New Approach to Modeling Polystyrene Production Process

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In the work the new approach to modeling the industrial process of polystyrene production has been submitted. The approach has been worked out with allowing for describing the peculiarities of the process kinetics in a reactor with accounting of the real structure of substances fluxes. The effective method for the identification of the parameters of the mathematical model has been developed. The undiscounted random factors are considered as a summary unobserved noise which is described with the help of Gauss law and forms the random sequences of the uncontrolled perturbations with a zero average value and with unit variance. Thus, according to the stochastic approach a few unobserved variables, which characterize a certain influence of the random factors, are included to the apriority model. On such an approach the mentioned above random factors are described in the form of additive time-correlated random perturbations. Persistency of the industrial process allows assuming that values of all the time-dependent factors at the moment depend only on the preceding moment. The novel methods for identifying the mathematical model have been applied to describing the polystyrene production process with the best evaluations of the process parameters.

1. Introduction

Polystyrene is one of the widespread polymer plastics. The demand for this polymer is on the increase in Kazakhstan. Depending on area of use the polystyrene of various grades is produced (Ham, 1973).
The main type of the apparatuses for industrial production of this polymer is a reactor with mixing devices. The analysis of the technology of polystyrene production revealed that polymerization process was sensitive to the technological conditions such as: different admixtures in the raw styrene, the decrease of the reactor work volume due to sticking the polymer to the walls of apparatus, and others factors (Penidis et al., 1992).
As polymerization process is conducted under the high temperature, the polymerized mass starts boiling, and density of the mixture changes through the air bubbles forming inside it. It also leads to increase of the load to the mixer (Herrera-Ordonez and Olayo, 2000).
All this factors also lead to a distortion between the real industrial process and ideal determinate model (Cawthon and Knaebel, 1989). These disturbing factors influence the quality of the finished polymer and, of course, its price (Xie et al., 2010).

2. Method of investigations

A lot of works are devoted to the description of the kinetics of polymerization process. Incidentally, the main problem arises while modeling the Trommsdorff's phenomenon (Meadows et al., 2003). That is too significant under the high conversion (Forni et al., 2000).
The experimental equation for the velocity of polymerization up to complete conversion is well-known (Penidis et al., 1992):

$$W = AF(C)\exp(-E/RT),\qquad(1)$$

where $F(C)$ is a function of conversion.

Except the kinetics, the other significant factor is the structure of substances fluxes in the reactor, which determines the efficiency of polymerization process (Cervantes et al., 2003). 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 residential time in the apparatus. Previous analysis showed a good agreement of the experimental data with the theoretical C-curves for the periodic process under the time more than 6 hours (Figure 1).

However, for the non-stop process the polymerized mass residence time inside the apparatus is less than 6 hours. It's 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 up-per 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 ^{o}C over the height of apparatus. The temperature at the upper part of reactor was higher than at the lower part (Figure 2).

The measures made at the different periods of the process also showed a considerable temperature difference. The densities of distribution can give visual information about this observation (Figure 3). The maximum of the density of temperature distribution is observed within the 71-72 ^{o}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.
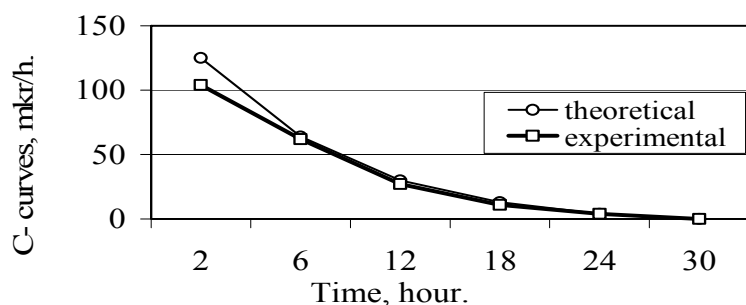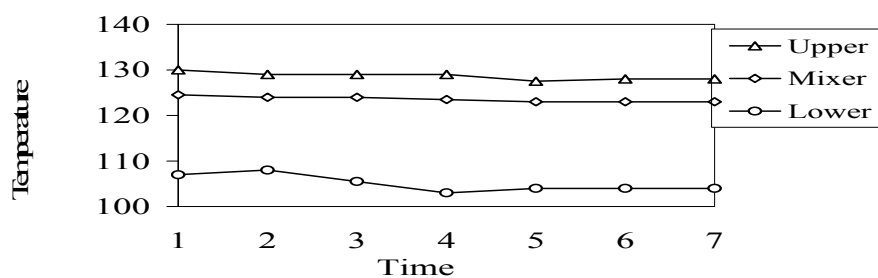

