Calculation of permissible monomer conversion in cascade polymerizers during the synthesis of general-purpose rubbers

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Abstract. The generalized model of combined chemical transformation and heat exchange is represented by a set of equations of the thermal balance and initial moments of MWD in stationary mode. A mathematical model of production process of synthesis of diene rubber on cobalt-based catalytic system consisting of kinetic and energy module is developed. The calculation algorithm of mathematical model of technological process of production of rubber SRDC on the basis of which numerical experiments are carried out is offered. The maximum permissible conversions are calculated. The influence of the initiator concentration, monomer and the temperature of the cascade input flow on the temperature of the cascade reactors and the conversion is researched.

The influence of temperature regime on polymerization processes is an important factor determining quantitative and qualitative characteristics of the resulting products [1-7]. In general, two important consequences of exothermic reaction nature affecting reactor operation and product properties can be identified. First, incomplete heat sink during the exothermic reaction leads to thermal autoacceleration and can cause reactor instability. Secondly, temperature changes affect such basic properties of the polymer as the average molecular weight, molecular weight distribution (MWD), as all kinetic constants depend on temperature [8-15].

To provide heat removal, the polymerization process is artificially stretched in time and carried out in the battery of polymerizers. The amount of monomer that can be polymerized in one battery unit is determined by the kinetics of the process and is limited to the maximum amount of heat that can be removed through heat transfer surfaces and by precooling the supplied product.

The calculation task may be to distribute the monomer feed into each polymerizer of the battery in such a way that the amount of polymer forming in the reactor does not exceed the amount determined...
by heat removal conditions. In polymerizers it is important to maintain the concentration of monomer not more than permissible for this purpose.

The permissible monomer conversion which provides heat removal in each unit is calculated as follows [16-22].

The main stage of reactor calculation consists in solving stationary equations at a given state of the initial mixture and at the required composition of reaction products [23, 24]. The thermal balance of solution polymerization process for the perfect-mixing reactor is follows:

\[
T_k - T_{k-1} + \frac{G_c \cdot c_x}{G_{\text{mix}} \cdot c_{\text{mix},k}} (1 - e^{-\frac{K_F \cdot F}{G_{\text{mix}} \cdot c_{\text{mix}}}}) (T_k - T_{\text{cool}}) = \frac{(-\Delta H) \cdot m_{\text{mon}}}{c_{\text{mix},k} \cdot \rho_{\text{mix},k}} I_0 M_0 (1 - x_k) \cdot \tau \cdot k_{p,k}^0 e^{-\frac{E}{RT_k}}
\]  

(1)

Designations are introduced. The right part of the equation is denoted through \(U_{k,1}\) and the left part through \(U_{k,2}\). The heat dissipation function \(U_{k,1}\) characterizes the temperature increase in the reactor due to the exothermic nature of the monomer polymerization reaction. The heat removal function \(U_{k,2}\) characterizes the temperature change in the reactor due to the input and output of the reaction mixture and due to heat transfer with the jacket.

For the first reactor:

\[
U_{1,1} = \frac{(-\Delta H) \cdot m_{\text{mon}}}{c_{\text{mix},1} \cdot \rho_{\text{mix},1}} M_0 \cdot k_{p,1}^0 e^{-\frac{E}{RT_1}} I_0 \tau \cdot \frac{1 + k_{p,1}^0 e^{-\frac{E}{RT_1}} I_0 \tau}{1 + k_{p,1}^0 e^{-\frac{E}{RT_1}} I_0 \tau}
\]

\[
x_1 = \frac{k_{p,1}^0 e^{-\frac{E}{RT_1}} I_0 \tau}{1 + k_{p,1}^0 e^{-\frac{E}{RT_1}} I_0 \tau}.
\]

\[
U_{1,2} = T_1 - T_{\text{in}} + \frac{G_c \cdot c_x}{G_{\text{mix}} \cdot c_{\text{mix},1}} (1 - e^{-\frac{K_F \cdot F}{G_{\text{mix}} \cdot c_{\text{mix}}}}) (T_1 - T_{\text{cool}}).
\]

The solution of equation (1) at \(k = 1\) is the temperature in the first reactor \(T_1\) when remaining parameters are fixed.

\[\text{Figure 1.} \ \text{Dependence function of heat dissipation } U_{1,1} \text{ and heat removal } U_{1,2} \text{ from the temperature in the first cascade reactor at } T_{\text{in}} = -10^0\text{C}, \ T_{\text{in}} = -10^0\text{C}, \ G_{\text{cool}} = 1000 \text{ kg/h, } G_{\text{mix}} = 8000 \text{ kg/h, } F = 36 \text{ m}^2, \ E=8.2 \text{ kcal/mol, } D_H = -1508000 \text{ J/kg} .\]

Temperature in the first reactor \(T_1 = 282.04\text{ K at } [\text{Co}] = 0.00002 \text{ mol/l, } M_0=1.22\text{mol/l}.\)

The conversion in the first reactor \(x_1\) is calculated at known \(T_1\) according to the formula:
\[ x_1 = 1 - \frac{c_{mix,1}P_{mix,1}}{(-\Delta H)\text{mon}M_0I_0\tau k_{p,1}^0e} \left( T_1 - T_{in} + \frac{G_{cool}c_{p,cool}}{G_{mix}c_{mix,1}} \left( 1 - e^{-\frac{K_{T,F}}{G_{mon,cool}}} \right)(T_1 - T_{cool}) \right) \] (2)

Consequently, \( x_1 = 0.367 \) according to the formula 2.

