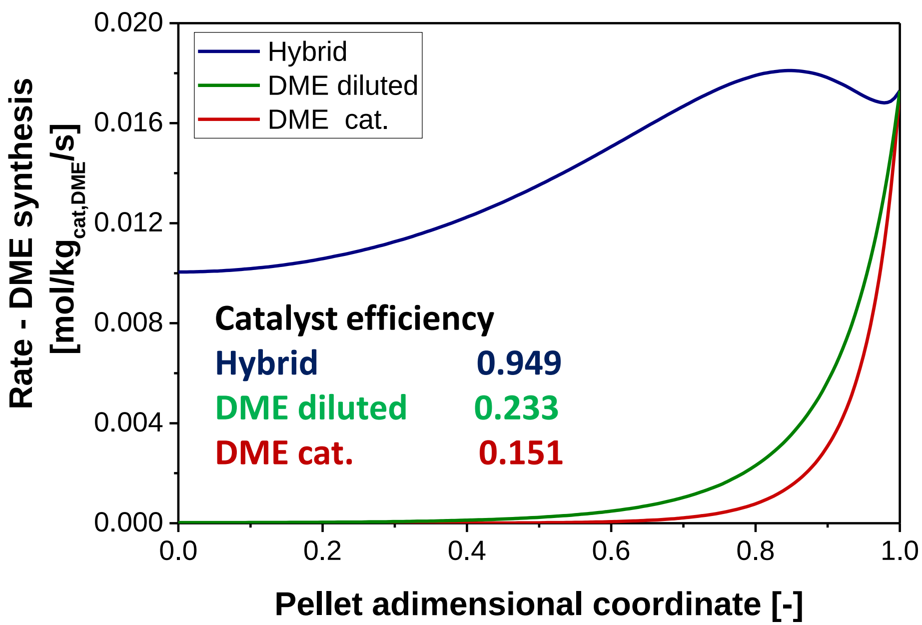


T = 511 K; P_{surf} = 50 bar; d_{pellet} = 4.85 mm; External surface composition: CO 20%, CO_2 17.5%, H_2 52.5%, H_2O 0.5%, MeOH 0.8%, DME 0.6 %, CH_4 8.3%.

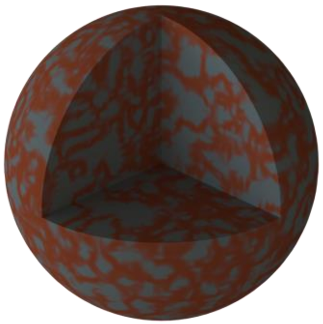
Dilution effects

Cat_{MeOH}/Cat_{DME} = 2 w/w

$$2\ CH_3OH \rightarrow CH_3OCH_3 + H_2O$$



Hybrid pellet



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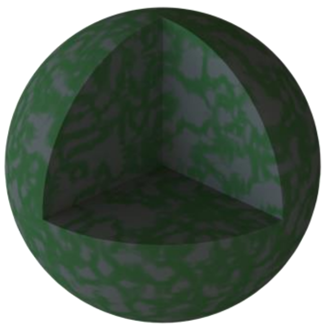
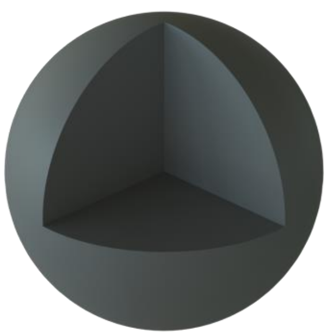


DME catalyst



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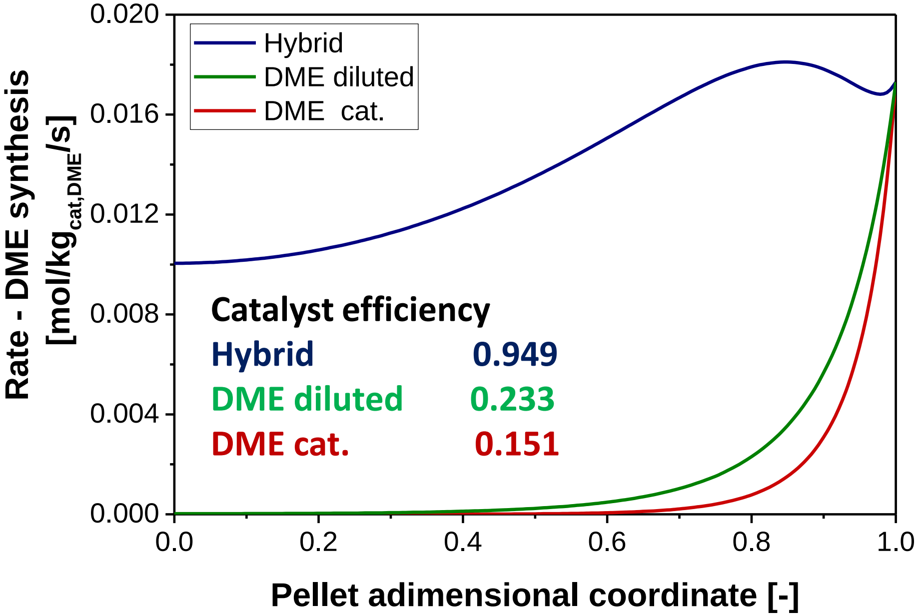

