

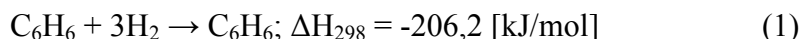
Hydrogenation of Benzene - Modeling of a Commercial Catalyst Bed.

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Hydrogenation of benzene to cyclohexane is an important case of the large-scale chemical processes. The reaction described by equation



is the first stage of a caprolactam production process according to the polish technology named CYCLOPOL. The industrial process is conducted in heterogeneous multitubular reactor at temperature in range 150-260°C on a commercial catalyst KUB-3 (manufacturer: Fertilizers Research Institute, Pulawy, POLAND). The main components of the KUB-3 catalyst are Ni, NiO, and Al₂O₃. Nickel is the active component of the catalyst while alumina is a structural promoter which provides the catalyst with high thermal stability. Physicochemical properties of the KUB-3 are as follows:

- chemical composition, wt. % NiO min. 45 (NiO to Ni reduction degree min. 40%), Al₂O₃ as a support
- balls of a diameter 4-6 mm
- density $1.0 \pm 0.1 \text{ kg/dm}^3$

Hydrogenation of benzene is conducted in two stages. Partial hydrogenation takes place in the first stage, under pressure 0.3 MPa in a shortage of hydrogen. In the second one, benzene is, in practice, completely hydrogenated to cyclohexane under pressure 1.0 MPa and an excess of hydrogen. In the catalyst bed there appears a reaction zone, which runs, step by step, along the reactor during its normal operation. The zone position change results from a progress of catalyst bed deactivation which is caused by sorption of sulphur compounds and coke deposition. Full deactivation process of the first catalyst bed lasts about 1-4 years. Nitrogen is the inert component of the reaction mixture.

Presented in the Table 1 model concerns the reactor at the first stage of benzene hydrogenation. It is assumed that catalyst is deactivated only by sorption of thiophene. The model is described by differential-algebraic equations set and contains mass balance equations for fluid and for pellet (for hydrogen, benzene, cyclohexane, nitrogen and thiophene) and heat balance equations for fluid and for pellet. The presented model is of a semiempirical type. It was developed using theoretical equations with experimental rate equation (fully described in [1]) and transfer coefficients were calculated from commonly accepted mass and heat transfer correlations [2]-[4]. Model equations set was solved using the authors' own program Estym_mh, which is able to solve differential equations by collocation on finite elements method. Results of the simulation were verified by comparison with single unit tube temperature measurements and are presented in Fig.1.

Typical results of simulations of the first stage reactor for hydrogenation of benzene are presented in Fig. 2. Catalyst bed was completely deactivated after approximately 3 years and 2 months. Such a result corresponds to the value presented above.

