Sorption enhanced dimethyl ether synthesis: process analysis and reactor modelling

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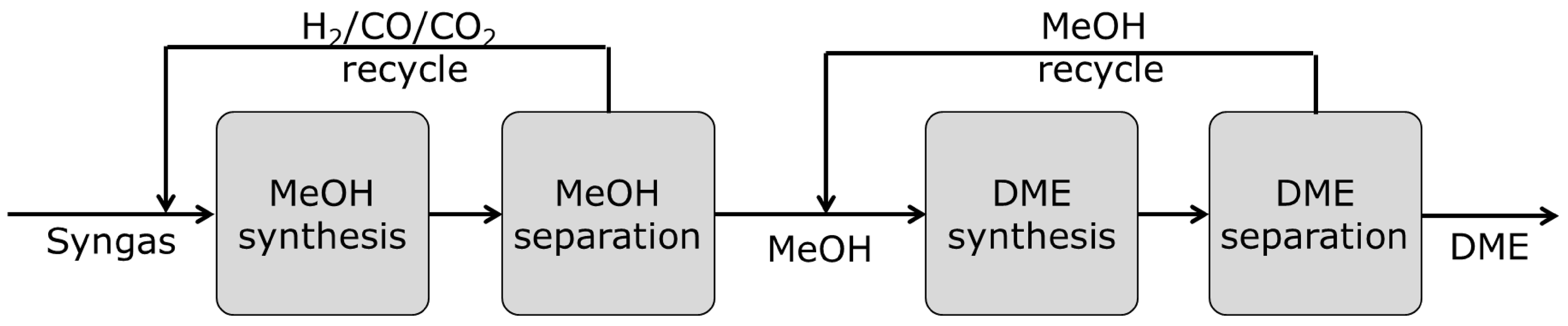
FLEDGED

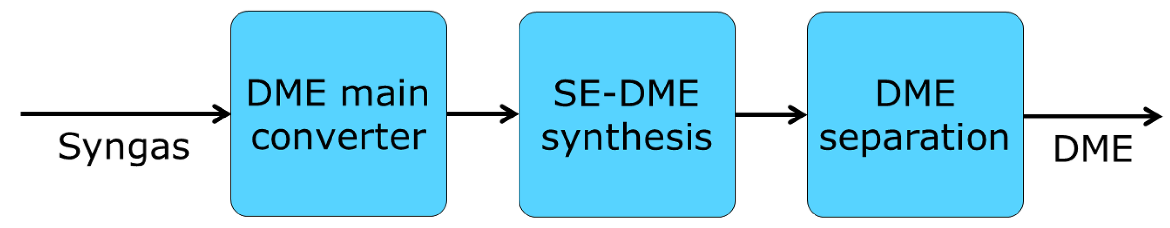
SE-DME PROCESS

In the SE-DME process, in-situ water removal is achieved through a steam adsorbent added into the direct DME synthesis catalytic bed. In this way, the single-pass DME yield is increased by overcoming thermodynamic limitations. This enables to eliminate the recycle typically used in conventional processes. The DME synthesis is characterized by exothermic reactions, as consequence the heat management plays a key role in control the thermodynamic and the kinetic of the process. This issue is here addressed by a 2D model analysis of the DME synthesis reactor.

