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Mathematical Models Of Polimerization Processes

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Abstract: The work presents a new approach of modeling industrial reactors to receive polymer plastics. The efficient method of identifying stochastic model is suggested, at which unaccounted chance factors are presented as integrated disturbances. The models, received at which allow to take into consideration both the structure of flows in reactors and kinetic peculiarities of the process.

Keywords: polymer plastic materials; chemical reactor; control system.

1 Introduction

Polystyrene is one of the widespread polymer plastics. The demand for this polymer is on the increase in Kazakhstan. Depending on sphere of use the polystyrene of various grades is produced. The main type of the apparatuses for industrial production of this polymer is reactor with mixing devices. The analysis of the technology of polystyrene production showed that the process is sensitive to the technological conditions such as: presence of admixtures in raw styrene, the decrease of a volume of reactor on account of sticking the polymer to the walls of apparatus, and others. As polymerization process is conducted under the high temperature the polymerized mass starts boiling, and density of the mass changes through the air bubbles forming inside it. It also leads to increase of load to the mixer. All this factors also cause a distortion between the real industrial process and ideal determinate model. These disturbing factors influence the quality of the finished polymer and, of cource, its price.

2 Main Part

A lot of works are devoted to the description of the kinetics of polymerization process. Incidentally, the main problem arises while modeling the Trommsdorffs phenomenon [1,2,3]. That is too significant under the high orderes of conversion. So experimental equation for the velocity of polymerization up to full conversion was obtained in [4]:

$$W = A\exp(-E/RT) * F(C) \tag{1}$$

where $F(C)$ is the function of conversion

Besides the kinetics the structure of substances fluxes in the reactor is the other significant factor, which determines the efficiency of polymerization process. Usually, the analysis of fluxes structure in the chemical reactors is realized with the help of the C- curves characterizing the distribution of the particles time being in the apparatus. Fig. 2.1 depicts the C-curve of the perfect mixing reactor [5]. Also theres the experimental curve obtained for the industrial reactor. A good match between experimental and theoretical C-curves is obvious. Its obvious also from Fig. 2.1 than we get a good match between experimental and theoretical C-curves for the periodic process under the time $\tau > 6h$.

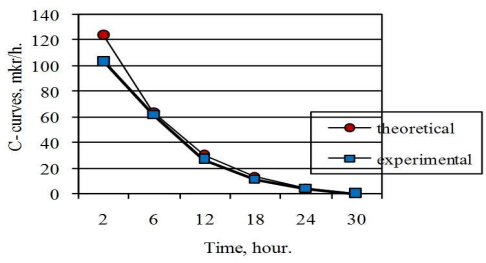

Fig. 2.1: C-curve of the perfect mixing reactor

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But for the non-stop process the time when the polymerized mass is inside the apparatus is less than 6 hours. Its proved by the statistic analysis of temperatures and of conversions in the non-stop polymerization process.

The process temperature was measured in three points over the height of each reactor: in upper part, in the middle part nearby the mixer and in the lower part. Our analysis showed that the temperature of process varies within the difference of about 200 C over the height of apparatus. As its depicted on the Fig. 2.1, the temperature at the upper part of reactor was higher than at the lower part.

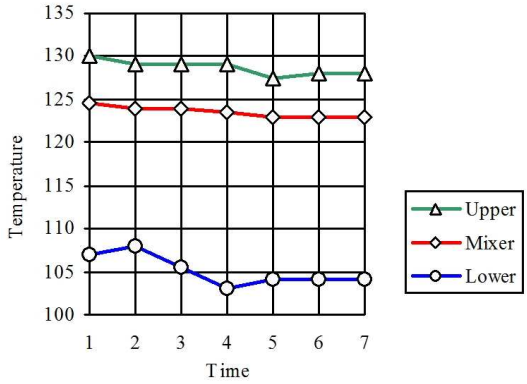

Fig. 2.2: The temperature over the height of reactor

The measuring made at the different periods of the process also showed a considerable temperature difference. The densities of distribution give visual information of this observation (Fig. 2.2). The maximum of the density of temperature distribution is observed within the 71-72 °C. It accords to the average temperature inside the reactor. This temperature difference is the evidence of significant discrepancy between the real process and the model of perfect mixing.