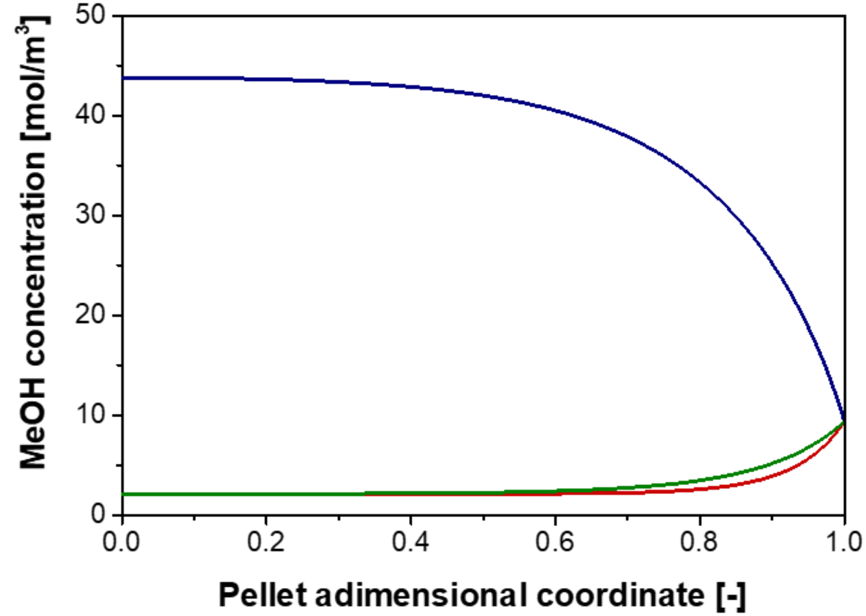

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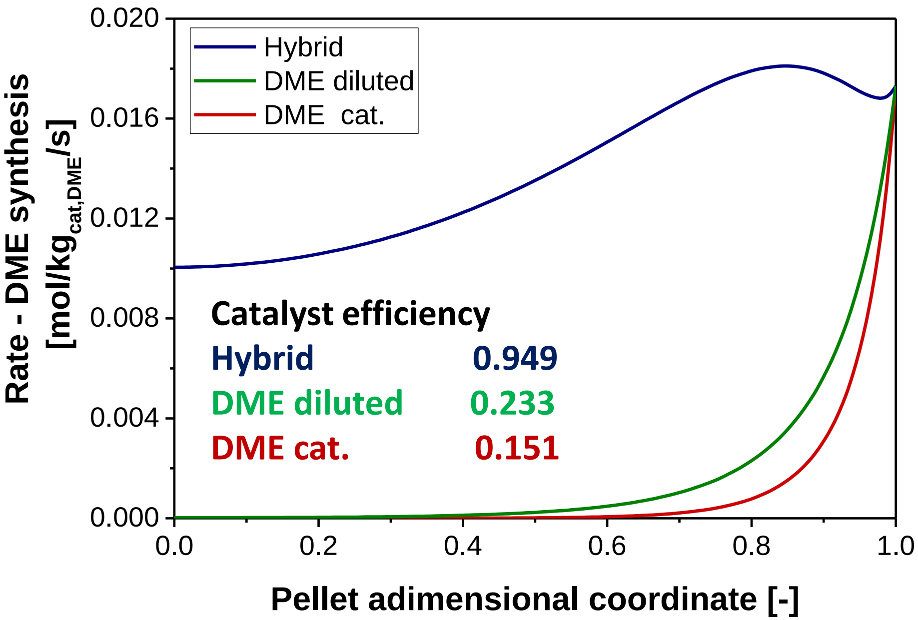
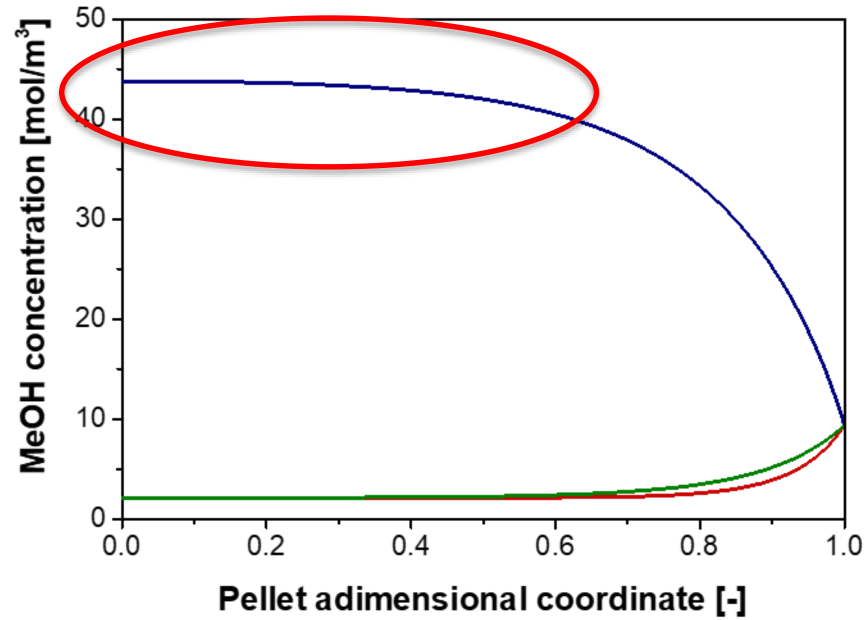
Dilution effects

Cat_{MeOH}/Cat_{DME} = 2 w/w

$$CO_2 + 3\,H_2 \rightarrow CH_3OH + H_2O$$
$$2\,CH_3OH \rightarrow CH_3OCH_3 + H_2O$$

$$R_{MeOH\,syn} = 2\,R_{DME\,syn}$$





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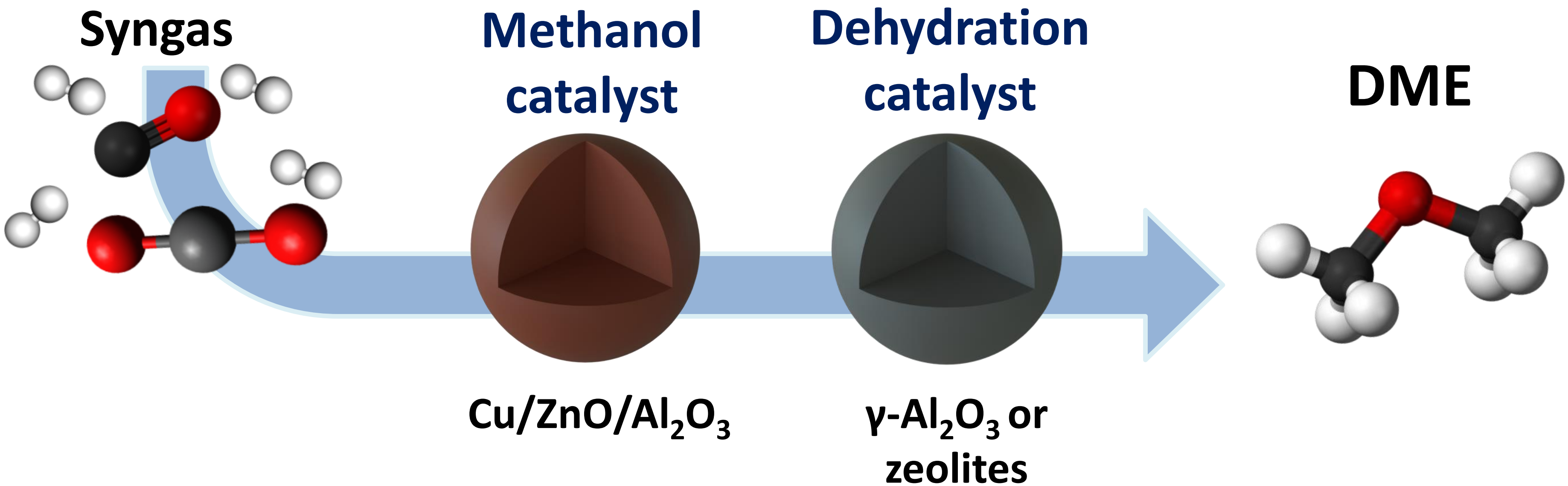
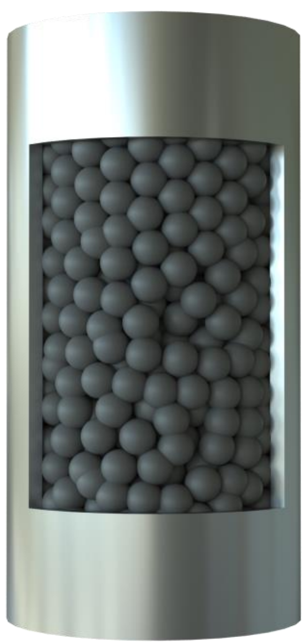
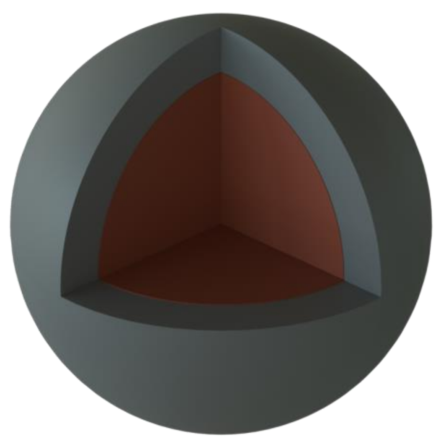
Catalyst configuration