The number-average, mass-average and sedimentation-average degree of polymerization of \( P_n \), \( P_w \), \( P_z \) at the output of the first reactor are calculated. \( P_{1,n} = 1297.63 \), \( P_{1,w} = 3033.34 \), \( P_{1,z} = 5622.84 \) kg/kmol are got.

The calculation of the second reactor is done by analogy.

\[ U_{2,1} = \frac{(-\Delta H)\text{mon}M_0}{c_{mix,2}P_{mix,2}} k_{p,2}^0e^{-\frac{E}{RT_2}}I_0\tau \left( 1 + k_{p,2}^0e^{-\frac{E}{RT_2}}I_0\tau \right) \]

\[ x_2 = \frac{x_1 + k_{p,2}^0e^{-\frac{E}{RT_2}}I_0\tau}{1 + k_{p,2}^0e^{-\frac{E}{RT_2}}I_0\tau} \]

where

\[ U_{2,2} = T_2 - T_1 + \frac{G_{mix}c_{x}}{G_{mix}c_{mix,2}} \left( 1 - e^{-\frac{K_{T,F}}{G_{mon,cool}}} \right)(T_2 - T_{cool}) \]

The solution of equation (1) at \( k = 2 \) is the temperature in the second reactor \( T_2 \) when remaining parameters (factory data) are fixed.

\[ T_{2,K} = 296.3 \text{ K at [Co]} = 0.00002 \text{ mol/l, M}_0 = 1.22 \text{ mol/l.} \]

The conversion in the second reactor \( x_2 \) is calculated at known \( T_2 \) according to the formula:

\[ x_2 = 1 - \frac{c_{mix,2}P_{mix,2}}{(-\Delta H)\text{mon}M_0I_0\tau k_{p,2}^0e^{-\frac{E}{RT_2}}} \left( T_2 - T_1 + \frac{G_{cool}c_{p,cool}}{G_{mix}c_{mix,2}} \left( 1 - e^{-\frac{K_{T,F}}{G_{mon,cool}}} \right)(T_2 - T_{cool}) \right) \] (3)

Consequently, \( x_2 = 0.65 \) is got.

The number-average, mass-average and sedimentation-average degree of polymerization of \( P_n \), \( P_w \), \( P_z \) at the output of the second reactor are calculated. \( P_{2,n} = 910.009 \), \( P_{2,w} = 2715.53 \), \( P_{2,z} = 6256.44 \) kg/kmol are got.
It is possible to calculate the permissible conversion and molecular mass characteristics at the output of the k-th cascade reactor by analogy.

The temperature in the first reactor was calculated when the process parameters are changed: the concentration of the initiator $I_0$ and the monomer $M_0$ in the input stream. The increase of the monomer concentration in the input flow leads to a change in the right part of the heat balance $U_{1,1}$ (line family in figure 3), and the left part of $U_{1,2}$ remains unchanged. The intersection of the heat removal line $U_{1,1}$ and the family of lines 1,2,3,... etc. of the heat dissipation $U_{1,2}$ (increasing the monomer concentration in the input stream is from 0.8 mol/l to 1.3 mol/l) leads to a significant increase in the temperature in the first reactor.

The calculations showed that increasing the initiator concentration leads to a significant increase in the temperature in the first reactor and the temperature in the second reactor significantly exceeds the allowable one.

The input flow temperature also significantly affects $T_1$ temperature and the monomer conversion in the first reactor. When the cooling of temperature of furnace-charge increases, the left part of the heat balance $U_{1,1}$ changes and $U_{1,2}$ remains constant. The conversion in the reactors increase with decreasing the cooling of furnace-charge (figure 5-6).

A mathematical model of technological process of production of synthesis of diene rubber on cobalt-based catalytic system (SRDC) consisting of kinetic and energy module is developed. The generalized model of combined chemical transformation and heat exchange is represented by a set of...
equations of the thermal balance and initial moments of MWD in stationary mode [7, 8]. The algorithm of calculation of mathematical model of technological process of production of rubber SRDC on the basis of which numerical experiments are carried out is offered. The maximum permissible conversions at the output of the first and second cascade reactor are calculated. The influence of the initiator concentration, monomer and the temperature of the cascade input flow on the temperature in the first and second cascade reactors is researched.

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