About an algorithm for modeling the isoprene polymerization process in the cascade of reactors using the Monte Carlo method

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Abstract. The article describes an algorithm for modeling the isoprene polymerization process based on the Monte Carlo method. The algorithm can be used to simulate polymerization processes carried out in batch or continuous mode. The possible polycentricity of the catalyst used is also taken into account. The model is based on this algorithm makes it possible to study the properties of the polymerization product and calculate the molecular weight distribution for different points in time.

1. Introduction

Currently, the production of polymer materials occupies one of the leading places in the domestic chemical industry. In this regard, studies of polymerization processes are of great interest to modern science. This area provides the best opportunities for studying statistical properties and factors influencing them and allows one to describe physical processes with high accuracy [1]. One of the most common polymer materials for industrial use is isoprene rubber [2]. This process is a complex technological process carried out in permanent Ziegler-Natta catalysts. This process is carried out continuously in the cascade of series-connected polymerizers. Each polymerizer is a stirred-tank reactor [3]. Studying the production of polyisoprene is a time-consuming process that becomes possible when building a mathematical model. That allows you to predict changes in the properties of the resulting product depending on the recipe and conditions of the process.

2. Using the Monte Carlo method in the construction of an algorithm for modeling the isoprene polymerization process carried out in batch mode

Kinetic and statistical approaches are conventionally distinguished for describing mathematical models of polymerization processes [4]. The kinetic approach consists of the preparation and solution of kinetic equations for the concentrations of all types of particles involved in the process. It can be successfully used to calculate averaged molecular characteristics of the polymer. The statistical approach is based on the calculation of the probabilities of reactions that are possible at a given point in time, and a random number that determines the type and amount of simulated reactions. Each link of the growing polymer chain is considered as a specific random process of conditional movement along the polymer molecule, while the probability of the random process is considered to be equal to...
the proportion of its corresponding molecules among all others in the reaction system. This approach is of interest for studying the structure of the polymer [5].

The Monte Carlo method implements this approach. It is based on imitation of the behavior of a chemical system taking into account the course of reactions. The model is a collection of particles corresponding to individual molecules or macromolecules. This allows you to accumulate information about the amount, length, and composition of the resulting polymer macromolecules and at any time to obtain the actual values of the molecular characteristics of the polymerization product. It allows you to observe the polymer in dynamics [6-7].

We apply a statistical approach to modeling the polymerization of isoprene. First, it is necessary to write out the kinetic scheme of the process, for which it is necessary to keep in mind the number of types of active sites involved in the process. It may depend on the conditions and methods of preparation of the catalyst. In paper [8], the application of a modified approach was considered using a tubular turbulent apparatus with a diffuser-confuser design in the technological scheme. It showed the presence of no more than two types of active sites in the system. The kinetic diagram of the isoprene polymerization process described in the work in the presence of a polycentric catalyst system has the form:

1. Chain propagation
   \[ P_i^j + M \xrightarrow{k_f^j} P_{i+1}^j, \]
2. Chain transfer to monomer
   \[ P_i^j + M \xrightarrow{k_d^j} Q_i + P_1^j, \]
3. Chain transfer to organoaluminium compound (OAC)
   \[ P_i^j + A \xrightarrow{k_c^j} Q_i + P_1^j, \]
4. Death of active sites
   \[ P_i^j \xrightarrow{k_d^j} Q_i, \]
5. Transition of active sites to each other
   \[ P_i^1 \xrightarrow{k_{12}^j} P_i^2, \]
   \[ P_i^2 \xrightarrow{k_{12}^j} P_i^1, \]
where \( M \) – monomer, \( A \) – organoaluminium compound, \( j, l = 1,2 \) – index, which characterizes the type of active site, \( P_i^j \) – active (“growing”) polymer chain of length \( i \) on \( j \) type of active sites; \( Q_i \) – inactive (“dead”) polymer chain of length \( i \), \( k_f^j, k_d^j, k_c^j, k_d^j, k_{12}^j \) – constants characterizing the reaction rate of chain propagation, transfer to monomer, transfer to organoaluminium compound, death of active sites and transition of active sites into each other, respectively [3].

Next, we describe the algorithm of modeling as a sequence of steps.

Step 1. Transform the rate constants of elementary reactions:
   \( \tilde{k} = k \) for first order reactions; \( \tilde{k} = \frac{k}{V \cdot N_A} \) for second order reactions (\( V \) – reaction volume (number of molecules), \( N_A \) – Avogadro number).

Step 2. Calculate the reaction rate for every reaction: \( R_i = \tilde{k}_i \cdot X_A \cdot X_B \), where \( \tilde{k}_i \) – the rate constant of \( i \)-th reaction, in which \( A \) and \( B \) reagents are involved; \( X_A, X_B \) – concentration of reagents. By summing them, we obtain the total reaction rate \( R_{\text{sum}} = R_1 + R_2 + \ldots + R_n \), where \( n \) is the number of elementary reactions of the kinetic scheme of the process.