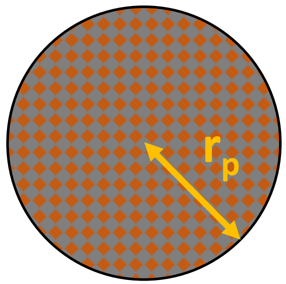
Core-shell pellet

G. Yang et al., J. Am. Chem. Soc., 132 (2010), 8129-8136
Y. Wang et al., Chem. Eng. J., 250 (2014), 248-256
W. Ding et al., Chem. Ing. Tech., 87 (6) (2015), 702-712

Catalyst configuration analysis

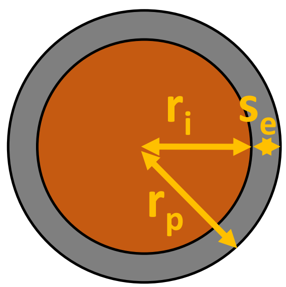
Cat_{MeOH}/Cat_{DME} **= 2 w/w**

Hybrid pellet



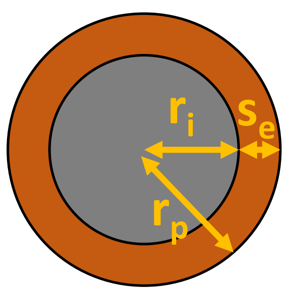
r_p=2.43 mm

Core-shell MeOH@DME



r_i=2.04 mm
s_e=0.39 mm

Core-shell DME@MeOH



r_i=1.80 mm
s_e=0.63 mm

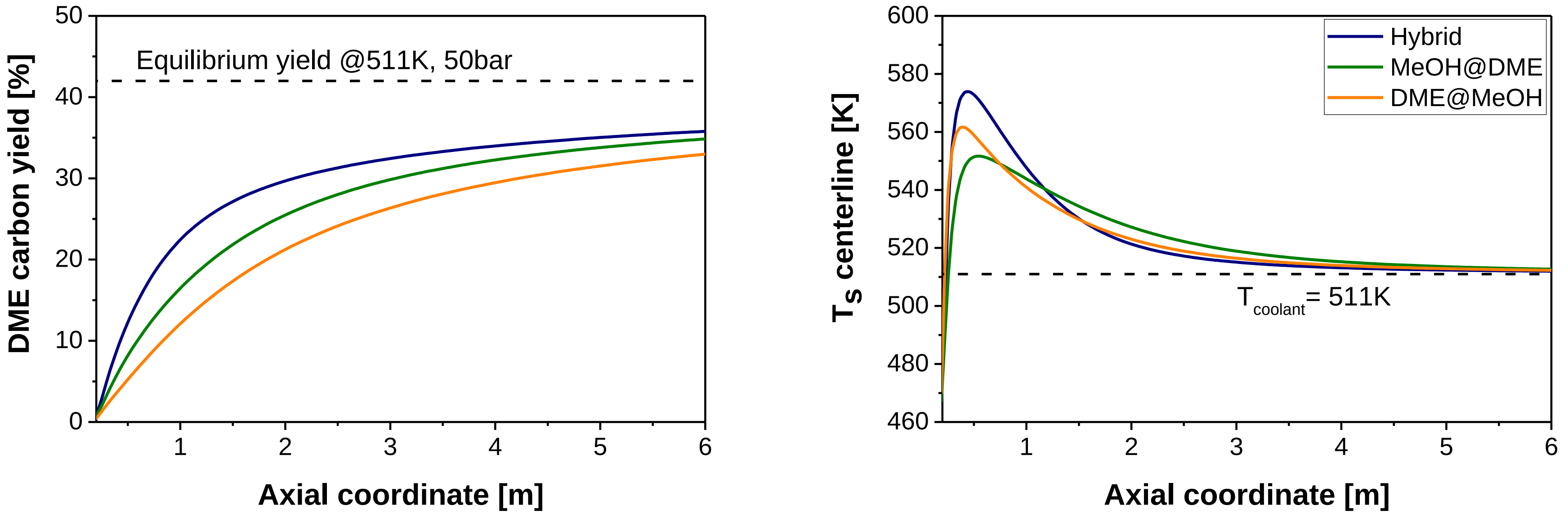
- **DME carbon yield**