Conventional process



SEDMES



THERMODYNAMIC ANALYSIS

Inlet stream

$M = \frac{H_2 - CO_2}{CO + CO_2} = 2$

$CO/CO_2 = 1.3$

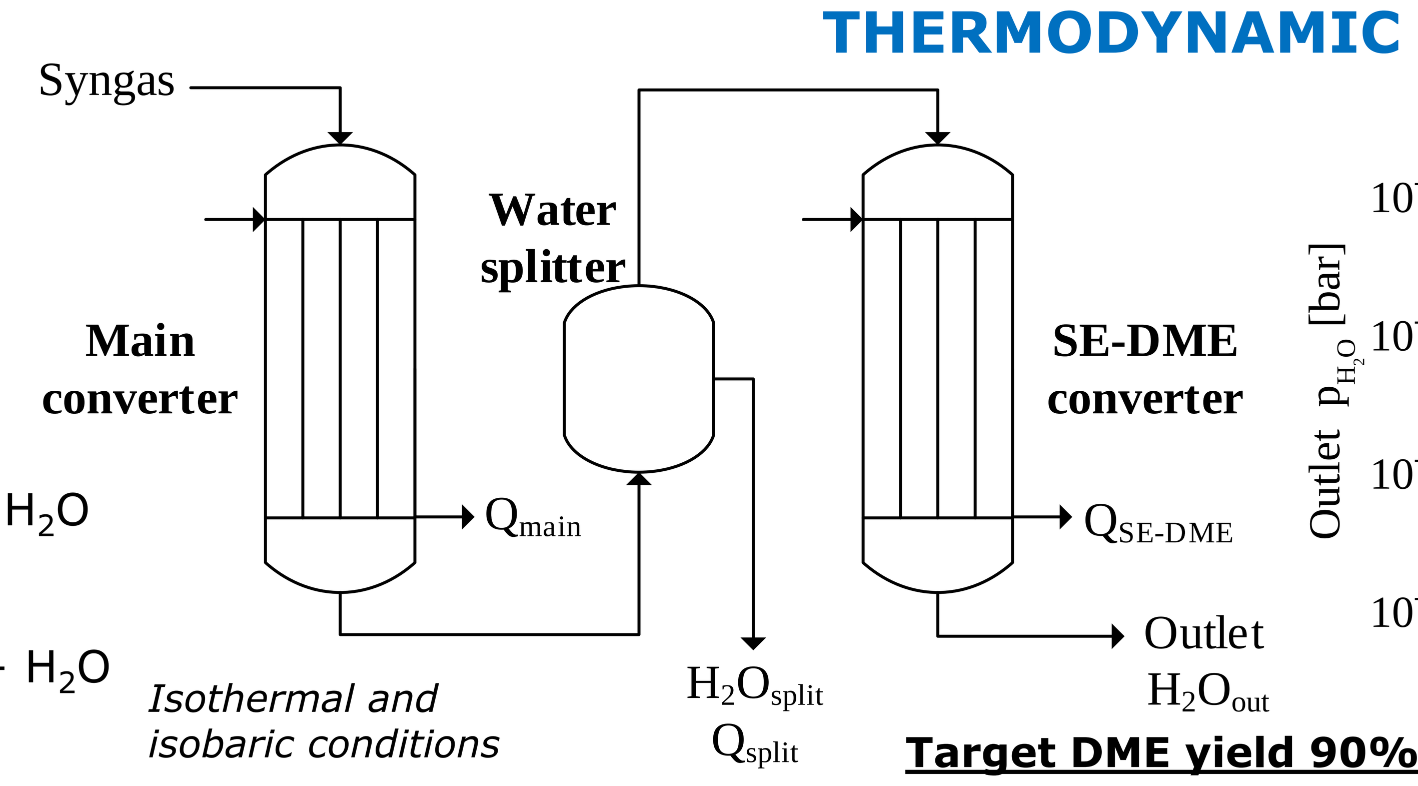
From biomass gassifier of a 100 MW_{th} plant

$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O$

$CO_2 + H_2 \leftrightarrow CO + H_2O$

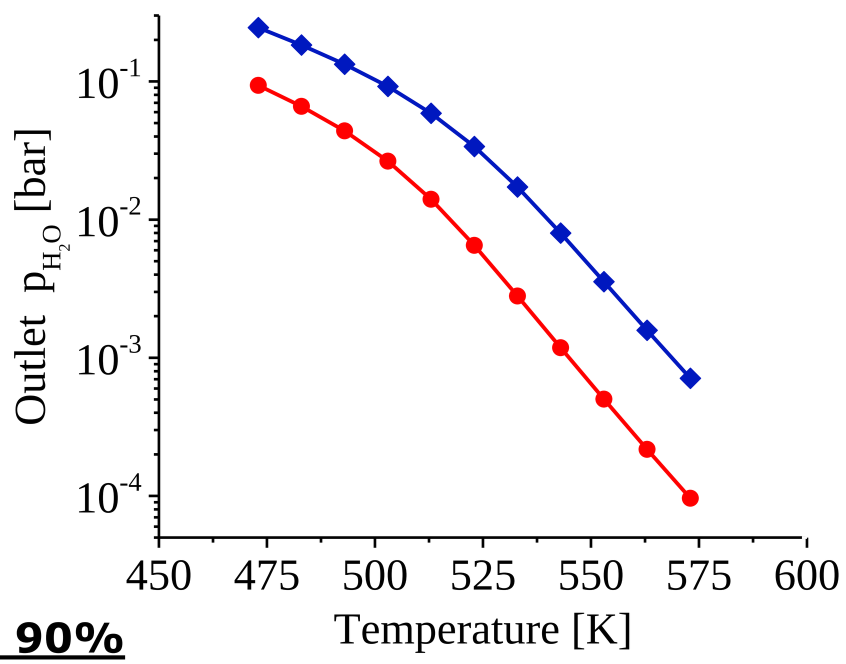
$2CH_3OH \leftrightarrow CH_3OCH_3 + H_2O$

