Modelling and simulation of a direct synthesis of dimethyl ether (DME) in a tubular reactor with a hybrid catalyst bed

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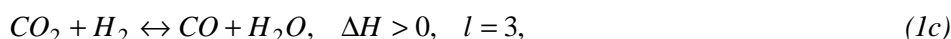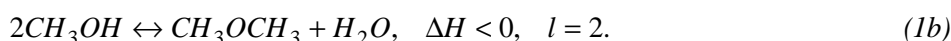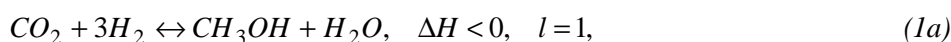
1. Summary

This work includes a modelling and simulation of dimethyl ether direct synthesis in a tubular type reactor with hybrid catalysts bed. The results of simulation show that the loading ratio of methanol synthesis and dehydration catalysts has a important influence on product yield.

Keywords: simulation, zeolite, hybrid catalyst bed, dimethyl ether

2. Extended Abstract

For a reaction system describing a direct synthesis of methyl ether from carbon dioxide and hydrogen:

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O, \quad \Delta H < 0, \quad l = 1, \qquad (1a)$$

$$2CH_3OH \leftrightarrow CH_3OCH_3 + H_2O, \quad \Delta H < 0, \quad l = 2. \qquad (1b)$$

$$CO_2 + H_2 \leftrightarrow CO + H_2O, \quad \Delta H > 0, \quad l = 3, \qquad (1c)$$

a mathematical model was created of an adiabatic tubular reactor with a plug flow. It was assumed that reference reagents are DME and CO_2. For carbon dioxide a change in number of moles was established, as concluded from reactions (1a) and (1c). Using the definition of the reaction progress number, ξ, running numbers of moles of DME and CO_2 were established. Defined was the dwell time, t and then a dimensionless time related to the maximum dwell time: $\tau = t \cdot t_{max}^{-1}$. Using these equations a differential control volume was written: $dV = \dot{F}_{ov} \cdot t_{max} \cdot d\tau$. The differential mass balance for individual reference compounds, including the initial conditions was written in the form:

$$\dot{F}_{on} \cdot d\left(y_{CO_2}^0 - \xi_1 - \xi_3\right) = -\dot{F}_{ov} \cdot t_{max} \cdot \rho_{z,1} \cdot r_1 \cdot d\tau, \qquad \xi_1(0) = 0, \quad (2a)$$

$$\dot{F}_{on} \cdot d\xi_2 = \dot{F}_{ov} \cdot t_{max} \cdot \rho_{z,2} \cdot r_2 \cdot d\tau, \qquad \xi_2(0) = 0, \quad (2b)$$

$$\dot{F}_{on} \cdot d\left(y_{CO_2}^0 - \xi_1 - \xi_3\right) = -\dot{F}_{ov} \cdot t_{max} \cdot \rho_{z,1} \cdot r_3 \cdot d\tau, \qquad \xi_3(0) = 0, \quad (2c)$$

$$\dot{F}_v \cdot \rho \cdot c_p \cdot dT = \left[\sum_{i=1}^{3}\left(-\Delta H_i\right)\cdot r_i \cdot \rho_{z,i}\right]\cdot \dot{F}_{ov}\cdot t_{max}\cdot d\tau, \qquad T(0)=T_p. \quad (2d)$$

In the set of equations (2) values appear that are related to the hybrid bed: $\rho_{z,1}$ means the density of catalyst in reaction (1a), and $\rho_{z,2}$ is the density of zeolite. The third reaction takes place in the presence of a catalyst of methanol synthesis. For further discussion the average density ρ_z of a hybrid bed was introduced, and also defined was a new value x as a dimensionless mass fraction of a zeolite catalyst in a mixed bed. Because of this, a notation $\rho_{z,1}=(1-x)\cdot\rho_z$ and $\rho_{z,2}=x\cdot\rho_z$ could be used. Used here was the established in the Ph.D. work (Anna Ptaszek, *Modelling of DME direct synthesis,* Gliwice, *2004*) kinetic equation of methanol dehydration on a zeolite catalyst:

$$r_2 = k \cdot \frac{K_{MeOH}^2 \cdot a_{p\,MeOH}^2 \cdot \left(1-\frac{a_{p\,H_2O}\cdot a_{p\,DME}}{K_{ap}\cdot a_{p\,MeOH}^2}\right)}{\left(1+K_{MeOH}\cdot a_{p\,MeOH}+K_{DME}\cdot a_{p\,DME}+K_{H_2O}\cdot a_{p\,H_2O}\right)^2} \quad (3)$$

Based on the available literature, selected were a methanol synthesis kinetics and kinetics of a reaction (1c) given by Vanden Bussche and Froment. Integrations of the system of equations (2) were performed for two sets of substrate compositions: $y_{H_2}^0=0.8$; $y_{CO_2}^0=0.2$ (fig.1a) and $y_{H_2}^0=0,.6$; $y_{CO_2}^0=0.2$ $y_{CO}^0=0.2$ (fig. 1b) under the following conditions: T_p=500 K, pressure changing from 1 to 5 MPa. In calculations it was also assumed that t_{max}=1, ρ_z=1000 and x=0.5. Therefore $\rho_{z,1}=\rho_{z,2}$=500.
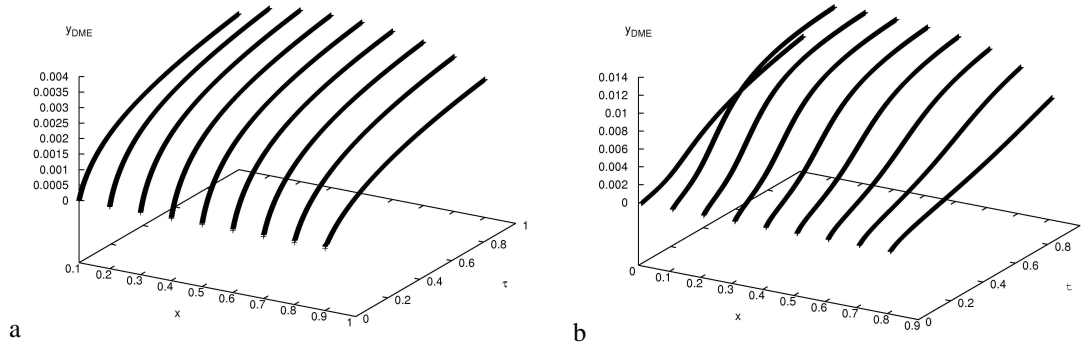

Figure 1: Dependence of DME molar fraction on dimensionless mass fraction of zeolite in a hybrid catalyst bed x and dimensionless time τ for two substrate compositions:
(a) $y_{H_2}^0=0.8$; $y_{CO_2}^0=0.2$, (b) $y_{H_2}^0=0.6$; $y_{CO_2}^0=0.2$; $y_{CO}^0=0.2$.

References

Vanden Bussche K. M, Froment G., (1996), *Journal of Catalysis,* 161, 1-10