$$Y_{DME} = \frac{2F_{DME}}{\left(F_{CO} + F_{CO_2}\right)_{in}}$$

- ***Reactor centerline temperature***
- ***Catalyst efficiency factor***

$$\eta_j = \frac{R_j^{cat,av}}{R_j^{cat,surf}}$$

Core-shell performances vs. hybrid



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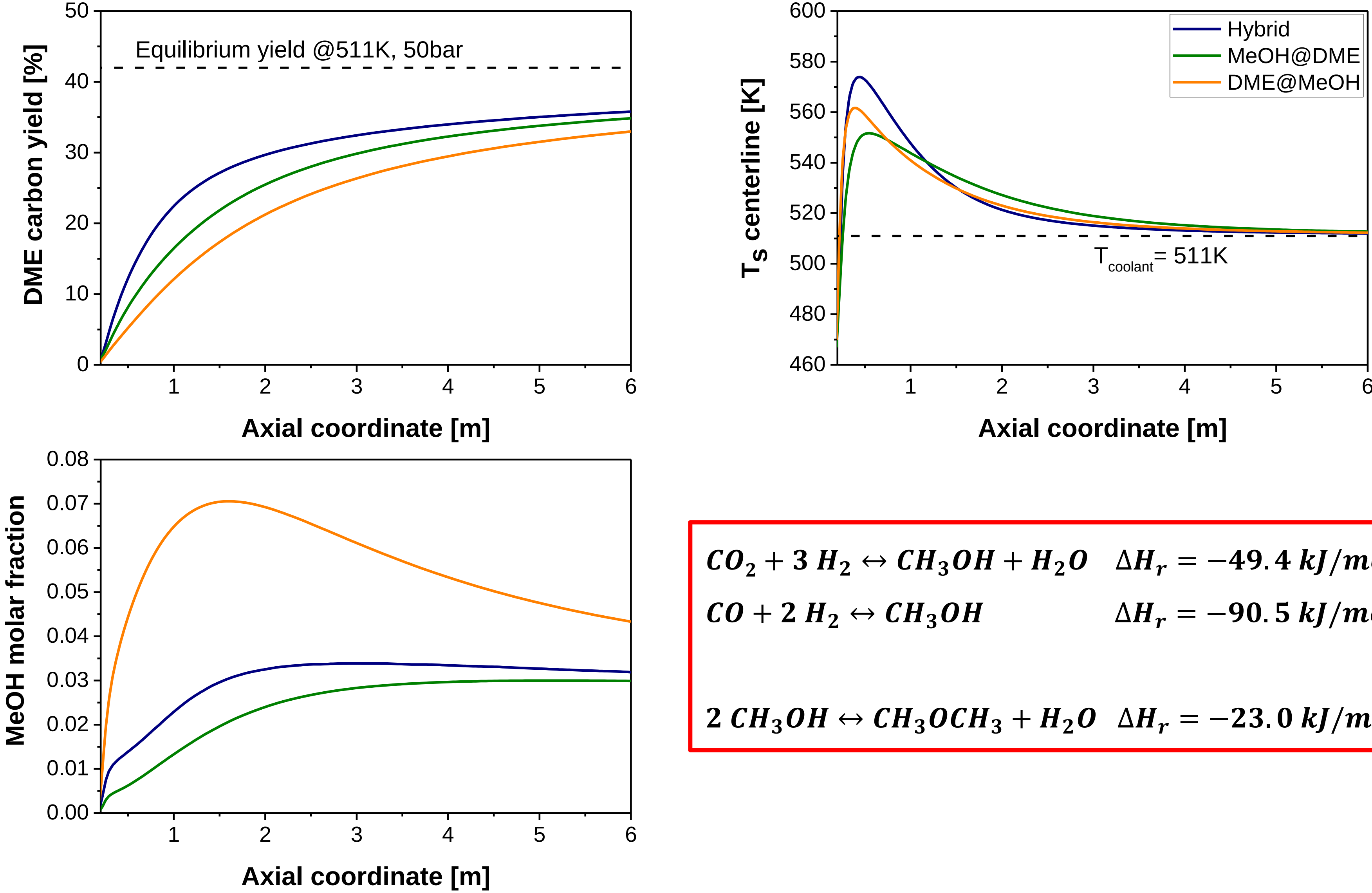
Core-shell performances vs. hybrid



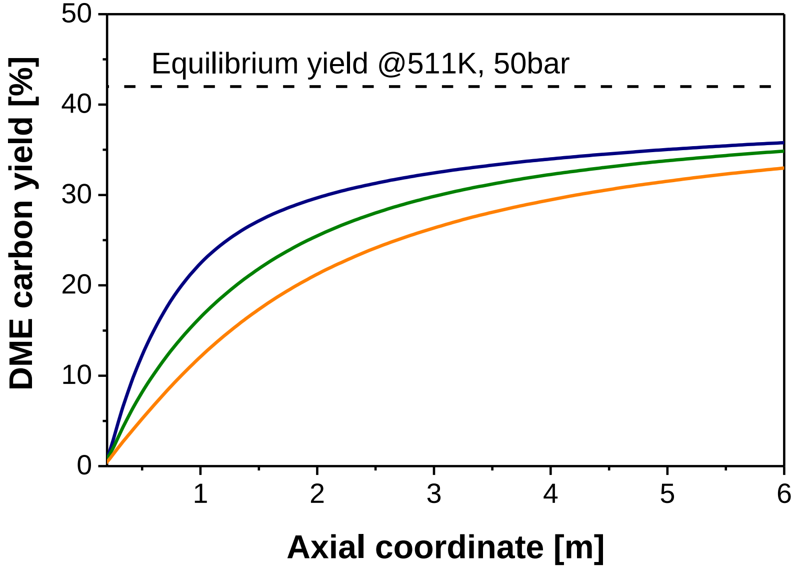
$$CO_2 + 3\,H_2 \leftrightarrow CH_3OH + H_2O \quad \Delta H_r = -49.4\ kJ/mol$$

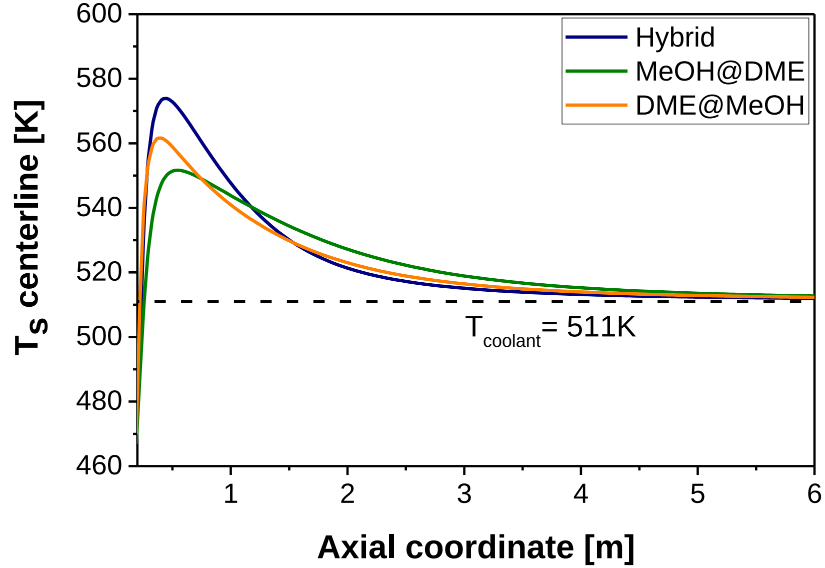
$$CO + 2\,H_2 \leftrightarrow CH_3OH \quad \Delta H_r = -90.5\ kJ/mol$$