Table 1. Model of reactor of hydrogenation of benzene

| mass and heat balance equations for fluid | mass and heat balance equations for catalyst pellet |
|--|---|
| <p>hydrogen mass balance</p> $\varepsilon_e \frac{\partial C_A}{\partial t} + \frac{\partial}{\partial x} (u C_A) - \varepsilon_e D_{L,A} \frac{\partial^2 C_A}{\partial x^2} =$ $= -k_{g,A} \frac{3}{R} (1 - \varepsilon_e) (C_A - C_{Ap}(r = R))$ <p>initial and boundary conditions</p> <p>$t = 0$ and $x \in (0, L)$: $C_A = C_{Ain}$</p> <p>$t > 0$ and $x = 0$: $u C_{Ao} = u C_A - \varepsilon_e D_{L,A} \frac{\partial C_A}{\partial x}$</p> <p>$t > 0$ and $x = L$: $\frac{\partial C_A}{\partial x} = 0$</p> $u = u_o \frac{C_{To} - C_{Ao}}{T_o - C_{Ao}}$ <p>mass balances for other components</p> $C_B = \frac{p}{R_g T} \left[\frac{\frac{C_{Bo}}{C_{To}} - \frac{1}{3} \frac{C_{Ao}}{C_{To}} \alpha_A}{1 - \frac{C_{Ao}}{C_{To}} \alpha_A} \right]$ $C_C = \frac{p}{R_g T} \left[\frac{\frac{C_{Co}}{C_{To}} + \frac{1}{3} \frac{C_{Ao}}{C_{To}} \alpha_A}{1 - \frac{C_{Ao}}{C_{To}} \alpha_A} \right]$ $C_D = \frac{p}{R_g T} \left[\frac{\frac{C_{Co}}{C_{To}}}{1 - \frac{C_{Ao}}{C_{To}} \alpha_A} \right]$ <p>poison mass balance</p> $\frac{\partial y_S}{\partial t} + \frac{1}{\varepsilon_e} \frac{\partial (u y_S)}{\partial x} - D_L \frac{\partial^2 y_S}{\partial x^2} =$ $= -k_{g,S} \frac{3}{R} \frac{(1 - \varepsilon_e)}{\varepsilon_e} (y_S - y_{Sp}(r = R))$ <p>initial and boundary conditions</p> <p>$t = 0$ and $x \in (0, L)$: $y_S = 0$</p> <p>$t > 0$ and $x = 0$: $u(1 - y_S) = -\varepsilon_e D_L \frac{\partial y_S}{\partial x}$</p> <p>$t > 0$ and $x = L$: $\frac{\partial y_S}{\partial x} = 0$</p> <p>heat balance</p> $\frac{\partial}{\partial t} \left(\sum C_i C_{pi} T \right) + \frac{\partial}{\partial x} \left(\frac{u}{\varepsilon_e} \sum C_i C_{pi} T \right) - D_{L,T} \frac{\partial^2 T}{\partial x^2} =$ $= -k_T \frac{3}{R} \frac{(1 - \varepsilon_e)}{\varepsilon_e} (T - T_K(r = 0)) + \frac{k_W}{\varepsilon_e} \frac{4}{D_K} (T_W - T)$ <p>initial and boundary conditions</p> <p>$t = 0$ and $x \in (0, L)$: $T = T_o$</p> <p>$t > 0$ and $x = 0$: $T_o = T - \frac{\varepsilon_e D_T}{u} \frac{\partial T}{\partial x}$</p> <p>$t > 0$ and $x = L$: $\frac{\partial T}{\partial x} = 0$</p> | <p>hydrogen mass balance</p> $\frac{\partial C_{Ap}}{\partial t} - \frac{1}{\varepsilon_p} \frac{1}{r^2} \frac{\partial}{\partial r} \left(\frac{D_{Aim}}{\tau} r^2 \frac{\partial C_{ip}}{\partial r} \right) = - \frac{(1 - \varepsilon_p)}{\varepsilon_p} \rho_s \cdot 3 \cdot r_B \cdot a(r)$ <p>initial and boundary conditions</p> <p>$t = 0$ and $r \in (0, R)$: $C_{Ap} = C_{Ap,in}$</p> <p>$t > 0$ and $r = 0$: $\frac{\partial C_{Ap}}{\partial r} = 0$</p> <p>$t > 0$ and $r = R$: $\frac{D_{mA} \varepsilon_p}{\tau} \frac{\partial C_{Ap}}{\partial r} = k_{g,A} (C_A - C_{Ap}(r = R))$</p> <p>mass balances for other components</p> $C_{Bp} = \frac{p}{R_g T} \left[\frac{\frac{C_{Bo}}{C_{To}} - \frac{1}{3} \frac{C_{Ao}}{C_{To}} \alpha_{Ap}}{1 - \frac{C_{Ao}}{C_{To}} \alpha_A} \right]$ $C_{Cp} = \frac{p}{R_g T} \left[\frac{\frac{C_{Co}}{C_{To}} + \frac{1}{3} \frac{C_{Ao}}{C_{To}} \alpha_{Ap}}{1 - \frac{C_{Ao}}{C_{To}} \alpha_A} \right]$ $C_{Dp} = \frac{p}{R_g T} \left[\frac{\frac{C_{Co}}{C_{To}}}{1 - \frac{C_{Ao}}{C_{To}} \alpha_{Ap}} \right]$ <p>diffusion coefficients</p> $\frac{1}{D_{mA}} =$ $= \frac{1}{D_{AB}} \left(y_{Bp} - \frac{1}{3} y_{Ap} \right) + \frac{1}{D_{AC}} \left(y_{Cp} + \frac{1}{3} y_{Ap} \right) + \frac{1}{D_{AD}} y_{Dp}$ $= \frac{1}{1 - y_{Ap}}$ <p>poison mass balance</p> $\frac{\partial y_{Sp}}{\partial t} + \frac{(1 - \varepsilon_p)}{\varepsilon_p} \rho_s \frac{\partial q}{\partial t} \frac{\Gamma^\infty}{C_{So}} = \frac{1}{\varepsilon_p} \frac{1}{r^2} \frac{\partial}{\partial r} \left(\frac{D_{Sm}}{\tau} \varepsilon_p r^2 \frac{\partial y_{Sp}}{\partial r} \right)$ <p>initial and boundary conditions</p> <p>$t = 0$ and $r \in (0, R)$: $y_{Sp} = 0$</p> <p>$t > 0$ and $r = 0$: $\frac{\partial y_{Sp}}{\partial r} = 0$</p> <p>$t > 0$ and $r = R$: $\frac{\varepsilon_p D_m}{\tau} \frac{\partial y_{Sp}}{\partial r} = k_{g,S} (y_S - y_{Sp}(r = R))$</p> <p>fouling kinetics</p> $\frac{\partial q}{\partial t} = k_a \cdot C_{So} \cdot y_{Sp} \cdot (1 - q)$ <p>$a(r) = 1 - q$</p> <p>heat balance</p> $\left((1 - \varepsilon_p) \rho_K C_{pK} + \varepsilon_p \rho_g C_{pg} \right) \frac{\partial T_K}{\partial t} - \lambda_{ef} \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial T_K}{\partial r} \right) =$ $= (1 - \varepsilon_p) (-r_B) (-\Delta H) \rho_{kat} a(r)$ $\Delta H = \sum_i v_i H_i$ <p>initial and boundary conditions</p> <p>$t = 0$ and $r \in (0, R)$: $T = T_o$</p> <p>$t > 0$ and $r = 0$: $\frac{\partial T}{\partial r} = 0$</p> <p>$t > 0$ and $r = R$: $\lambda_{ef} \frac{\partial T}{\partial r} = k_T (T - T_K(r = R))$</p> |