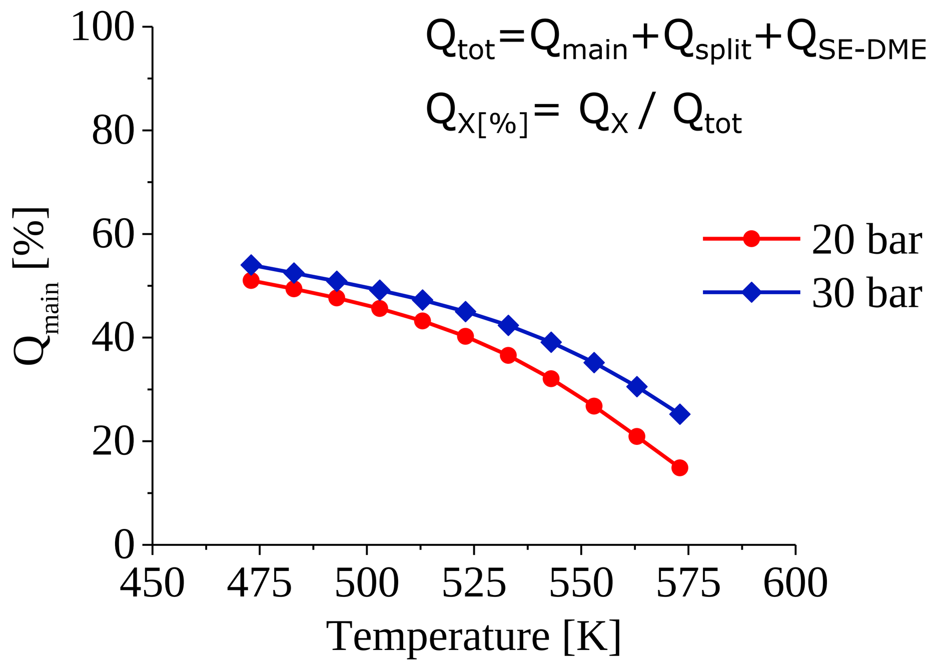
$H_2O \rightarrow H_2O_{ads}$



Isothermal and isobaric conditions

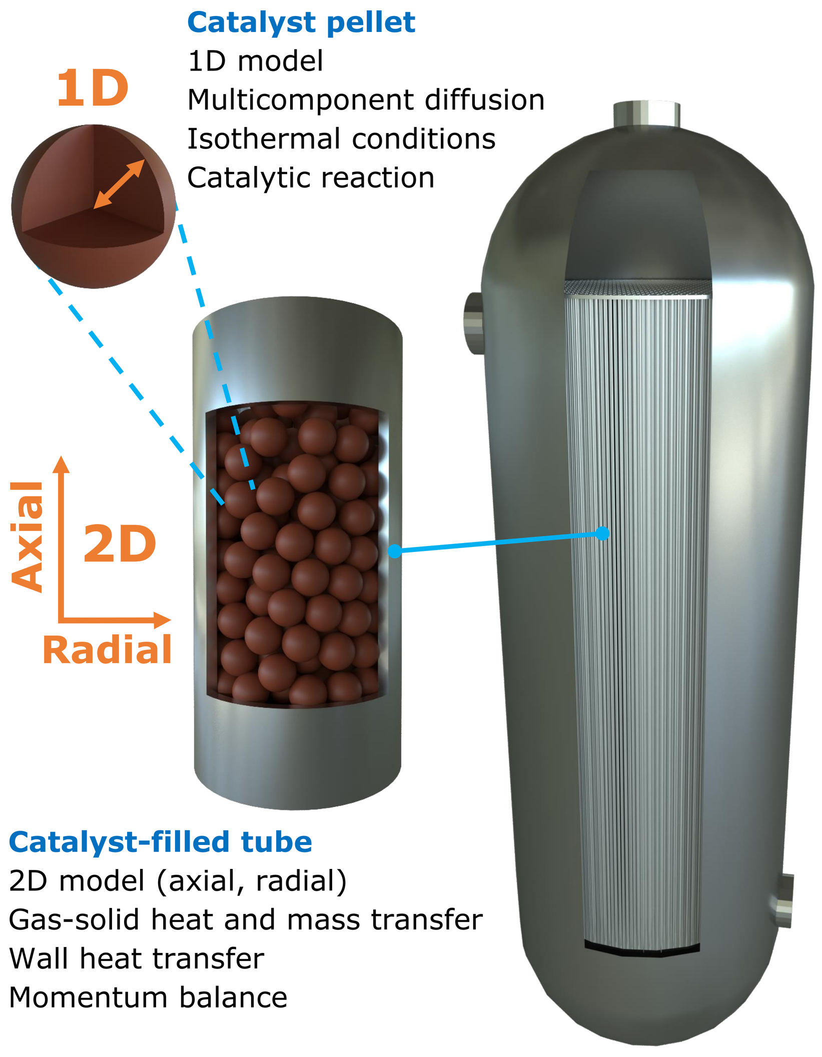
Target DME yield 90%





REACTOR MODEL

- Multi Tubular Reactor with external cooling
- Packed Bed Catalyst
- Single tube model
- 2D + 1D Reactor Model
- Heterogeneous (gas + solid)
- gPROMS commercial software



gPROMS PSE

MAIN CONVERTER MODEL EQUATIONS

MASS BALANCES

		Boundary conditions
$-W_t \frac{\partial \omega_{i,g}}{\partial z} + \rho_g D_{er,i}\left(\frac{\partial^2 \omega_{i,g}}{\partial r^2} + \frac{1}{r}\frac{\partial \omega_{i,g}}{\partial r}\right) + \rho_g K_{m,i} a_v(\omega_{i,s} - \omega_{i,g}) = 0$	**Gas phase (2D)**	• $z = 0;\ r[0,R]$ $\quad \omega_{i,g} = \omega_{i,g}^0$ • $z(0,L];\ r = 0$ $\quad \frac{\partial \omega_{i,g}}{\partial r} = 0$ • $z(0,L];\ r = R$ $\quad \frac{\partial \omega_{i,g}}{\partial r} = 0$