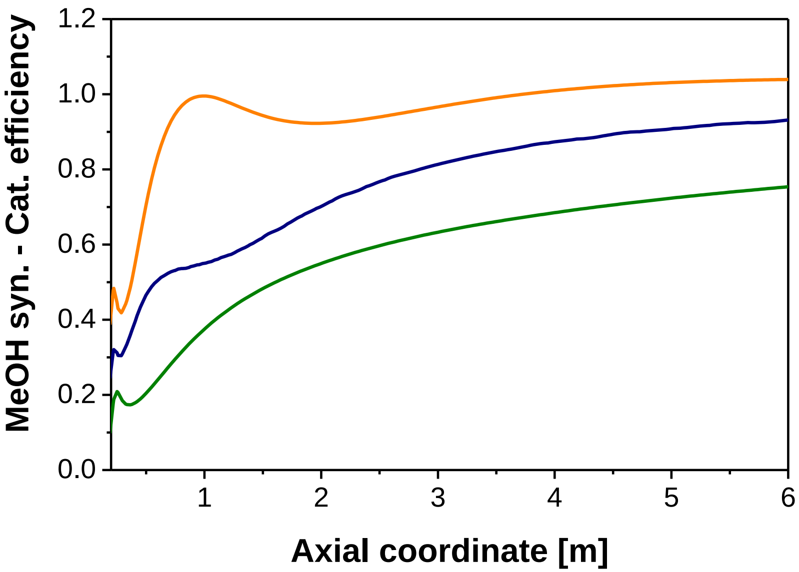
$$2\,CH_3OH \leftrightarrow CH_3OCH_3 + H_2O \quad \Delta H_r = -23.0\ kJ/mol$$

T_{inlet} = 323 K; P_{inlet} = 50 bar; GHSV = 1407 h^{-1}; M=(H_2-CO_2)/CO_x=1; CO/CO_2=1.3; D_{tube} = 25.65 mm; L_{tube} = 6 m; d_{pellet} = 4.85 mm; Cat_{MeOH}/Cat_{DME} = 2 w/w.

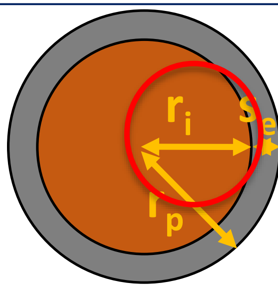
Core-shell performances vs. hybrid







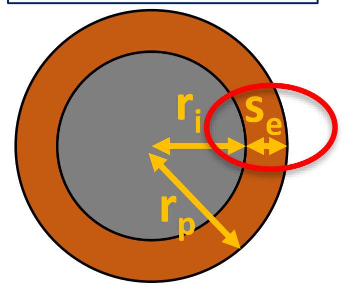
Core-shell MeOH@DME



r_i=2.04 mm

s_e=0.39 mm

Core-shell DME@MeOH



r_i=1.80 mm

s_e=0.63 mm

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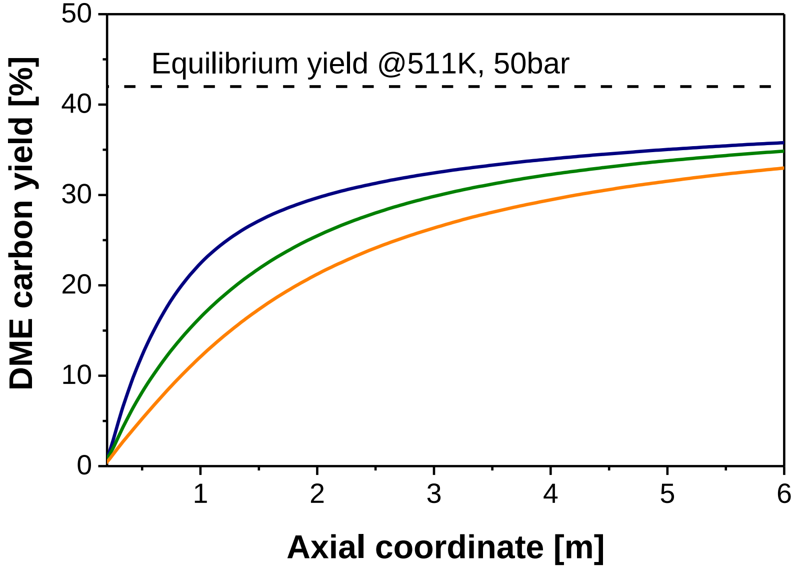
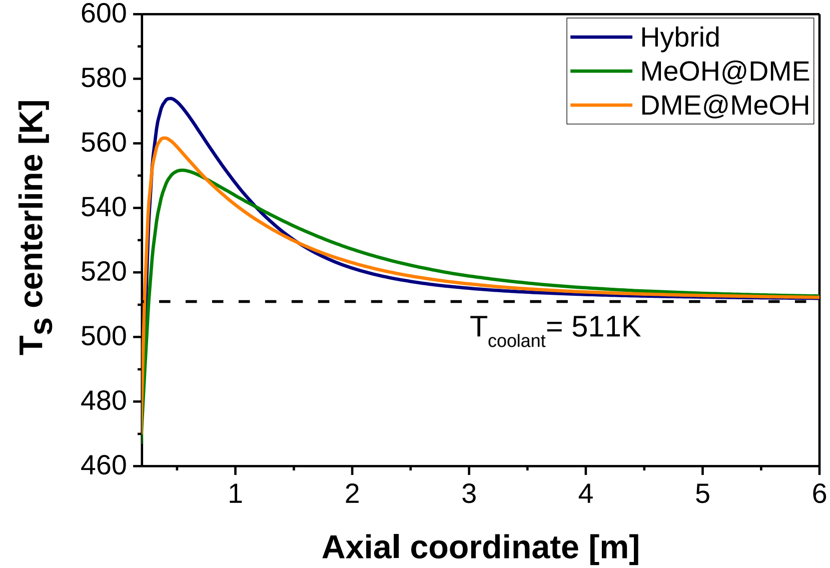
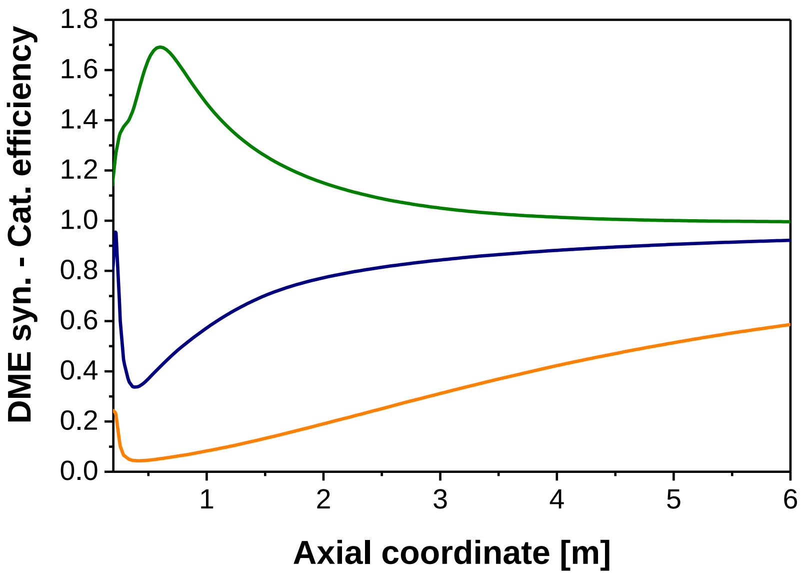
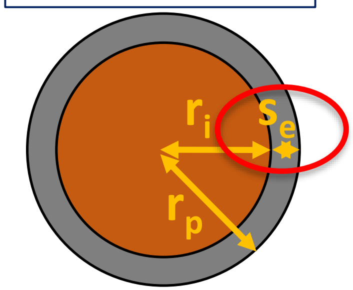
Core-shell performances vs. hybrid