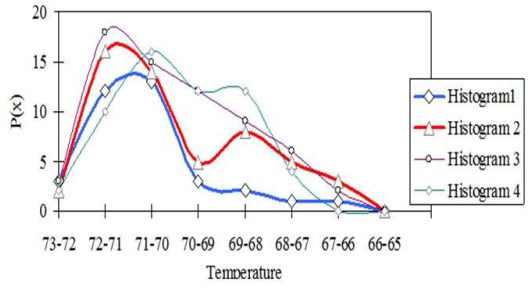

Fig. 2.3: The densities of the temperature distribution

Estimations for cross-correlation functions of temperatures and styrene conversion were obtained on the basis of observation over the process in the reactor for the long period. Maximum points of cross-correlation functions accord to the time lag about 5-6 hours, what corroborates the maximum of correlation between process parameters at that period and accords also to the average time of polymerized mass being inside the reactor.

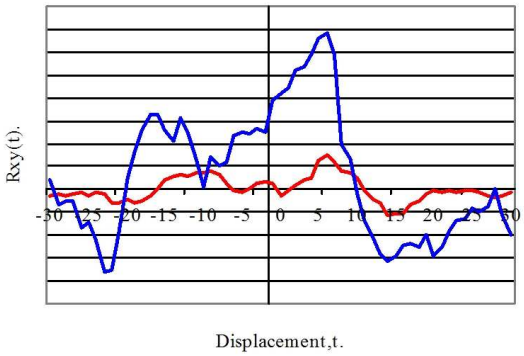

Fig. 2.4: Cross-correlation function

Determinate static model of styrene polymerization can be written as

$$y_j = y_{j-1} + A_{x_j} \tag{2}$$

where A is a certain coefficient;
j is a number of reactor;
y_j and x_j are the input and output variables calculated from the formulas :

$$\frac{C_{jn}}{F(C_{jn})} = y_j n;\ \exp(-E/RT_{jn}).\tau_j = x_{jn} \tag{3}$$

where C_{jn} is the styrene conversion;
T_j is the time being of the polymerized mass in the reactor. Dynamic linearized model of the polymerization process can be written in discrete form as

$$y_{jn+1} = \theta_{1j}\, y_{jn} + \theta_{2j}\, y_{j-1n} + A_{x_{jn}}$$
$$\theta_{1j} = 1 - 1/\tau_j\ \theta_{2j} = 1 - \theta_{1j} \tag{4}$$

j = 1,m ; m is the total number of reactors.
The equations (2), (3), (4) describe the averaged state of polymerization process under the idealized conditions. In order to investigate the process under the real conditions we observed the polymerization of styrene in two connected reactors with mixing devices. A profound investigation of the chemical and physical nature of these processes requires considerable expenses and due to this its sufficiently difficult. A combined stochastic model is more effective, because it takes into account all these

factors. Incidentally, the determinate model is all the same the main basis of our consideration. In the present work we offer the new approach to modeling the industrial process of polystyrene production. This approach allows for the peculiarities of the kinetics of reactor under the real structure of substances fluxes. We also offer the effective method for the identification of the parameters of the model developed. Thus, under the stochastic approach a few unobserved variables, which characterize a certain influence of the random factors, are included to the apriority model. Adequation of the stochastic model is evaluated according to the minimum of the accepted criterion. On such an approach the above random factors are described in the form of additive correlated random perturbations. Persistency of the industrial process allows to assume that values of all the time-dependent factors at this moment depend only on the preceding moment. Thus, the time-correlated noise is observed in the considered object. That is proved by the statistical investigations. I.e. undiscounted factors are considered as a summary unobserved noise, which is described by Gauss law. These factors are uncorrelated in time and between each other. They form the random sequences of the uncontrolled perturbations with a naught average value and with unit variance. The model of noise in autoregressive form reads

$$V_n = \lambda_{n-1} + \sigma\varepsilon_n \tag{5}$$

Stochastic model of the process dynamic at (n+1)-moment with allowance for the influence of the correlated perturbations is such as one

$$y_{jn+1} = \theta_{jn} + (1-\theta)y_{j-1n} + A_j X_{jn} + V_{jn+1} \tag{6}$$

As a result we have the stochastic model, with correlated perturbations.

$$y_{jn+1} = (\theta+\lambda_j)y_{jn} + (1-\theta)y_{j-1n} - \theta\lambda_j y_{j-1n-1} + A_j X_{jn} - A_j\lambda_{jn-1} + \sigma\varepsilon_{jn} \tag{7}$$

The expression can be presented in the more convenient form

$$y_{jn+1} = \sum 0 a_{ji} y_j(n) + \sum_{i=0}^{1} b_{ji} y_{j-1}(n) + \sum_{i=0}^{1} c_{ij} x_j(n-1) + \sigma\varepsilon_{jn} \tag{8}$$

