Investigation of the effect of continuous operation of the polymerization process in the presence of Ziegler-Natta catalysts on the molecular characteristics of the product

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Abstract. A mathematical model of the process of producing polyisoprene in the presence of various catalytic systems of the Ziegler-Natta type is constructed in the article. When developing a mathematical model, the polycentric nature of the applied catalytic system was taken into account and the modular construction principle was applied, which allows calculations to be made both for the batch mode of the process and for the continuous mode. An analysis was also made of the influence of the hydrodynamic regime on the polymerization rate and the molecular characteristics of the resulting product using the example of a titanium-containing catalyst system.

1. Introduction

Trends in modern chemical production often lead to the need to study processes using mathematical modeling methods. A mathematical description of these processes allows to solve the problems of forecasting, optimization of manufacturing, and in the future to carry out planned synthesis of products with desired properties. Here is an example of a mathematical description of the process for producing synthetic isoprene caoutchouc by polymerization of isoprene in the presence of Ziegler-Natta catalysts. By the constructing of the mathematical model, we will use the modular construction principle: the kinetic module describing the kinetics of the production process occurring in one reactor will be supplemented by a macrokinetic module that takes into account hydrodynamic mechanisms. This approach will allow us to constantly analyze the difference in the behavior of the characteristics of the product obtained as a result of periodic and continuous regime of conducting the production process.

2. The construction of a mathematical model for describing the periodic process of isoprene polymerization

Traditionally, the construction of such a model involves the use of a kinetic approach, which consists in the composition and numerical solution of kinetic equations for the concentrations of all types of particles involved in the process. For a correct description of the kinetic mechanism, it is necessary to have information about the number of types of active centers[1], which present in the polymerization system. Various factors can influence their number, and among the main ones is the nature of the formation of the catalyst and the method of its preparation[2]. In industrial manufacturing is used a modified approach using a diffuser-confuser constructions in the technological scheme of a tubular
turbulent apparatus [3,4]. Previous studies [5] showed that in the case of applying this approach to the preparation of the catalytic complex, a maximum of 2 types of active sites are present in the system.

The kinetic scheme describing the polymerization of isoprene in the presence of a polycentric catalyst system will take the form [6,7]:

1. Chain growth
   \[ P_i^j + M \xrightarrow{k_{p}} P_{i+1}^j, \]

2. Chain transfer to monomer
   \[ P_i^j + M \xrightarrow{k_{m}} Q_i + P_i^j, \]

3. Chain transfer to organoaluminum compound (OAC)
   \[ P_i^j + A \xrightarrow{k_{a}} Q_i + P_i^j, \]

4. The death of active centers
   \[ P_i^j \xrightarrow{k_{d}} Q_i, \]

5. Transition of active centers to each other
   \[ P_i^j \xrightarrow{k_{t}} P_i^2, \]
   \[ P_i^2 \xrightarrow{k_{t2}} P_i^j, \]

where \( M \) is monomer, \( A \) is concentration of OAC, \( j, l = 1,2 \) characterizes the type of active center, \( P_i^j \) is the active ("growing") polymer chain length \( i \) on \( j \) the type of active centers; \( Q_i \) – inactive ("dead") chain of the polymer length \( i \), \( k_{p}, k_{m}, k_{a}, k_{d}, k_{t}, k_{t2} \) – constants characterizing the reaction rate of chain growth, transfer to monomer, transfer to organoaluminum compound (OAC), death of active centers and transition of active centers to each other, respectively. In this mechanism, reaction 5 is assumed to be irreversible. The reaction of the transition of active centers is embedded in the kinetic scheme for its adequacy in the description of experimentally observed dependences.