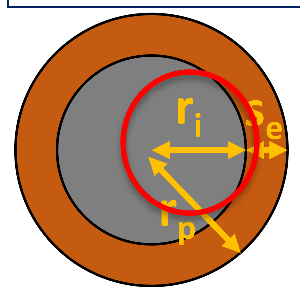
Core-shell MeOH@DME



r_i=2.04 mm

s_e=0.39 mm

Core-shell DME@MeOH



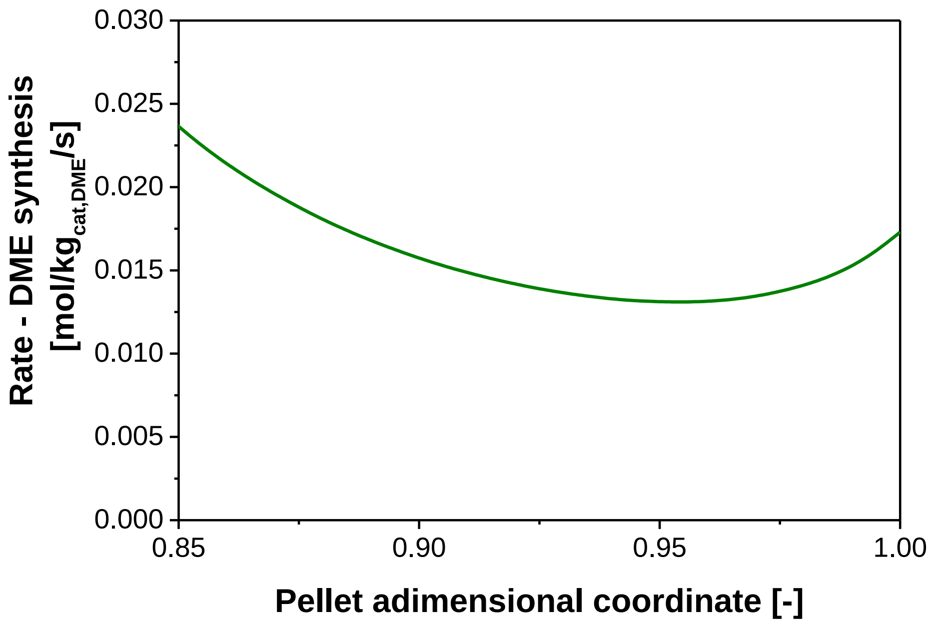
r_i=1.80 mm

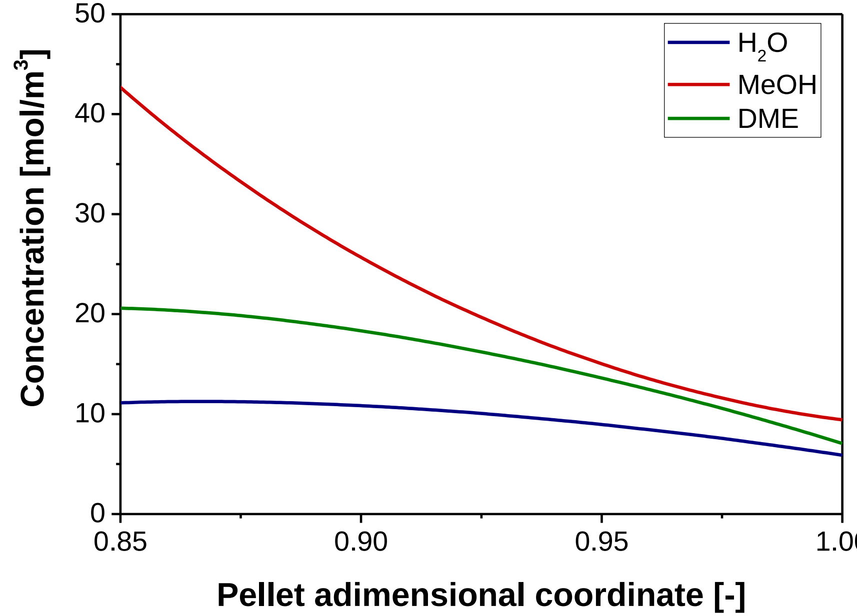
s_e=0.63 mm

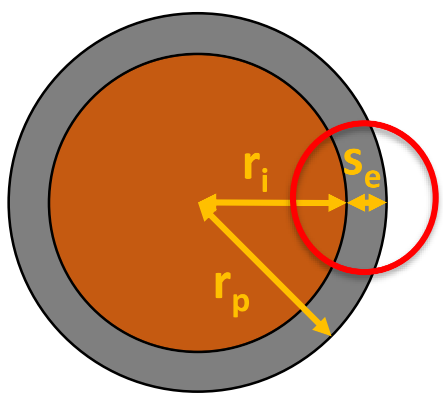
T_{inlet} = 323 K; P_{inlet} = 50 bar; GHSV = 1407 h^{-1}; M=(H_2-CO_2)/CO_x=1; CO/CO_2=1.3; D_{tube} = 25.65 mm; L_{tube} = 6 m; d_{pellet} = 4.85 mm; Cat_{MeOH}/Cat_{DME} = 2 w/w.

Core-shell performances: MeOH@DME

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







r_i=2.04 mm

s_e=0.39 mm

$$\eta_{DME\ syn} = \frac{R_{DME\ syn}^{cat,av}}{R_{DME\ syn}^{cat,surf}}$$

T = 511 K; P_{surf} = 50 bar; d_{pellet} = 4.85 mm; External surface composition: CO 20%, CO_2 17.5%, H_2 52.5%, H_2O 0.5%, MeOH 0.8%, DME 0.6 %, CH_4 8.3%.

Conclusions

- A 2D+1D heterogeneous single tube model of a direct DME synthesis multitubular reactor has been used to study the effects of diffusion phenomena in different catalysts configurations (hybrid pellet, mechanical mixture, core-shell).