$\rho_g K_{m,i} a_v(\omega_{i,g} - \omega_{i,s}) + \rho_s \xi \sum_{j=1}^{NR} \nu_{ij} R_j^{eff}\, MW_i = 0$	**Interphase continuity**	
$\frac{\partial}{\partial x}\left(D_{eff,i}\frac{\partial C^s{}_i}{\partial x}\right) + \rho_s \sum_{j=1}^{NR} \nu_{ij} R_j = 0$	**Solid pellet (1D)**	• $x = 0;\ z[0,L];\ r[0,R]$ $\quad C_i^s = C_{i,s}$ • $x = r_{eq};\ z[0,L];\ r[0,R]$ $\quad \frac{\partial C_{i,s}}{\partial x} = 0$

ENERGY BALANCES

$-W_t C_{p,g}\frac{\partial T_g}{\partial z} + \lambda_{er}^g\left(\frac{\partial^2 T_g}{\partial r^2} + \frac{1}{r}\frac{\partial T_g}{\partial r}\right) + h a_v(T_{surf} - T_g) = 0$	**Gas phase (2D)**	• $z = 0;\ r[0,R]$ $\quad T_g = T_g^0$ • $z(0,L];\ r = 0$ $\quad \frac{\partial T_g}{\partial r} = 0$ • $z(0,L];\ r = R$ $\quad h_w(T_g - T_{cool}) = -\lambda_{er}\frac{\partial T_g}{\partial r}$
$h a_v(T_g - T_{surf}) + \rho_s \xi \sum_{j=1}^{NR} R_j^{eff}(-\Delta H_{R,j}^0) = 0$	**Interphase continuity**	

