The use of the model of kinetics of ethylbenzene dehydrogenation to estimate the state variables and catalyst performance under unsteady conditions

A P Popov¹, S G Tikhomirov¹, O G Neizvestny² and Kh E Kharlampidi³
¹FSBEI HE Voronezh State University of Engineering Technology, Voronezh, Russia
²FSBEI HE Voronezh State Technical University, Voronezh, Russia
³FSBEI HE Kazan National Research Technological University, Kazan, Russia

E-mail: aleksej_p_91@mail.ru; tikhomirov_57@mail.ru; o.neizvestnyi@mail.ru

Abstract. The article considers the application of the mathematical modeling method to describe the dynamics of the catalytic layer state variables of the styrene production reactor. This method was carried out using a kinetic approach for description of chemical transformations, which occurs in a multicomponent gas mixture. The main physical processes, affecting the decrease in catalytic activity during operation, are considered and the relationship between them is described. A method for increasing the efficiency of the catalytic system in terms of ACS (automated controlling system) synthesis is proposed. The mathematical formulation of the problem of creating a predictive program control system under unsteady conditions is completed. Mathematical software has been developed that allows us to evaluate activity and predict the dynamics of changes in such production efficiency indicators as ethylbenzene conversion and styrene selectivity. In that framework, the blocking of catalyst active centers, proceeding by the sequential mechanism of coke formation, is classified as a deactivating factor. The distribution patterns of carbon along the length of the reaction space at different times of the catalyst inter-reactivation period, depending on changes in the mixture component concentrations and the temperature condition, are revealed. Based on the production data, the calculation and approximation of raw materials conversion values and selectivity for the target product were carried out taking into account the accumulation of carbon on the layer surface, as well as the variation of process parameters such as temperature, pressure of the reaction mixture and partial pressures of the components.

1. Introduction
Since the 80s of the XX century, in scientific works, scientists noted that the level of chemical technology and the chemical industry is determined by the perfection of the catalysts and the ability to ensure their effective use in carrying out chemical-technological processes. For catalytic processes, the main state parameters are indicators such as catalyst activity, feed conversion and selectivity for the target product. At the same time, a decrease in catalyst activity during the operation of process equipment is the main side effect that characterizes most processes.

According to literature sources, the catalytic activity of industrial plants decreases as a result of the following processes: coke (carbon) deposits on active centers; "poisoning” of the reaction accelerator surface by the contact poisons or sintering under the action of high temperatures and water vapor; abrasion of particles; fatigue of the layer surface; and also a change of strength, structure and surface of the catalyst as a result of aging processes. All these processes lead to a gradual or sharp, uniform or non-uniform decrease in the effective surface of the layer, which in turn causes a deviation of the
physical parameters of the reaction environment from the nominal values, as well as a change in the hydrodynamic characteristics of the chemical reactor [1, 2].

The premature occurrence of these processes, as well as the inability to control, prediction and manage their dynamics, is one of the main problems of the petrochemical industry [3]. This is a causal factor in the inefficient operation of catalytic systems.

One of the innovative solutions in this area is the use of the Industry 4.0 technologies to develop new or transform existing chemical synthesis process control systems. The strategy for the formation and continuous expanding knowledge bases with information in the form of possible scenarios of changes in catalytic activity depending on the course of various physical and chemical factors of decontamination is an appropriate plan for achieving this goal. For this, it is necessary to use such advanced technologies as modeling and predicting, storage and processing of big data, and design of control neural networks. Ultimately, all this, within the framework of the model-based design paradigm, will provide information for the development of control actions that allow us to timely estimate the decrease in catalytic activity in an industrial condition.

The basis for reaching a new level of catalytic systems operation is the creation of a mathematical description of the dynamics of chemical transformations. For this, all possible factors causing a decrease in catalytic activity must be taken into account in time, along the length of the reaction space and inside the pores of the catalyst.