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Step 3. Calculate the probability of each reaction at a given time: 

\[ p_i = \frac{R_i}{R_{sum}}, \quad i = 1..n. \]

It's obvious that 

\[ p_1 + p_2 + \ldots + p_n = 1. \]

Step 4. Generate a uniformly distributed random number \( r \) on the segment from 0 to 1 and choose such value \( k \) that there is an inequality: 

\[ \sum_{i=1}^{k-1} p_i < r < \sum_{i=1}^{k} p_i. \]

Therefore, as a result of the simulation choice, the reaction under the index \( k \) should occur.

Step 5. Continuing reasoning similarly we will build whole scheme of carrying out the reaction.

3. Modification of the algorithm of Monte Carlo modeling for the isoprene polymerization process carried out in the continuous mode

In industrial conditions the process under study is carried out in the cascade of reactors in continuous mode. For this reason, the concept of "reaction time" loses its meaning. Therefore, it is worth talking only about a certain average residence time in the reactor as a random variable that is characterized by a probability distribution function.

Paper [9] describes the need to consider the residence time distribution for the processes taking place in the cascade of reactors. We denote the probability that a particle spends time from \( t \) to \( t + dt \) in the current reactor as \( p(t)dt \). The calculation of value \( p(t) \) depends on the type of reactors used. Reactors used in industry to conduct the process under study are continuous stirred tank reactors for which \( p(t) \) is calculated by the formula:

\[ p(t) = \left( \frac{n}{\tau} \right)^n \frac{t^{n-1}}{(n-1)!} e^{-\frac{nt}{\tau}}, \quad (1) \]

where \( n \) is the amount of reactors in the system, \( \tau \) – the average residence time of the reaction mixture in one reactor (h) [10]. It should be noted that the peak of the curve constructed according to distribution (1) corresponds to the average residence time of the reaction mixture in one reactor.

Since the process of isoprene polymerization considered in the paper proceeds in the cascade of 2 continuous stirred tank reactors [3], the residence time distribution has the form shown in Figure 1. The interval [0, 3] with a step of 0.05 h was chosen, since in this case the possible variants of the particle’s residence time form an exhaustive event.

![Figure 1. Residence time distribution of particles for the cascade of two continuous stirred tank reactors.](image)

The generation of the residence time is carried out similarly to the choosing of the reaction. The probabilities of possible values of the residence time are sequentially located on the interval [0, 1] (an
integral distribution curve is constructed), then a random number \( r \) is generated and the corresponding value of the residence time is selected (Figure 2).

![Figure 2. Integral curve of residence time distribution.](image)

Transform the previously constructed algorithm.

Step 5. For the selected reaction, we calculate the time of its modeling \( \Delta t_j \) according to the formula

\[
\Delta t = \frac{1}{R_{sum}} \ln \left( \frac{1}{t_2} \right)
\]

and for each particle formed or destructed as a result of step 4, we calculate its exit time from the current reactor \( t_{ex} \):

\[
t_{ex} = t + t_{dm},
\]

where \( t \) – current time of process modeling from its beginning, \( t_{dm} \) – residence time of the molecule in the current reactor, calculated according to the distribution (1).

Step 6. Repeat the steps from 3 to 6 for each reactor of the cascade \( j = 1, m \).

Step 7. Change the total time of modeling by increasing it by the minimum reaction modeling time among all reactors

\[
t = t + \min_{j=1, m} \Delta t_j.
\]

Step 8. For each reactor in the cascade, we transfer to the next reactor all molecules whose exit times are less than the total time of process: \( t_{ex} < t \). After that, we will return to step 2.

Step 9. Continuing the discussion and repeating the sequence of steps 2 to 9, we will build the complete process modeling scheme. In this case, it is necessary to add a new portion of the reaction mixture to the first reactor with a given period, with the calculation of the residence time, calculated according to the distribution (1) for each new particle.

4. Features of the software implementation of the algorithm

Since the algorithm of the Monte Carlo method imitates the propagation of a polymer at the particle level, in the case of a software implementation of the algorithm, the proper organization of storage of all the source and received data is necessary. Information about the state of particles in the reactors of the cascade is stored in a common array, the dimension of which is equal to the number of reactors in the cascade. Each cell of the array contains a vector (dynamic array), in which stored information depends on the type of molecule:

• to monomer molecules and OAC corresponding dynamic array comprises exit time of a particle from the current of the reactor (the transition to the next reactor);
• for growing (active) and “dead” (inactive) polymer macromolecules for each type of active site, the dynamic array contains information about the amount of monomer in the chain.
It should be noted that the polymer macromolecules correspond to similar arrays for storing their exit time from the current reactor (ordered according to the increase in exit time). When a particle is transferred to the next reactor, it is removed and the remaining objects are indexed automatically.

The described storage organization, thanks to the advantages of the Monte Carlo method, allows obtaining information on the total amount of polymer macromolecules in each of the reactors, the length and composition of each chain, the values of the molecular weight and viscosity characteristics of the polymer, in particular, the total molecular weight distribution and separately for each type of active sites.

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6. References
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