It can be shown that well-known methods [6,7,8] are ineffective in case of correlated perturbations. Though we often cant carry out the active experiment in the industrial conditions, the databases about the process parameters can be always used. So we elaborated the new method for identification unknown parameters of the model proposed. According to this method databases are produced in the form of time series. Thus the two main problems of identification are solved:

1. Identification of the parameters of the determined model of styrene polymerization. This model is described by the equations (1,2).
2. Identification of the combined stochastic model with allowance for the correlated perturbations. This model is presented by the equations [6,7]. To evaluate the parameters of model (7) and (8) the equations of Yul-Woker's type was offered in [8]. They include the second moments of the distribution:

$$R_{yy}(k) = (\theta+\lambda)R_{yy}(k+1) - \theta\lambda_{yy}(k+2) + AR_{xy}(k+1) - A\lambda_{xy}(k+2) \tag{9}$$

$$R_{xy}(k) = (\theta+\lambda)R_{xy}(k+1) - \theta\lambda_{xy}(k+2) + AR_{xx}(k+1) - A\lambda_{xx}(k+2) \tag{10}$$

solution of any two of this equation allows for obtaining the optimum evaluations of the model parameters. It can be shown that the minimum squares method is a special case of the suggested method under the uncorrelated noise. Evaluations for the model parameters obtained by the minimum squares method follow from the simultaneous solution of the certain equations of Yul-Wokers type with k=0 [9]. The Yul-Wokers equations are such ones for the static model:

$$(1-\theta)R_{xy}(k) = AR_{xx}(k), k \geq \tag{11}$$

Appropriate correlations for calculating the evaluations of dynamic model parameters are given by :

$$R_{yy}(k+1) = \theta_{yy}(k) + AR_{xy}(k) \tag{12}$$

$$R_{xy}(k+1) = \theta_{xy}(k) + AR_{xx}(k) \tag{13}$$

The root-mean-square error of the prognosis of output variable per unit the one- step was accepted as the identification criterion. According to this criterion equations of Yul-Wokers type were suggested for calculating the evaluations of the model parameters. The root-mean-square error of the prognosis for the model parameters and evaluations of the second moments according to the dynamic system with correlated perturbations can be written as

$$\begin{aligned}\sigma &= \frac{1}{N}\sum_{n-1}^{N}[y_{n+1} - \widehat{y}_{n+1}]^2 \\ &= \frac{1}{N}\sum_{n=1}^{N}[y_{n+1} - (\theta+\widehat{\lambda})y_{n-1} - \widehat{A}x_n \\ &= \widehat{A}\widehat{\lambda}x_{n-1}]^2 \\ &= \phi_1\widehat{R_{yy}}(0) + \phi_2\widehat{R_{yy}}(1) + \phi_3\widehat{R}_{yy}(2) + \phi_4\widehat{R}_{yy}(-1) \\ &\quad + \phi_{5\widehat{R}_{xy}}(0) + \phi_6\widehat{R}_{xy}(1) + \phi_7\widehat{R}_{xy}(2) \\ &\quad + \phi_8\widehat{R}_{xx}(o) + \phi_9\widehat{R}_{xx}(1)\end{aligned} \tag{14}$$

The results of calculations for the two above models as well as appropriate identification criterions are shown in the Tables 1, 2.

Table 1: The results of calculations for the first above model

Statics		Dynamics	
$A_{st.}10^{12}$	$\delta_{st.}$	$A_{din.}10^{10}$	$\delta_{din.}$
0,07	1,65	1,23	1,058
0,67	1,74	1,78	1,069
1,33	2,06	1,50	1,061
1,76	2,39	1,66	1,066
2,18	2,81	1,57	1,063
2,01	2,62	1,18	1,059

Table 2: The results of calculations for the two above model

$A.10^{12}$	θ	δ
40,66	0,37	3,45
23,67	0,105	8,20
0,16	1,76	1,09
1,33	3,08	0,60
2,50	0,23	0,92

Analysis of the results obtained showed that account of the object dynamics allows for decreasing the prognosis dispersion for 40-50%. Account of the correlated perturbations at the object output allows for degreasing the prognosis dispersion for 60-70%. Evaluations of A and λ calculated with k=2;4 give a minimum prognosis dispersion δ. So, the mathematical model of the styrene polymerization carried out with allowance for the correlated perturbations gives the best prognosis. Therefore, its the most exact one.

3 Conclusion

The main contribution of the present paper:

1. The novel concept for mathematical modeling the technological process has been proposed. The approach proposed allows for adapting the model to the various production conditions with sufficiently accuracy.

2. The novel method for identifying the mathematical model gives the best evaluations of the parameters of the industrial process.

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