The preparation of styrene by dehydrogenation of ethylbenzene is one of the most complicated catalytic processes occurring at the interface between the solid and gas phases since:

1. Inside the reactor stages, a heterogeneous gas-phase endothermic reaction of thermal decomposition of ethylbenzene proceeds, the mechanism of reaction is serial-parallel with the formation of a large number of by-products [4]:
   - decomposition of ethylbenzene, resulting in the formation of styrene, hydrogen, benzene and ethylene;
   - hydrogenation of ethylbenzene with the formation of toluene and methane;
   - carbon emissions resulting from the decomposition of methane, as well as the conversion of methane by water vapor.

2. The catalytic layer of the reactor is fixed, and at the input to the reaction zone, the feed is mixed with superheated water vapor.

Therefore, the used catalytic layer is influenced by at least five physicochemical processes resulting in a decrease in catalyst effective surface:

![Diagram of physical and chemical processes](image)

**Figure 1.** Correlation of the main physical and chemical processes of the decontamination of the catalytic layer of the stages in the styrene production reactor.

The nature of the decrease in the layer activity is due to the direct influence of these processes on each other. The sintering rate of the catalyst is greatly influenced by water vapor, accelerating this process. The deposited coke leads to uneven sintering of the catalytic particles, since it provides protection for active centers at high temperatures. During the dehydrogenation of ethylbenzene, in addition to carbon, hydrogen, methane and carbon oxides can also be included in the composition of coke. As a result of incorrect catalyst charge into the reactor and implementation of process control
with significant deviations of the technological parameters from the specified nominal values, early decontamination occurs. All of these processes accelerate the aging of a catalytic substance particles.

Thus, from the point of view of engineering cybernetics, in order to create and implement a neural network algorithm of predicting software control, it is necessary to develop and verify a module of an integrated dehydrogenation model. That will allow to accurately calculate the physical and chemical aspects of the decrease in activity in conjunction with non-steady-state kinetic models of chemical transformations, reactivation and sintering process kinetics.

Work on the study of the kinetics unsteadiness, as well as the prediction of the catalytic layer condition using the methods of simulation and computational mathematics was carried out by many scientific teams for various types of reactors and catalytic layers [5–11]. The reviews of the created mathematical models and methods for describing reactors with fixed and fluidized catalyst beds are presented in [11–13]. The main disadvantage of these works is the fact that, using various methods of modeling the process kinetics, one of the possible negative factors is usually chosen as decontamination. Russian articles describe the processes of coking [6, 7] and poisoning of catalysts [8, 9]. In foreign articles, much attention is paid to the processes of sintering of layer particles [14–16]. Insufficient attention has been paid to the issues of creating complex models that take into account the multiply connected parameters of decontamination processes.

A small number of such studies has been carried out in relation to styrene production processes. Among others, one can note the work on controlling the process of styrene synthesis based on a mathematical description of the decrease in catalyst activity due to chemisorption of reagents [17].

As the dehydrogenation proceeds, the catalyst layer decontamination is the main reason for the decrease in the concentration of the target styrene product, the change in ethylbenzene conversion and styrene selectivity, as well as the increase in coolant flow rate to compensate for this side effect. Therefore, the stabilization of these values at a given level over a long period, providing a program transition to other values of controlled parameters, as well as predicting their decline during operation using modern technological methods, tools and solutions, is an urgent scientific and production problem.

2. Materials and methods

When choosing methods to solve the problem, it is necessary to take into account the following features of the process, as well as the results of previously performed work in the field of technical chemistry of heterogeneous processes:

- according to the dynamics of physicochemical transformations inside the reaction zone, one of the stages in the development and verification of a predictive model of the styrene production process according to the previously described mechanism is the preparation of a mathematical description of the decrease in the catalytic activity of the reactor using models describing the kinetics of the main and side reactions during the separation of hydrogen from ethylbenzene charge [18–21];