others

$$C_T = \frac{p}{R_g T}$$

$$C_{T0} = \frac{p_0}{R_g T_0}$$

$$\alpha_A = 1 - \frac{C_A}{C_{A0}} \frac{C_{T0} - C_{A0}}{\frac{T_0}{T} C_{T0} - C_A}$$

$$\alpha_{Ap} = 1 - \frac{C_{Ap}}{C_{A0}} \frac{C_{T0} - C_{A0}}{\frac{T_0}{T} C_{T0} - C_{Ap}}$$

$$q = \frac{\Gamma}{\Gamma^\infty}$$

$$y_{sp} = \frac{C_S}{C_{S0}}$$

Symbols

α - conversion

c- concentration

y- mole fraction

T – temperature

x – reactor coordinate

r – pellet coordinate

indexes

A – hydrogen

B – benzene

C – cyclohexane

D – nitrogen

S – poison (thiophene)

0 – reactor inlet

in – initial value

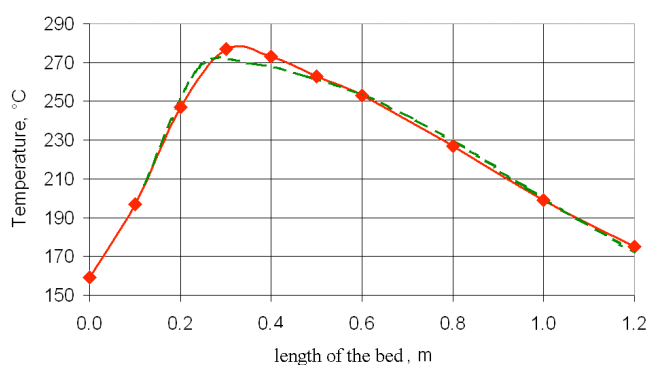


Fig. 1. Verification of the model with experimental data from the single unit tube; solid line – results of experiments, dashed line – results of simulations

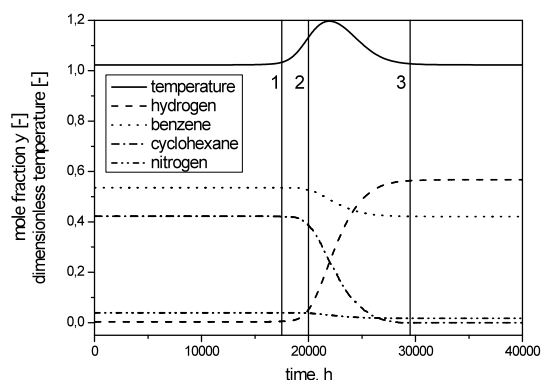


Fig. 2. Reactor outlet concentrations and temperature for process with catalyst deactivation vs. time
Line 1 – no changes in outlet composition and temperature are observed
Line 2 - changes in outlet composition and temperature are noticed
Line 3 – catalyst bed is deactivated

Literature

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3. S. Bretsznajder, *Własności gazów i cieczy*, WNT, Warszawa, 1962
4. L. K. Doraiswamy, M.M. Sharma, *Heterogeneous Reactions vol. 1*, Wiley, 1984.