Figure 1: C-curve of the perfect-mixing reactor

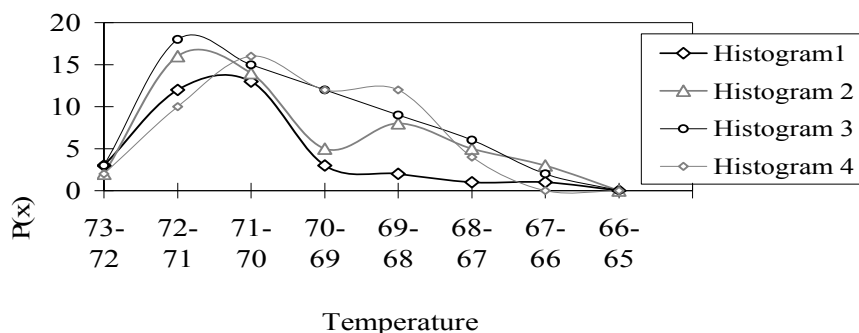Figure 2: temperature (^{o}C) over the height of the reactor in time (s)

Figure 3: the densities of temperature (s) 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 correspond to the time lag about 5-6 hours, what confirms the maximum of correlation between process parameters at that period and accords also to the average time of polymerized mass being inside the reactor.

Dynamic linearized model of the polymerization process can be written in discrete form as

$$Y_{j,n+1} = \theta_{1,j} Y_{j,n} + \theta_{2,j} Y_{j-1,n} + AX_{j,n},$$ (2)

The experimental equation for the velocity of polymerization up to complete conversion is well-known ():

$$\theta_{1,j} = 1 - 1/\tau_j, \quad \theta_{2,j} = 1 - \theta_{1,j}$$ (3)

$Y_{j,n}$ and $X_{j,n}$ are the input and output variables calculated from the formulas:

$$Y_{j,n} = C_{j,n}/F(C_{j,n}); \qquad X_{j,n} = \tau_j \exp(-E/RT_{j,n}).$$ (4)

Here $C_{j,n}$ is the styrene conversion, τ_j is the residential time of the polymerized mass in the reactor.

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 those processes requires considerable expenses and due to this it's sufficiently difficult (Li et al., 2005). A combined stochastic model is more effective, because it takes into account all these factors. So, the determinate model remains all the same the main basis of our consideration.

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 stochastic model with allowance for the influence of the correlated perturbations in the bounds of the model of noise in autoregressive form reads

$$Y_{j,n+1} = (\theta + \lambda_j)Y_{j,n} + (1-\theta)Y_{j-1,n} - \theta\lambda_j Y_{j,n-1} - (1-\theta)\lambda_j Y_{j-1,n} + A_j X_{j,n} - A_j \lambda_j X_{j,n-1} + \sigma\varepsilon_{j,n}$$ (5)

It can be shown that well-known methods () are ineffective in the case of correlated perturbations. Though we often can't carry out the active experiment in the industrial conditions, the databases about the process parameters can be always used.

According to the elaborated method the 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 Eqs. (1, 2).

2. Identification of the combined stochastic model with allowance for the correlated perturbations. This model is presented by Eq. (5).

To evaluate the parameters of model (5) the equations of Yul-Woker's type (Box et al., 2013) were chosen.