- the use of vacuum technology for the dehydrogenation of ethylbenzene, when the total pressure inside the reaction zone is equal to or less than atmospheric. In this pressure range, to estimate the degree of decrease in the activity of catalyst particles, it is important to know the partial pressures of the components of the reaction stream interacting with the granular catalyst bed, as well as the values of water vapor pressures and the total pressure of the mixture. It should be noted that the highest value of the sintering rate of the catalyst under the influence of water vapor occurs when the partial pressure in the range from 0 to 0.1 MPa [2];

- the interconnection of the main physical and chemical factors of catalytic layer decontamination determines the dependence of the dynamics of an irreversible decrease in activity and a decrease in the effective layer surface on the rate and spatial orientation of coke formation.

Thus, increasing the catalyst operation efficiency cannot be realized without an automated control system (ACS). The main task of ACS is to quickly calculate and change the process mode parameters, which are the control actions [22].
For the process under consideration, the core of the ACS is mathematical support (MS), for the formation, layout and validation of which it is necessary to apply the method of complicated mathematical models. What is necessary to solve the most important tasks at the stages of synthesis of a predictive control system:

1. Development of models of internal reactor processes taking into account new factors (for this process, these factors are partial pressures and partial molar volumes of reagents, as well as the concentration and distribution of coke in the reactor space).

2. Providing the effect of saturation with information of the predictive ACS knowledge base in the field of possible scenarios of catalyst aging while minimizing uncertainty factors.

From the point of view of system analysis and theory of automatic control, the blocking of the catalyst active centers by coke is an internal immeasurable perturbation action for the process. Thus, based on the chosen methods, a description of the mechanism of carbon deposits formation on the catalytic layer is developed. It is used to calculate and determine a reliable predictive horizon for changes in the following parameters: the total concentration of coke, its distribution along the length of the reactor at various points in time of the process.

In summary, the MS of management system includes:

- a model of the dehydrogenation kinetics, which is a system of differential equations describing the dynamics of changes in the reagent concentrations, depending on the process parameters: partial pressure of the components, temperature of the mixture, reaction steam rate:

\[
\frac{d\mathbf{x}}{dt} = F_r(\mathbf{x}, \mathbf{u}, \mathbf{k}(l)), \quad z = A, \ldots, P
\]

\[
n(0) = n_0, \quad k_q(0) = k_0^q, \quad q = 1, \ldots, 7
\]

\[
\mathbf{x} = \{T(l), V_{\text{sm}}^\text{maw}(l), P_A(l), \ldots, P_p(l), a(l), S(l)\}
\]

\[
\mathbf{u} = \{T_m(0), T_p(0), R_m, R_p, R_g, S(0)\}
\]

\[
\mathbf{k} = (k_1(l, V_{\text{sm}}^\text{maw}(l), P_A(l), T(l)), k_2(l, T(l)), k_3(l, V_{\text{sm}}^\text{maw}(l), P_p(l), T(l)), k_4(l, V_{\text{sm}}^\text{maw}(l), P_p(l), V_{\text{cm}}^\text{maw}(l), P_c(l), T(l)))
\]

Where:

- \(n_A, n_B, n_C, n_D, n_K, n_F, n_G, n_H, n_K, n_P\) - amount of styrene, ethylbenzene, hydrogen, benzene, ethylene, toluene, methane, carbon, carbon monoxide and water vapor, respectively, mol;

- \(k_1\) is the styrene formation rate constant, s\(^{-1}\);

- \(k_2\) is the rate constant of the reverse reaction of the styrene formation, 1 / (mol s);

- \(k_3\) is the rate constant for the formation of benzene and ethylene, s\(^{-1}\);

- \(k_4\) is the rate constant for the formation of toluene and methane, 1 / (mol s);

- \(k_5\) is the rate constant for the formation of carbon and hydrogen, s\(^{-1}\);

- \(k_6\) is the rate constant for the formation of carbon monoxide and hydrogen, 1 / (mol s);

- \(k_7\) is the rate constant for the formation of methane and water vapor, 1 / (mol s);