MOMENTUM BALANCE

$\left(\frac{\rho_g}{W_t^2} - \frac{1}{P}\right)\frac{\partial P}{\partial z} + \frac{1}{T_g}\frac{\partial T_g}{\partial z} + MW_g \sum_{i=1}^{NC} \frac{1}{MW_i}\frac{\partial \omega_{i,g}}{\partial z} + 2 f_m a_v = 0$	**Gas phase (2D)**	• $z = 0;\ r[0,R]$ $\quad P = P^0$

MAIN CONVERTER PARAMETERS ANALYSIS

Operating conditions

P_{in} = 30 bar
T_{in} = 323 K
T_{cool} = 511 K
Feed: M = 2; CO/CO$_2$ = 1.3

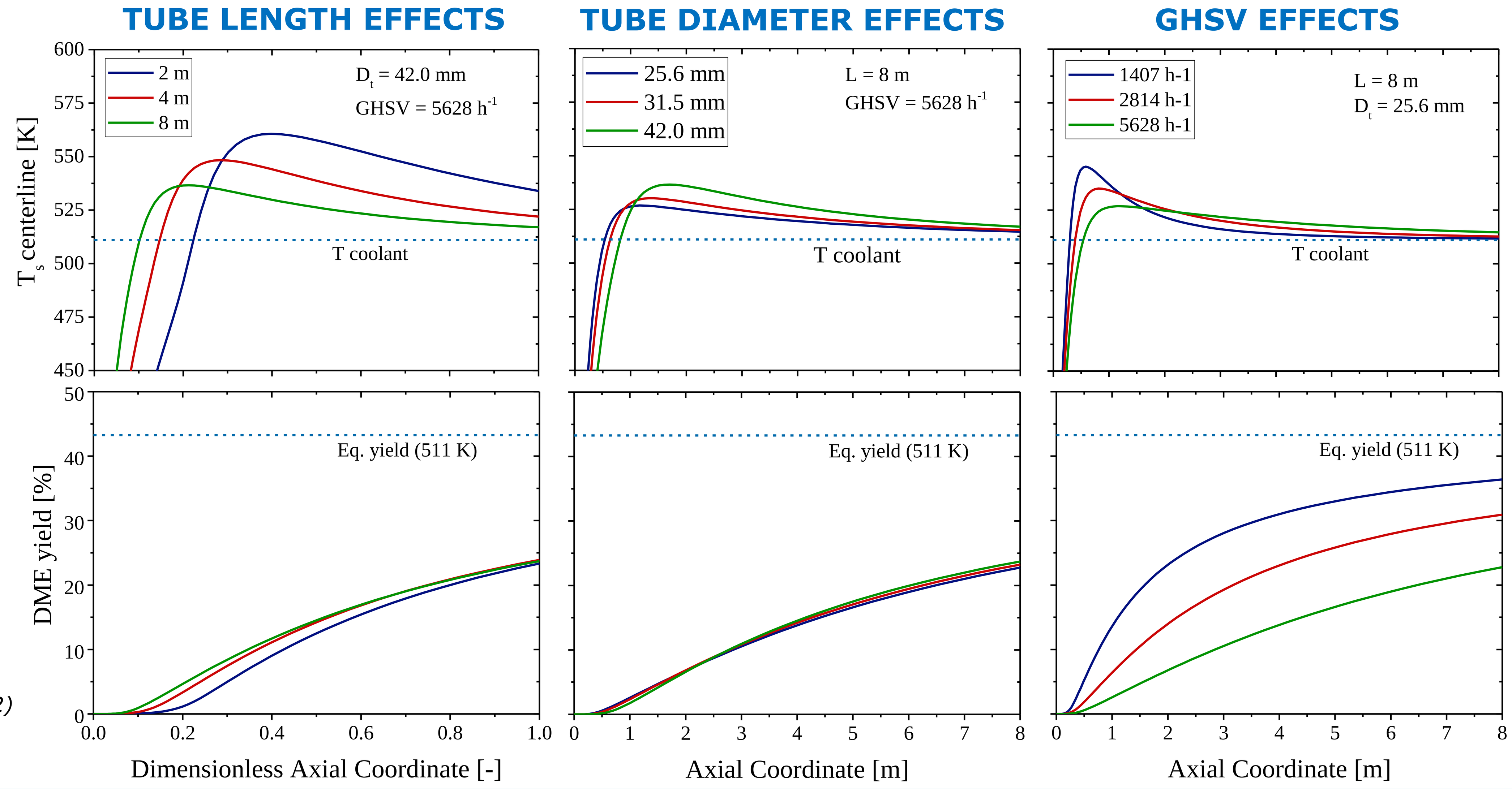
Cylindrical pellets

d_p = 6 mm
h_p = 3.5 mm
MeOH/DME cat. v/v ratio 2:1
$\rho_{s,MeOH}$ = 1712 kg/m^3
$\rho_{s,DME}$ = 1284 kg/m^3