- The hybrid configuration has shown the best performances in terms of DME yield, but it is reported in literature that can suffer from deactivation issues.

- In the case of the mechanical mixture the DME yield is strongly limited by the diffusion-reaction phenomena.

- The core-shell configuration MeOH@DME reaches a satisfying DME yield with lower interface contact between the two catalysts than in the hybrid pellet.

Thank you for your attention!

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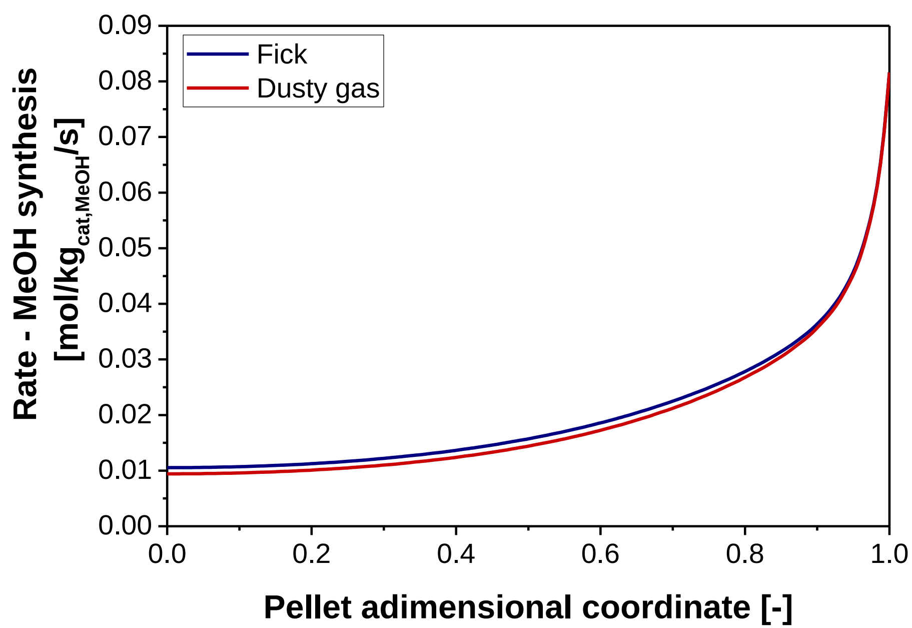
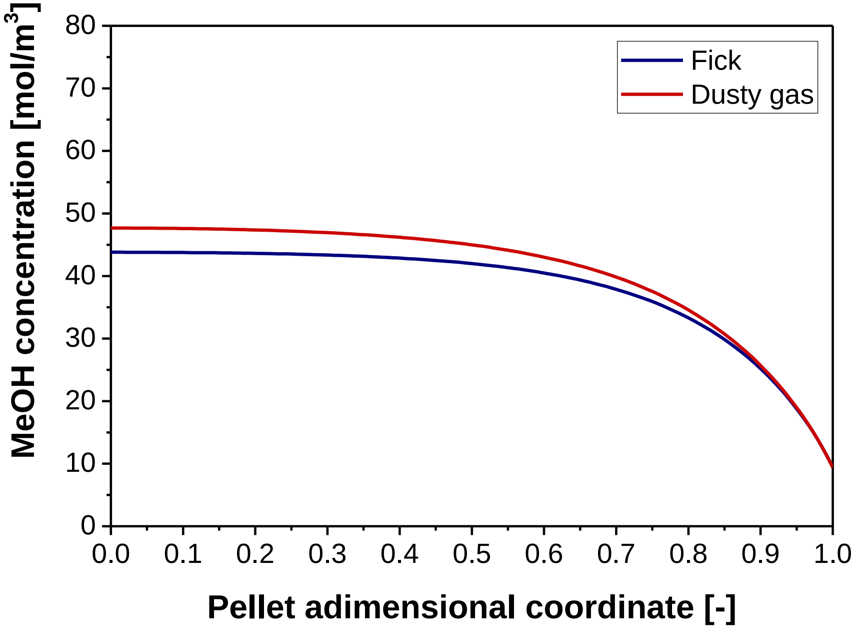
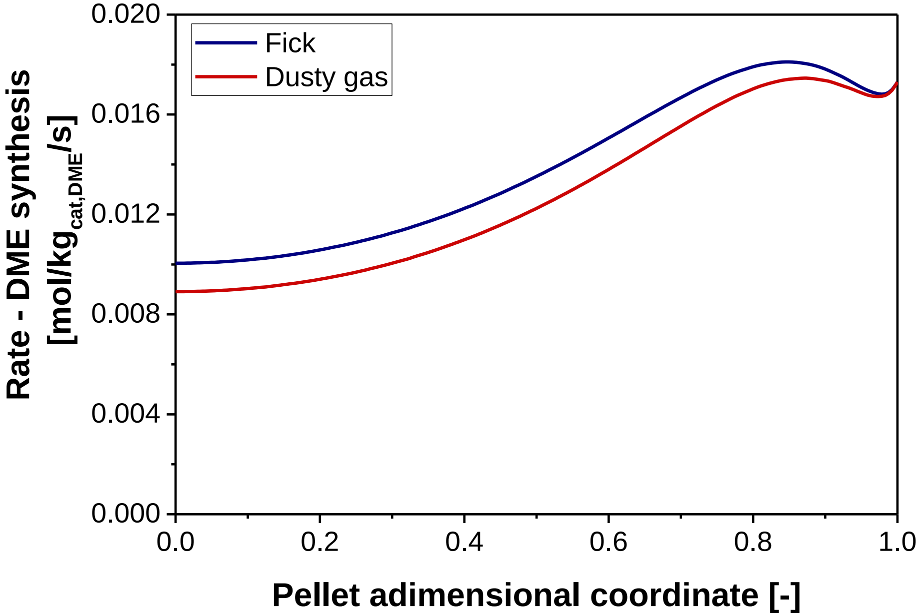
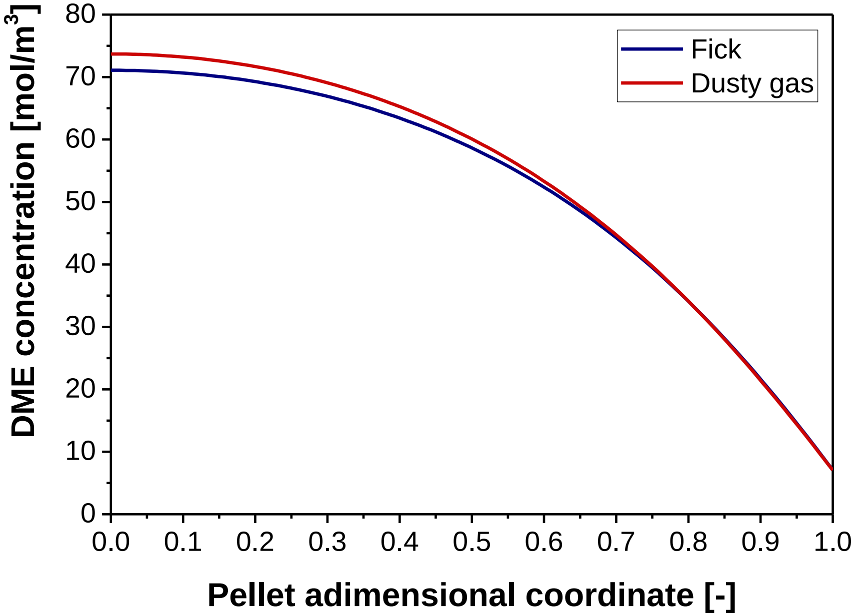
Fick model vs. Dusty gas model