Estimating model parameters can be obtained by solving the Yul-Woker's equations (Berdieva et al., 2013) under the conditions

$$\sum_{i=1}^{n} Y_{n-i}\varepsilon_i = 0; \qquad \sum_{i=1}^{n} X_{n-i}\varepsilon_i = 0; \qquad (6)$$

However, the determination of the parameters under these conditions is not always possible to minimize the magnitude of the mean square error of the forecasted output variable. Note that the estimates of the parameters with the minimal deviation can be obtained from these relations in a particular case. Therefore, in the far-follows we can obtain estimates of the parameters for different values of the quasi-stationarity range by checking where these estimates are larger than standard deviation. This allows us in some cases to simplify the calculation procedure.

The root-mean-square error of the prognosis of output variable per unit of the one step was accepted as the identification criterion. According to this criterion equations of Yul-Woker's type were suggested for calculating the evaluations of the model parameters.

As the polymerization process is non-stationary, so the identification procedure we propose to convene on a sliding interval. In order to account the non-stationarity of polymerization processes, the special algorithm on a sliding range, which is called quasi-stationary intervals, have been proposed (Berdieva et al., 2013).

For this purpose, the weight function $W[n,k,p]$, which takes into account the non-stationarity has been introduced:

$$W(n,k,p) = \begin{cases} 1, & if\ (n-k) \le p, \\ 0, & if\ (n-k) > p \end{cases} \qquad (7)$$

Here n is the discrete time (the number of measurement); p is the algorithm memory (quasi-stationary interval); k is the current range of quasi-stationarity.

This weighting function is of relay type. For non-stationary processes the usual method of least squares leads to loss of information. Therefore, we use an adaptive method of least squares.

In this approach the Yul-Woker's equations (Box et al., 2013) include autocorrelation and cross-autocorrelation functions in the form of second moments of the distribution:

$$R_{XY}(k,n) = \frac{1}{p+1-k}\sum_{i=n}^{p+1-k} X_i Y_{i+k}; \ R_{XX}(k,n) = \frac{1}{p+1-k}\sum_{i=n}^{p+1-k} X_i X_{i+k};$$

$$R_{YY}(k,n) = \frac{1}{p+1-k}\sum_{i=n}^{p+1-k} Y_Y X_{i+k}. \qquad (8)$$

Thus, the procedure becomes a multi-step.

3. Results and discussion

The estimates of the correlation function were used in the identification procedure using equations Yule – Uoker. Estimate means square error calculated by the known scheme (Berdieva and Ospanova, 2012a), wherein the coefficients of the mathematical model and correlation functions were time-dependent (Figures 4, 5, 6).
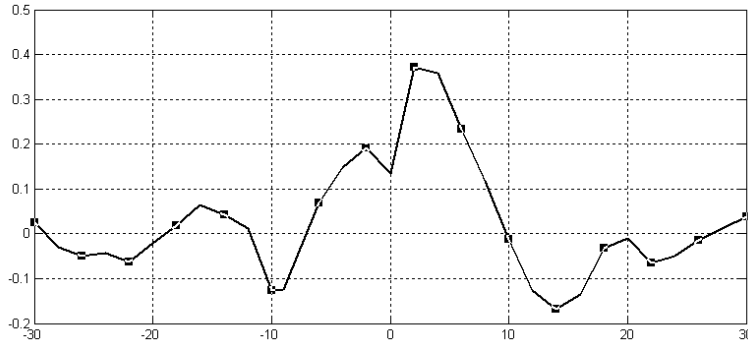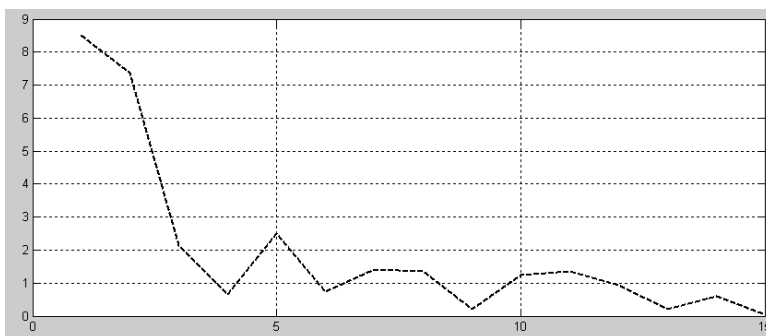

