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

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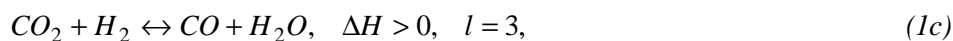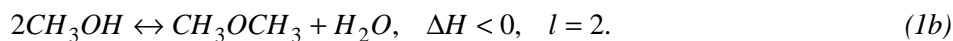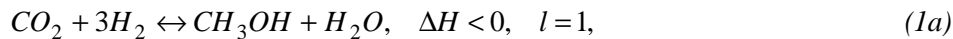[b]Faculty of Food Technology, Agricultural University of Cracow, Balicka 122, 30-149 Cracow, Poland

Abstract

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

1. Introduction

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 direct synthesis of DME,* Gliwice, *2004*) kinetic equation of methanol dehydration on a zeolite catalyst:

$$r_{1b} = k \cdot \frac{K_{MeOH}^2 \cdot a_{pMeOH}^2 \cdot \left(1 - \dfrac{a_{pH_2O} \cdot a_{pDME}}{K_{ap1b} \cdot a_{pMeOH}^2}\right)}{\left(1 + K_{MeOH} \cdot a_{pMeOH} + K_{DME} \cdot a_{pDME} + K_{H_2O} \cdot a_{pH_2O}\right)^2} \qquad (3)$$

Based on the available literature, selected were a methanol synthesis kinetics and kinetics of a reaction (1c) given by Vanden Bussche and Froment. In these equations reaction rates were expressed as functions of partial pressures of reagents, because the reactive mixture was treated as the ideal one. Since this work used a different composition of substrate mixture for calculations prior to applying the above equations, therefore the calculations were conducted of reagent activity coefficients for a seven-component mixture under various pressures. Calculations have shown that their pressure activity values are significantly outside of the interval given by Vanden Bussche and Froment. In order to introduce the necessary corrections into kinetic equations, kinetic data was generated based on the original equations. This information was used to estimate coefficients of pre-exponential parameters $k_{1a}^{'}$ and $k_{1c}^{'}$ for new kinetic equations that consider pressure activity

$$r_{1a} = k_{1a}^{'} \cdot \frac{a_{pCO_2} \cdot a_{pH_2} \cdot \left(1 - \dfrac{a_{pH_2O} \cdot a_{pMeOH}}{K_{ap1a} \cdot a_{pH_2}^3 \cdot a_{pCO_2}}\right)}{\left(1 + K_1 \cdot \dfrac{a_{pH_2O}}{a_{pH_2}} + \sqrt{K_2 \cdot a_{pH_2}} + K_3 \cdot a_{pH_2O}\right)^3} \qquad (4)$$

$$r_{1c} = k_{1c}^{'} \cdot \frac{a_{pCO_2} \cdot \left(1 - \dfrac{a_{pH_2O} \cdot a_{pMeOH}}{K_{ap1c} \cdot a_{pH_2}^3 \cdot a_{pCO_2}}\right)}{\left(1 + K_1 \cdot \dfrac{a_{pH_2O}}{a_{pH_2}} + \sqrt{K_2 \cdot a_{pH_2}} + K_3 \cdot a_{pH_2O}\right)} \qquad (5)$$

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 $\rho_{z,1} \dot{=} \rho_{z,2}$=500.

2. Results

At first, analysed were the results obtained for a mixture of substrates consisting exclusively of hydrogen and carbon dioxide. Figure 1a shows the relationship between the molar fraction of ether and a dimensionless time τ and pressure p. Presented results demonstrate a small production of ether. The increase in pressure does not increase the amount of ether generated. When analysing the final value of the molar fraction of ether, one can see a small local maximum. This effect can be explained by a rate-reducing effect of water generated in the reaction system. In the range of lower pressures not enough water is generated to significantly reduce the rate of methanol synthesis. As the pressure increases the quantity of water becomes significant. That the presence of water implies the reduction in rate of methanol synthesis, and as a result: the reduction in rate of synthesis of methyl ether. The catalyst used in ether synthesis is not sensitive to the presence of a large amount of water in the reaction mixture.

On the following charts (fig. 1b) shown are the conclusions form the calculations obtained for a mixture of substrates of a composition: $y_{H_2}^0 = 0.6$, $y_{CO_2}^0 = 0.2$, $y_{CO}^0 = 0.2$.