$$D_{ij} = \frac{0.0143\, T_g^{1.75}}{P\sqrt{\frac{2000}{\frac{1}{MW_i}+\frac{1}{MW_j}}}\left[\left(\sum v_i\right)^{1/3} + \left(\sum v_j\right)^{1/3}\right]^2}$$

Fuller et al., 1969

$$D_{eff,i} = \frac{\frac{\varepsilon_p}{\tau}}{\frac{1}{D_{K,i}} + \frac{1}{D_{i,mix}}}$$

Bosanquet, 1944

$$D_{i,mix} = \left(\sum_{j=1, j\neq i}^{NC} \frac{x_{j,g}}{D_{ij}}\right)^{-1}$$

Reid et al., 2001

$$D_{er,i} = \varepsilon\left(D_{i,mix}\sqrt{\varepsilon} + 0.1\, d_{pe}\, v\right)$$

Wakao et Funazkri, 1978

$$D_{K,i} = 9700\, r_p \sqrt{\frac{T_s}{MW_i}}$$

Bosanquet, 1944

$$Sh_i = \frac{K_{m,i} d}{D_{i,mix}} = 1.26 Re_{d_{pe}} Sc_i^{1/3}\left(\left(\frac{1-(1-\varepsilon)^{5/3}}{2-3(1-\varepsilon)^{1/3}+3(1-\varepsilon)^{5/3}-2(1-\varepsilon)^2}\right)^{-0.5} Re_{d_{pe}}\right)^{-2/3}$$

Pfeffer, 1964

$$\frac{\lambda_{er}^{g}}{\lambda_g} = \varepsilon + \frac{1-\varepsilon}{0.22\,\varepsilon^2 + \frac{2}{3}\left(\frac{\lambda_g}{\lambda_{cat}}\right)} + \frac{Re_{d_{pa}} Pr}{8.65\left[1 + 19.4\left(\frac{d_{pa}}{d_t}\right)^2\right]\frac{d_{pv}}{d_{pa}}}$$

Specchia et Sicardi, 1980

$$h_w = \frac{\lambda_g}{d_{pv}}\left(2\varepsilon + \frac{1-\varepsilon}{0.0024\left(\frac{d_t}{d_{pv}}\right)^{1.58} + \frac{1}{3}\left(\frac{\lambda_g}{\lambda_{cat}}\right)}\right) + h_{w,conv}$$

Specchia et Sicardi, 1980

$$Nu = \frac{h_{w,cond}\, d_{pa}}{\lambda_g} = \begin{cases} Re_{d_{pa}} < 1200\,, & 0.0835 Re_{d_{pa}}^{0.91} \\ Re_{d_{pa}} \geq 1200\,, & 1.23 Re_{d_{pa}}^{0.53} \end{cases}$$

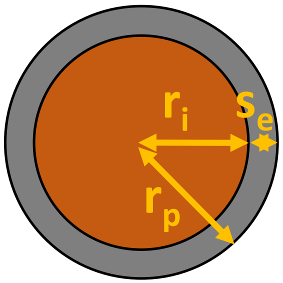
$$Nu = \frac{h\, d_{pe}}{\lambda_g} = 1.26 Re_{d_{pe}} Pr^{1/3}\left(\left(\frac{1-(1-\varepsilon)^{5/3}}{2 - 3(1-\varepsilon)^{1/3} + 3(1-\varepsilon)^{5/3} - 2(1-\varepsilon)^2}\right)^{-0.5} Re_{d_{pe}}\right)^{-2/}$$

Pfeffer, 1964

Eisfeld et Schnitzlein, 2001

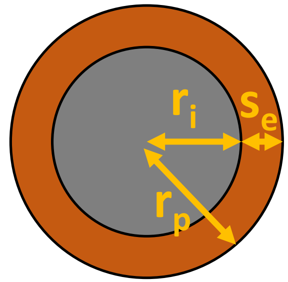
$$f_m = 23.75 \frac{\left(1 + \frac{2}{3\frac{d_t}{d_{pe}}(1-\varepsilon)}\right)^2}{\frac{d_p W_t}{\mu_g}} \frac{(1-\varepsilon)^2}{\varepsilon^3} + 0.125 \frac{\left(1 + \frac{2}{3\frac{d_t}{d_{pe}}(1-\varepsilon)}\right)}{\left(2\left(\frac{d_{pe}}{d_t}\right)^2 + 0.77\right)^2} \frac{(1-\varepsilon)}{\varepsilon^3}$$

Catalyst configuration analysis – core-shell



r_p=2.43 mm
r_i=2.03 mm
s_e=0.39 mm

MeOH@DME



r_p=2.43 mm
r_i=1.80 mm
s_e=0.63 mm

DME@MeOH

Cat_{MeOH}/Cat_{DME} = 2 w/w

1D solid mass balances

$$\frac{1}{x^2}\frac{\partial}{\partial x}\left(D_{eff,i}\, x^2 \frac{\partial \omega_i^s}{\partial x}\right) + \frac{\rho_s}{\rho_g} MW_i \sum_{j=1}^{NR} \nu_{ij} R_j = 0$$

Boundary conditions

$$\begin{cases} \omega_{surf} = \omega_i^s & r = r_p \\ D_{eff,i}\dfrac{\partial \omega_i^s}{\partial x}|_{r_{i+}} = D_{eff,i}\dfrac{\partial \omega_i^s}{\partial x}|_{r_{i-}} & r = r_i \\ \dfrac{\partial \omega_i^s}{\partial x} = 0 & r = 0 \end{cases}$$

MeOH@DME

$R_1, R_2 = 0 \qquad r > r_i$

$R_3 = 0 \qquad r < r_i$

DME@MeOH

$R_3 = 0 \qquad r > r_i$

$R_1, R_2 = 0 \qquad r < r_i$

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

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

3) $2\, CH_3OH \leftrightarrow CH_3OCH_3 + H_2O$