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

\[ C_6H_6 + 3H_2 \rightarrow C_6H_{12}; \Delta H_{298} = -206.2 \text{ [kJ/mol]} \]  (1)

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 ± 0.1 kg/dm³

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

hydrogen mass balance
\[ \dot{m}_A + \frac{\partial}{\partial x} (u_m x_A) - \dot{m}_{DL,A} \frac{\partial^2 C_A}{\partial x^2} = 0 \]

mass balances for other components

\[ C_B = \frac{P}{R_e T} \begin{bmatrix} \frac{1}{C_{Bo}} & 1 \frac{C_{Ao}}{C_{To}} \frac{\alpha_A}{\alpha} \\ \frac{1}{C_{To}} & \frac{3}{C_{To}} \frac{\alpha_A}{\alpha} \end{bmatrix} \]

mass balances for catalyst pellet

hydrogen mass balance
\[ \frac{\partial C_{Ap}}{\partial t} + \frac{1}{u_m^2} \frac{\partial}{\partial x} \left( u_m x_{Ap} \right) - \frac{1}{\rho_p} \frac{\partial C_{Ap}}{\partial \tau} = \frac{1}{\rho_p} \frac{\partial}{\partial \tau} \left( r_p x_{Ap} \frac{\partial C_{Ap}}{\partial \tau} \right) \]

mass balances for other components

\[ C_{Bp} = \frac{P}{R_e T} \begin{bmatrix} \frac{1}{C_{Bo}} & 1 \frac{C_{Ao}}{C_{To}} \frac{\alpha_A}{\alpha} \\ \frac{1}{C_{To}} & \frac{3}{C_{To}} \frac{\alpha_A}{\alpha} \end{bmatrix} \]

initial and boundary conditions

\[ t = 0 \text{ and } \tau = R: C_{Ap} = C_{Ap,in} \]

fouling kinetics
\[ \frac{\partial q}{\partial \tau} = \eta \left( \frac{\partial q}{\partial \tau} \right) \]

\[ q(t) = 1 - q \]

heat balance
\[ \frac{\partial}{\partial \tau} \left( \xi \frac{C_p}{T_{K}} \right) - \frac{1}{C_{To}} \left( \frac{\partial}{\partial \tau} \right) \left( \frac{\partial T}{\partial \tau} \right) = \lambda_C - 1 \frac{\partial}{\partial \tau} \left( r \frac{\partial T}{\partial \tau} \right) \]

\[ C_H = \sum v_i H_i \]

poison mass balance
\[ \frac{\partial y_S}{\partial \tau} + \left( \frac{1}{u_m^2} \frac{\partial}{\partial x} \right) \left( \frac{1}{C_{Bo}} \right) \frac{\partial y_S}{\partial x} = \frac{1}{\rho_p} \frac{\partial}{\partial \tau} \left( r_p \frac{\partial y_S}{\partial \tau} \right) \]

initial and boundary conditions

\[ t = 0 \text{ and } \tau = R: y_S = 0 \]

heat balance
\[ \frac{\partial}{\partial \tau} \left( \xi \frac{C_p}{T_{K}} \right) - \frac{1}{C_{To}} \left( \frac{\partial}{\partial \tau} \right) \left( \frac{\partial T}{\partial \tau} \right) = \lambda_C - 1 \frac{\partial}{\partial \tau} \left( r \frac{\partial T}{\partial \tau} \right) \]

\[ C_H = \sum v_i H_i \]

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\[ C_{Bp} = \frac{P}{R_e T} \begin{bmatrix} \frac{1}{C_{Bo}} & 1 \frac{C_{Ao}}{C_{To}} \frac{\alpha_A}{\alpha} \\ \frac{1}{C_{To}} & \frac{3}{C_{To}} \frac{\alpha_A}{\alpha} \end{bmatrix} \]

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status

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\[ C_H = \sum v_i H_i \]
Others

\[ C_T = \frac{p}{R_g T}, \quad C_{T0} = \frac{p_0}{R_g T_0} \]
\[ \alpha_A = 1 - \frac{C_A}{C_{A0}} \frac{T_0}{T} \frac{C_{T0} - C_A}{C_{T0} - C_{A0}} \]
\[ \alpha_{Ap} = 1 - \frac{C_{Ap}}{C_{A0}} \frac{T_0}{T} \frac{C_{T0} - C_{Ap}}{C_{T0} - C_{A0}} \]
\[ q = \frac{T}{1^e} \]
\[ y_{sp} = \frac{C_S}{C_{So}} \]

Symbols

- \( \alpha \) - conversion
- \( c \) - concentration
- \( y \) - mole fraction
- \( T \) - temperature
- \( x \) - reactor coordinate
- \( r \) - pellet coordinate
- \( A \) - 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