- \(V_{\text{sm}}^\text{maw}(l), V_{\text{cm}}^\text{maw}(l), V_{\text{cm}}^\text{maw}(l), V_{\text{cm}}^\text{maw}(l), V_{\text{cm}}^\text{maw}(l)\) - partial volume of styrene, ethylbenzene, hydrogen, methane, carbon monoxide and water vapor, respectively, 1 / mol;

- \(P_A(l), P_B(l), P_C(l), P_p(l), P_g(l), P_c(l)\) - partial pressures of styrene, ethylbenzene, hydrogen, methane, carbon monoxide and water vapor, respectively, Pa;

- \(V\) is the volume of the reaction mixture, l;

- \(a(l)\) is the activity of the catalytic system;

- \(T(l)\) is the temperature in the reactor stage, K;
is the value of the ratio of the water vapor pressure and ethylbenzene mixture pressure; 

is the fuel gas flow rate, m³/s;

is the water vapor flow rate, m³/s;

is the ethylbenzene charge flow rate, m³/s.

- a model for calculating catalytic activity depending on the amount of carbon deposits:

\[
\Delta n_{j,i}^{\text{C}} = n_{j+1,i}^{\text{C}} - n_{j,i}^{\text{C}}, \quad i = 0, \ldots, L; \quad j = 0, \ldots, 12000;
\]  

where

\[
\Delta n_{j,i}^{\text{C}} \text{ is the amount of carbon substance deposited during the passage of the reaction environment through the } i\text{-th section of the catalytic layer at time } j, \text{ mol;}
\]

\[
n_{j+1,i}^{\text{C}} \text{ is the amount of carbon substance in the } (i+1)\text{-th section of the catalyst at time } j, \text{ mol;}
\]

\[
n_{j,i}^{\text{C}} \text{ is the amount of carbon substance in the } i\text{-th section of the catalyst at time } j, \text{ mol.}
\]

\[
\text{sum}_{j,i}^{\text{C}} = \sum_{m=1}^{i} n_{m-1,i}^{\text{C}} + \Delta n_{j,i}^{\text{C}},
\]  

where

\[
\text{sum}_{j,i}^{\text{C}} \text{ is the integral amount of carbon substance accumulated in the } i\text{-th section of the reaction space at time } j, \text{ mol.}
\]

\[
\text{Act}_{j,i} = \exp \left( - \frac{\text{sum}_{j,i}^{\text{C}}}{C_{\text{max}}} \right)
\]  

is the activity value of the i-th site of the catalytic surface at time j, mol.

\[C_{\text{max}}\] is the maximum value of the carbon deposits content, mol [11].

The assumptions adopted when modeling the processes of coke deposition:

- the dehydrogenation reaction proceeds in the kinetic area;

- the catalytic surface is homogeneous;

- coke formation on the catalytic surface is multilayer and proceeds at the same rate, regardless of the surface coking degree and the number of active sites of the catalyst;

- only carbon molecules are part of coke deposits;

- the mechanism of blocking active centers by coke is sequential.

Figure 2. Coke formation mechanism.
When conducting a computational experiment to study the dynamics of the coke deposits formation, the catalytic layer was divided into sections of a fixed length, for each of which the value of activity was estimated depending on the current values of the reaction mixture temperature, partial pressures of the reagents, and also on the integral amount of carbon deposited.

3. Results and discussion
As a result of a computational experiment, we obtained the distribution of the amount of carbon substance deposited on the surface of the catalytic sections along the length of the reaction zone at the following reactor operating times: 200, 4000, 8000, and 12000 hours. The calculations are based on production data of the change in the initial temperature of the reaction mixture at the inlet to the reactor, which are presented in Table 1 [23].