When analysing shown results, one can notice a significant increase in the quantity of obtained ether, in comparison to results described previously.
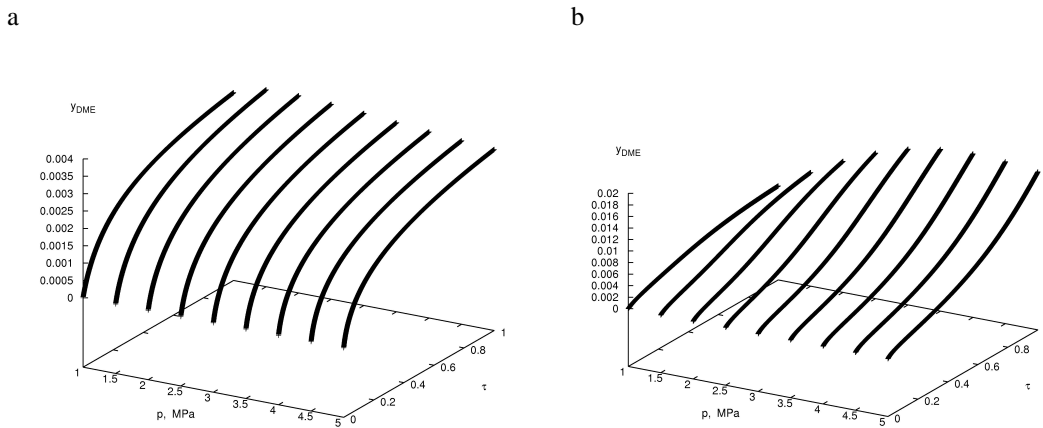
a   b

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

This is caused by water that is used up in the water gas reaction. On the chart (fig. 1b) showing the relationship between $y_{DME}(1)$ and pressure (end data points on the line $y_{DME}=y_{DME}(\tau)$) one can additionally observe the presence of a local maximum concentration of DME at the exit of the reactor. In the range of average pressures, the increase of methanol synthesis rate, based on le Chatelier rule stimulates generation of

DME. Further pressure p increase does not increase the rate of dehydration of MeOH, so this reaction „does not keep up" with the increased generation of methanol.

On subsequent figure 2 presented is the relationship between the molar fraction of DME and τ and the composition of the hybrid bed. Figure 2a shows results obtained for substrates consisting exclusively of hydrogen and carbon dioxide in 4:1 proportion respectively, at the total pressure of 2 MPa. The maximum amount of dimethyl ether at the exit from the reactor can be obtained in a bifunctional bed, in which the zeolite catalyst consists of 20%-40% of the total mass. The further increase in the contribution of HZSM-5 in the mixed bed implies a small drop in the value of y_{DME} at the exit from the reactor. Figure 2b illustrates the relationship between y_{DME} and dimensionless time τ and mass fraction of zeolite catalyst x in hybrid bed for a mixture of substrates: hydrogen, carbon dioxide and carbon monoxide. For x within an interval 0.1 - 0.3 of molar fraction of methyl ether, y_{DME} assumes maximum values. As the fraction of zeolite catalyst increases in the bed, the quantity of methyl ether decreases. If γ-Al_2O_3 was a catalyst for dehydration of methanol then, as indicated by literature (Ng et all), it would have to constitute 67% of hybrid bed. Such a significant quantity of catalyst must compensate its large drop in activity caused by presence of water. When analysing calculation results presented above, one can notice that in the case of HZSM-5 even a 40% wt. fraction in the hybrid bed ensures an acceptable degree of reaction of methanol to ether.
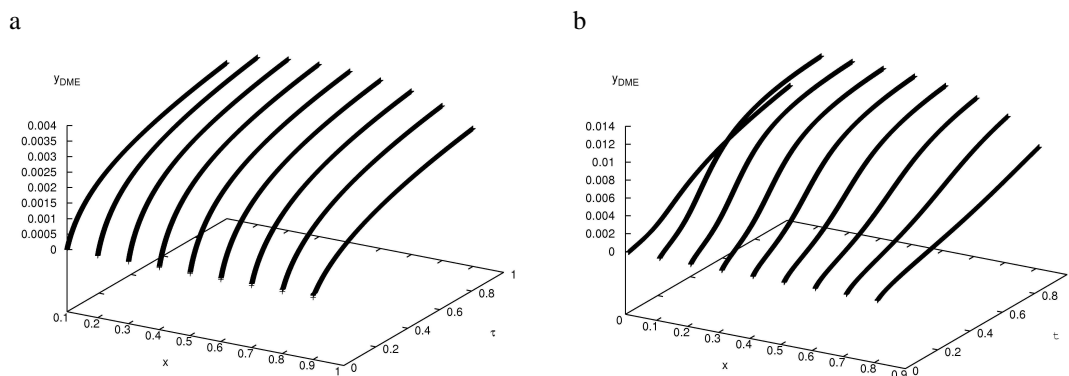

Figure 2: Dependence of DME molar fraction on dimensionless mass fraction of zeolite in a hybrid catalyst bed x and dimensionless time τ for two substrate compositions: (a) $y_{H_2}^0 = 0.8$; $y_{CO_2}^0 = 0.2$, (b) $y_{H_2}^0 = 0.6$; $y_{CO_2}^0 = 0.2$; $y_{CO}^0 = 0.2$.

References

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