Writing the equations of material balance for each component of the reaction, we obtain a system of differential equations of large dimension (of the order of \( 10^5-10^6 \)). Previously for solving such systems was successfully used the method of moments [8], which allows to lead the system to a final form for the purpose of further numerical solution. To analyze molecular weight distribution, the concepts of the moments of active and inactive chains are introduced, which differ in the type of active center at its end.

\[
\begin{align*}
\mu_i^j &= \sum_{i=2}^{\infty} i^j P_i^j, \\
&= \sum_{i=2}^{\infty} i^j P_i^2, \\
\mu_i^2 &= \sum_{i=2}^{\infty} i^2 P_i^2, \\
\eta_i^j &= \sum_{i=2}^{\infty} i^j Q_i^j, \\
&= \sum_{i=2}^{\infty} i^j Q_i^2.
\end{align*}
\]

(1)

In addition, it is necessary to find the derivative moments of active and inactive chains on the residence time:

\[
\begin{align*}
\frac{d\mu_i^j}{dt} &= \sum_{i=2}^{\infty} i^j \frac{dP_i^j}{dt}, \\
&= \sum_{i=2}^{\infty} i^j \frac{dP_i^2}{dt}, \\
\frac{d\mu_i^2}{dt} &= \sum_{i=2}^{\infty} i^2 \frac{dP_i^2}{dt}, \\
\frac{d\eta_i^j}{dt} &= \sum_{i=2}^{\infty} i^j \frac{dQ_i^j}{dt}, \\
&= \sum_{i=2}^{\infty} i^j \frac{dQ_i^2}{dt}.
\end{align*}
\]

(2)

Based on the written out kinetic scheme, taking into account the law of the acting masses, we write a system of ordinary differential equations characterizing the change in the concentrations of all reagents acting in the system.
Using the mathematical method of moments, we transform the resulting system to a system of differential equations of finite dimension regarding to the statistical moments of the molecular weight distribution of polyisoprene:

\[
\begin{align*}
\frac{dM}{dt} &= -M \left( k_1^1 + k_2^1 \right) + \sum_{i=0}^{\infty} P_i^1 \left( k_1^i + k_2^i \right) + \sum_{i=0}^{\infty} P_i^2 \left( k_1^2 + k_2^2 \right) - M \mu_0^1 \left( k_1^1 + k_2^1 \right) - M \mu_0^2 \left( k_1^2 + k_2^2 \right), \\
\frac{dA}{dt} &= -A \left( k_1^1 \sum_{i=0}^{\infty} P_i^1 + k_2^1 \sum_{i=0}^{\infty} P_i^2 \right), \\
\frac{dP_1^1}{dt} &= -k_1^1 MP_1^2 + \left( k_1^1 M + k_1^1 A \right) \sum_{i=2}^{\infty} P_i^1 - k_1^1 P_1^1 - k_1^2 P_1^2 - k_1^2 P_1^1, \\
\frac{dP_1^2}{dt} &= -k_2^1 MP_1^2 + \left( k_2^1 M + k_2^1 A \right) \sum_{i=2}^{\infty} P_i^2 - k_2^2 P_2^1 + k_1^2 P_1^1 - k_2^1 P_1^2, \\
\frac{dQ_1^1}{dt} &= k_1^1 MP_1^1 + k_1^1 AP_1^1 + k_1^1 P_1^1, \\
\frac{dQ_2^2}{dt} &= k_2^2 MP_2^2 + k_2^2 AP_2^2 + k_2^2 P_2^2.
\end{align*}
\]

(3)

Using the mathematical method of moments, we transform the resulting system to a system of differential equations of finite dimension regarding to the statistical moments of the molecular weight distribution of polyisoprene:

\[
\begin{align*}
\frac{dM}{dt} &= -MP_1^2 \left( k_1^1 + k_2^1 \right) - MP_2^2 \left( k_1^2 + k_2^2 \right) - M \mu_0^1 \left( k_1^1 + k_2^1 \right) - M \mu_0^2 \left( k_1^2 + k_2^2 \right), \\
\frac{dA}{dt} &= -k_1^1 AP_1^1 - k_2^1 AP_1^2 - k_1^1 A \mu_0^1 - k_2^1 A \mu_0^2, \\
\frac{dp_1^1}{dt} &= -k_1^1 MP_1^1 + \mu_0^1 \left( k_1^1 M + k_1^1 A \right) - k_1^1 P_1^1 - k_1^2 P_1^2, \\
\frac{dP_2^2}{dt} &= -k_1^2 MP_2^2 + \mu_0^2 \left( k_1^2 M + k_1^2 A \right) - k_1^2 P_2^1 + k_1^2 P_1^2, \\
\frac{dQ_1^1}{dt} &= k_1^1 MP_1^1 + k_1^1 AP_1^1 + k_1^1 P_1^1, \\
\frac{dQ_2^2}{dt} &= k_1^2 MP_2^2 + k_2^2 AP_2^2 + k_2^2 P_2^2.
\end{align*}
\]

(4)
\[
\begin{align*}
\frac{d\mu_0^2}{dt} &= (k_m^2 M + k_n^2 A + k_p^2) \mu_0^2, \\
\frac{d\mu_1^2}{dt} &= 2k_m^2 MP_0^1 + k_r^2 M \mu_0^1 - (k_m^2 M + k_n^2 A + k_p^2) \mu_1^1 + k_n^2 \mu_0^2, \\
\frac{d\mu_2^2}{dt} &= 2k_m^2 MP_0^2 + k_r^2 M \mu_0^1 - (k_m^2 M + k_n^2 A + k_p^2) \mu_2^1 + k_n^2 \mu_0^2, \\
\frac{d\mu_0^3}{dt} &= (k_m^1 M + k_n^1 A + k_p^1) \mu_0^1, \\
\frac{d\mu_1^3}{dt} &= (k_m^0 M + k_n^2 A + k_p^2) \mu_1^1, \\
\frac{d\mu_2^3}{dt} &= 4k_m^1 MP_0^1 + k_r^1 M \mu_0^1 + 2k_r^1 M \mu_1^1 - (k_m^1 M + k_n^2 A + k_p^2) \mu_2^1 + k_n^2 \mu_0^2, \\
\frac{d\mu_0^4}{dt} &= 4k_m^2 MP_0^2 + k_r^2 M \mu_0^1 - (k_m^2 M + k_n^2 A + k_p^2) \mu_2^1 + k_n^2 \mu_0^2, \\
\frac{d\mu_1^4}{dt} &= (k_m^1 M + k_n^1 A + k_p^1) \mu_1^1, \\
\frac{d\mu_2^4}{dt} &= 8k_m^3 MP_0^3 + 3k_m^1 M (\mu_2^2 + \mu_1^1) + k_m^2 M \mu_0^1 - (k_m^3 M + k_n^2 A + k_p^2) \mu_2^1 + k_n^2 \mu_0^2, \\
\frac{d\mu_0^5}{dt} &= 8k_m^2 MP_0^2 + 3k_m^1 M (\mu_2^2 + \mu_1^1) + k_m^2 M \mu_0^1 - (k_m^2 M + k_n^2 A + k_p^2) \mu_2^1 + k_n^2 \mu_0^2, \\
\frac{d\eta_0^1}{dt} &= (k_m^1 M + k_n^1 A + k_p^1) \mu_0^1, \\
\frac{d\eta_1^2}{dt} &= (k_m^0 M + k_n^2 A + k_p^2) \mu_1^1, \\
\frac{d\eta_2^3}{dt} &= (k_m^1 M + k_n^1 A + k_p^1) \mu_2^1, \\
\end{align*}
\]

where \( \mu_0^i, \mu_1^i, \eta_0^i, \eta_1^i \) - are the moments of the molecular weight distribution of active and inactive chains respectively. The initial conditions for system (4) have the form:

\[
\begin{align*}
M(0) &= M_0, A(0) = A_0, \\
P_i^j(0) &= P_i^j, Q(0) = 0, \\
\mu_0^i(0) &= \mu_1^i(0) = \eta_0^i(0) = \eta_1^i(0) = 0, i = 0, \ldots, 3.
\end{align*}
\]

The constructed system of differential equations (4) with initial conditions (5) is a mathematical model\([6,7]\) of the process of the polymerization of isoprene on a titanium-containing catalyst system taking into account the dynamics of active centers.