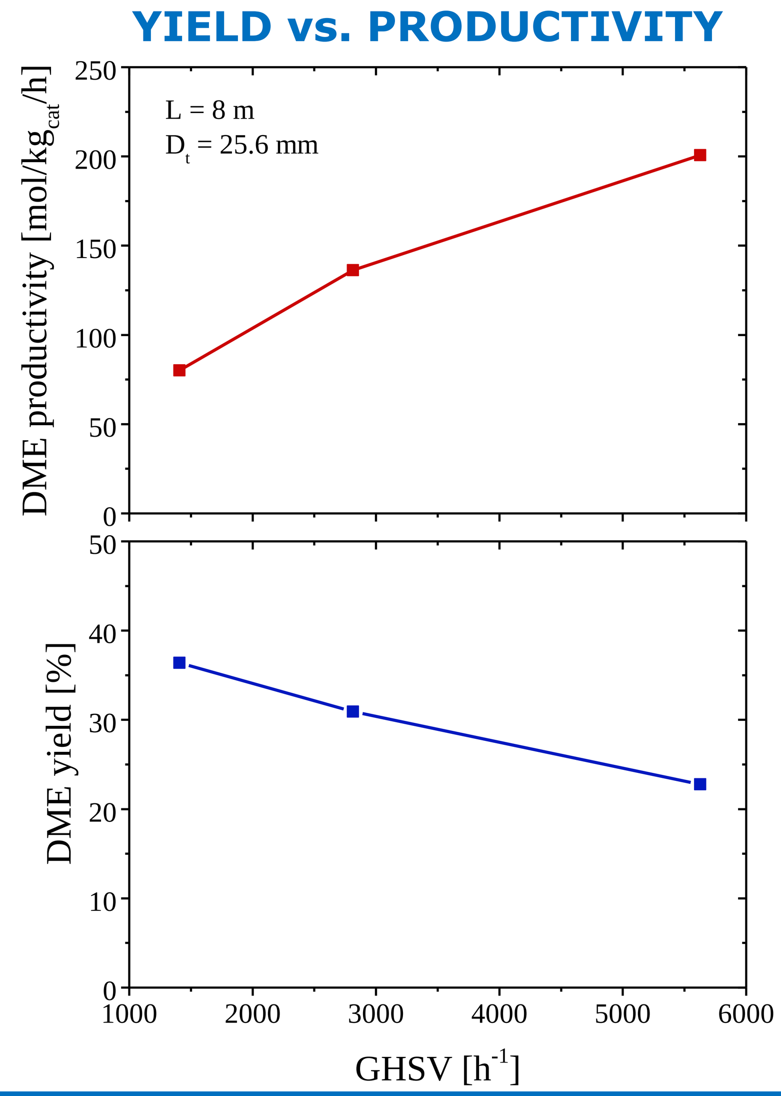
$$Y_{DME} = \frac{2F_{DME}}{(F_{CO} + F_{CO_2})_{in}}$$

Kinetic model:
Bercic et al., Ind. Chem. Eng. Res. 31 (1992)
Vanden Bussche et al., J. Catal. 161 (1996)
Ng et al., Chem. Eng. Sci. 54 (1999)

TUBE LENGTH EFFECTS / TUBE DIAMETER EFFECTS / GHSV EFFECTS



YIELD vs. PRODUCTIVITY



CONCLUSIONS

- The thermodynamic analysis has shown that a main converter positioned upstream to the process is required in order to reduce the heat duty to the SE-DME synthesis reactor.
- The heat management is a critical issue: geometrical parameters, as tube length and diameter, should be properly tuned to prevent excessively high hot-spots.
- The main converter DME yield can be increased adopting low GHSV, however this negatively affects the productivity and increases capital costs (N tubes).

ACKNOWLEDGEMENTS

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