Table 1. The temperature of the reaction mixture at the inlet to the reactor.

| Operating time, h | Temperature, °C |
|------------------|-----------------|
| 200              | 603             |
| 4000             | 602             |
| 8000             | 603             |
| 12000            | 607             |

The simulation results in the form of graphs of the distribution of the amount of carbon deposited, changes in temperature, methane concentration, accumulation of carbon deposits and changes in catalytic activity are shown in figure 3–7 respectively.

Figure 3. Change in the amount of carbon substance deposited on the catalytic surface sites at different times of reactor operation.

The distribution paths of carbon along the length of the reaction space, presented in figure 3, show that during operation there are a change in the maximum amount of precipitated deposits at the
active centers of the catalyst and a shift of this value along the length of the layer while transforming the shape of the distribution graph.

![Graph showing temperature decrease along reaction zone length](image)

**Figure 4.** The decrease in temperature of the reaction mixture along the length of the reaction zone.

![Graph showing methane formation kinetics](image)

**Figure 5.** Kinetic curves of methane formation ($n^G$).

An analysis of the data obtained allows us to conclude that the highest value of the layer surface coking (figure 6) occurs in those parts of the reaction space where methane concentration is high. In this case, the graphs of changes in methane concentration and the amount of substance of deposited carbon monotonously increase. The results are consistent with the sequential mechanism of carbon
deposition and graphs of changes in the concentration of methane (figure 5) and carbon (figure 3). The decrease in catalytic activity is shown in figure 7.

![Graph showing carbon accumulation along length of catalytic surface](image)

**Figure 6.** Distribution of carbon accumulation along the length of the catalytic surface.

![Graph showing catalytic activity changes](image)

**Figure 7.** Dynamics of changes in the catalytic layer activity.

A comparison of the experimental and calculated data using model (1–4) characterizing the operation of the catalytic system and the process efficiency is shown in figure 8–9 and in table 2. In figure 8–9 \( K_{\text{exp}}(t) \) – are the experimental values of ethylbenzene conversion, \( K_{\text{ras}}(t) \) – are the ethylbenzene conversion values obtained using model (1–4), \( S_{\text{exp}}(t) \) – are the experimental values of selectivity for styrene, \( S_{\text{ras}}(t) \) – are the selectivity values for styrene obtained using the model (1–4).
Figure 8. Change in the conversion of ethylbenzene during 12000 hours of reactor operation.

Figure 9. Change in styrene selectivity over 12,000 hours of styrene production reactor.

Table 2. The experimental and calculated values of ethylbenzene conversion and styrene selectivity comparison results.

| Operating time, h | $\Delta K(t)$, % | $\Delta S(t)$, % |
|-------------------|-------------------|-------------------|
| 200               | 0.05              | 0.29              |
| 4000              | 0.04              | 0.28              |
| 8000              | 0.07              | 0.11              |
| 12000             | 0.07              | 0.34              |

where $\Delta K(t)$ is the value of the % RE of ethylbenzene conversion calculation; $\Delta S(t)$ is the value of the % RE of styrene selectivity calculation.
As can be seen from table 2, the values characterizing the operation of the dehydrogenation catalyst calculated according to model (1–4) are consistent with the theoretically obtained data [23].

4. Conclusion

The simulation results, presented in table 2 and in figure 8–9, showed the possibility of using the obtained dependences to describe the dynamics of the catalyst state variables under unsteady conditions. Thus, a automated control system mathematical support of the dehydrogenation reactor was developed, which allows to evaluate the catalytic activity and predict the dynamics of changes in ethylbenzene conversion and styrene selectivity. The forecast is carried out taking into account the place of coke accumulation on the catalytic surface of the reaction zone and such process parameters as temperature, pressure and consumption of raw materials.

Due to the fact that during the dehydrogenation of ethylbenzene charge, some of the reactions are related to side reactions of the Fischer – Tropsch process. Based on the results obtained, it is advisable to study the effect of the contact gas composition on the amount of chemical reactions products adsorbed by the catalyst in addition to carbon particles. In the future, this will allow us to calculate the kinetics of the processes of reactivation and sintering of the catalytic system under consideration.

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