3. **Building a mathematical model to describe a continuous process**

In large-scale production, a continuous mode of conducting the process is assumed, since it does not require constant regulation of technological parameters, since it has stability, uniformity and firmness of the process. We supplement the model describing the kinetics of the production process with macrokinetic mechanisms that take into account the influence of the hydrodynamic regime in the reaction zone\([9,10]\).
The polymerizers used are ideal mixing reactors, since they are structurally equipped with a stirrer, which is typical for liquid-phase polymerization processes. Therefore, in the system there are no possible temperature and concentration gradients in the reactor.

For ideal mixing reactors there are recurrence relationships between the moments of molecular weight distribution:

\[
\theta \frac{dm_j^{(k)}}{dt} = m_j^{(k-1)} - m_j^{(k)} + \theta \left( \frac{dm_j^*}{dt} \right)^{(k)}.
\]

Expression (6) can be converted to the form

\[
\frac{dY^{(k)}}{dt} = \frac{Y^{(k-1)} - Y^{(k)}}{\theta^{(k)}} + \overline{R}_y^{(k)},
\]

where \(\theta^{(k)}\) - is the residence time of the reaction mixture in the \(k\)-th reactor of the cascade, and a kind \(\overline{R}_y^{(k)}\) is determined by the adopted kinetic module.

Expression (7) allows to expand the system of differential equations describing the polymerization of isoprene in the presence of various catalytic systems.

4. Computational Experiment

On purpose to study the influence of the periodic/continuous regime of the process on the molecular characteristics of the obtained product, a computational experiment was conducted for the polymerization of isoprene process on a titanium-containing catalyst system under the following conditions close to the conditions of actual operating continuous production:

- catalytic system – TiCl₄-TIBA-piperylene-DFO;
- isoprene – 1.388 mol/l;
- OAC – 0.0014 mol/l;
- active centers – 0.0028 mol/l;
- the concentration of active centers was set in the amount of 2.2%;
- the number of reactors involved in the cascade – 2 (for a continuous process);
- average residence time 30 minutes in one polymeriser (60 min. for the entire cascade).

The numerical calculation of the resulting system of differential equations describing the periodic/continuous regime of the process was carried out using the Adams-Bashfort method [11]. The kinetic parameters were taken from the work[12]. Figures 1-3 show the changes in the conversion and the averaged molecular characteristics of time for both the periodic and continuous regimes of the process.

**Figure 1.** The dependence of conversion values on time (line – periodic regime, dotted line - continuous regime of the process).
Figure 2. The dependence of the values of the number average molecular weight on time (line – periodic regime, dotted line - continuous regime of the process).

Figure 3. The dependence of the values of the weight average molecular weight on time (line – periodic regime, dotted line - continuous regime of the process).

5. Analysis of the results
It can be seen from the given figures that, that for the process under study, by the transition from periodic to continuous regime of conducting there is an increase of conversion, which indicates an increase in the reaction rate and the influence of the hydrodynamic regime. In addition, higher values of averaged molecular characteristics are observed. The difference is noticeable even for the case of a small number of the used reactors. The industrial manufacturing of some popular brands of caoutchouc involves the use of more than 10 cascade reactors, for which the influence of continuous regime will have a stronger role.

Therefore, the hydrodynamic effect can be considered as one of the levers of influence on the molecular characteristics of the resulting product. The constructed mathematical model and the numerical methods used for the calculations make it easy to evaluate the influence of the continuous regime of the process for other catalytic systems.
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7. References
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