Figure 4: cross-correlation function Rxy(k,n)

Figure 5: autocorrelation function Ryy(k,n)
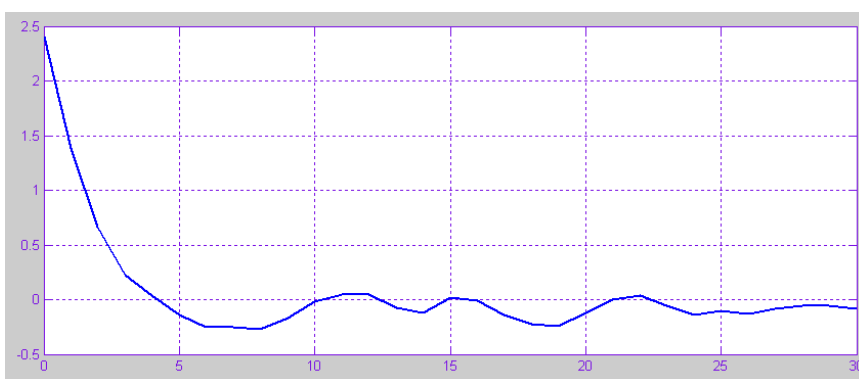

Figure 6: autocorrelation function Rxx(k,n)

To calculate the coefficients of the model by described methods, the measured values of conversion and temperature were used applying to the industrial process styrene polimerization in two serially connected mixing reactors.

Analysis of the results shows that account of dynamic factors while evaluating the model parameters of the object allows us to reduce the variance of the forecast up to 40-50%. Account of the correlated perturbations at the object output allows decreasing the prognosis dispersion up to 60-70% (Berdieva and Ospanova, 2012b).

So, the mathematical model of the styrene polymerization carried out with allowance for the correlated perturbations gives the best prognosis for control parameters. Therefore, it's more exact mathematical description of the process.

Accounting for correlated noise at output of the object reduces the variance estimates of the forecast by 60-70%. Estimates of the model coefficients calculated under the shifts k = 2, 4, give a minimum estimate of the variance of the forecast of 0.60.

However, it should be meant that some values of control parameters ($\lambda > 3$ in Eq. 5, particularly) may correspond to the absence of physical sense of the process characteristics, since the model describes the instability of the model in the case of unobserved noise.

Comparison between estimates of model parameters of the first and the second reactors shows that the pre-exponential factor of the model for the first reactor is greater than for the second reactor. The error of the model for the second reactor is lower.

This fact explains the features of the process occurring in the reactor: the reaction rate of polymerization in the second reactor is lower and disturbing factors are lower too. At the same time, the prognosis by the usual least square method did not allow to decrease the error.

So, comparison between results of analyzing by the considered methods for constructing estimates of parameters of the models for the first and second reactors shows that in both cases (in the first and second reactors) the best forecast estimates of the parameters were obtained using sliding interval method with the correlated noise.

4. Conclusions

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.

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

For monitoring the industrial process in real-time regime according to the submitted mathematical model, it is recommended to carry out the identification of the mathematical model parameters with accounting of the correlations between perturbations with the help of sliding interval approach.

The submitted method was applied to constructing the mathematical models of the styrene polymerization in industrial reactors. During the detail study of the kinetics of styrene polymerization as well as of the flow structure in the apparatuses, it can be concluded that this method relies both on a methodology for constructing deterministic models and on mathematical tools for constructing the stochastic models.

Such rational approach to the construction of mathematical models for industrial processes using a database of technological parameters in the real-time regime showed its relevance from the point of view of best reliability. The submitted method allows us to pass over the scaling problem in a sense, inasmuch as conclusions on the base of the results obtained on pilot plants is not reliable for the simulation of large industrial reactors. It helps also to avoid the problem of large-scale transition (Musabekova et al., 2014).

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