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NEURAL NETWORK MODELLING OF THE PROCESS OF METHYLBUTENE DEHYDRANATION INTO ISOPRENE

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ABSTRACT

The process of C_5H_{10} hydrocarbon dehydrogenation consists of turning isopenthane into methylbutene and its compounds, or into isoprene with an oxide ferric potassium catalyst. When operating in a commercial reactor for several thousand hours, a ferric potassium catalyst gradually loses its activity. In the commercial operation, the catalyst is activated at times with water vapour. However, frequent regenerations are unfavourable as they result in a gradual change in the treatment phase content of the catalyst in the circle: reaction – regeneration. Thus, it is typical to modernize the isoprene production processes on the basis of hydrocarbon material. Namely, to construct new mathematical models, making it possible to forecast properties of the basic process factors. This paper is devoted to the construction of a mathematical model using differential equations and an artificial neural network for the catalyst process of methylbutene dehydrogenation into isoprene, providing the reagent changes in time and reactor length. Simultaneously, the given neural network made it possible to consider the peculiarities of the chemical process and foresee the concentration of the target product (isoprene), and how they depended on the changes in the parameters of the setting and composition of the source substances of the reaction compound.

Keywords: direct problem of chemical kinetics, neural networks, multifactorial model, dehydrogenation of methylbutenes.

INTRODUCTION

The necessary criterion to calculate a commercial process is to be aware of kinetic and mathematical models. It is necessary, above all, to study the kinetics of the catalyst reaction in detail to gain a better understanding of the physical and chemical essence of the catalyst reaction. This will involve the mathematical modelling of the catalyst process and specification of the conditions of its commercial implementation. Further, based on the kinetic model, it may be necessary to investigate the process at the higher levels that the models of the catalyst grain correspond to, such as the model of the catalyst layer, of the catalyst reactor and of the setting. Each level contains models of lower levels and balances that show the level-to-level transfer. This approach makes it possible to carry out the detailed modelling of chemical technological processes. However, the obtained models are quite complex and their calculations require more time and resource-intensive inputs. When modelling, a number of simplifications and constraints are introduced and can significantly distort the results.

An alternative approach to modelling chemical-technological processes can be an artificial neural network. A neural network allows one to give up complex mathematical models, and instead consider peculiarities of chemical processes at the same time.

The process to construct a neural network consists of two stages. In the first stage, the software design and activation functions of neurons are set up. In the second stage, weighing coefficients of neuron correlations are sorted out. The second stage is also called network training. The advantageous implementation of neural networks is an ability to come to terms with the changes in the chemical process through the retraining or readjustment of the network.

Kinetic level

To construct a kinetic model, pentene isomers were united into the group component of $i\text{-}C_5H_{12}$, methylbutenes into the components of $i\text{-}C_5H_{10}$, isoprene isomers into the component of $i\text{-}C_5H_8$, all cracking products into the component of CP.

In study [1], a four-stage scheme of the changes for theC_5 hydrocarbon dehydrogenation process was given. The reaction scheme can be presented in the following way:

$$\begin{aligned} i-C_5H_{12} &\leftrightarrow i-C_5H_{10}+H_2 \\ i-C_5H_{10} &\leftrightarrow i-C_5H_8+H_2 \\ i-C_5H_8 &\rightarrow v_1\{coke\}+v_2H_2+v_3CP \\ \frac{1}{2}C\{coke\}+H_2O &\rightarrow \frac{1}{2}CO_2+H_2 \end{aligned} \quad (1)$$

The corresponding equations of hydrocarbon dehydrogenation velocities are given in the form of equations:

$$\begin{aligned} W_1 &= \frac{k_{+1}C_1 - k_{-1}C_2C_4}{(1+b_{11}C_1+b_{12}C_2+b_{13}C_4)^2}, \\ W_2 &= \frac{k_{+2}C_2 - k_{-2}C_3C_4}{(1+b_{21}C_2+b_{22}C_3+b_{23}C_4)^2}, \\ W_3 &= \frac{k_3C_3}{1+b_3C_4}, \\ W_4 &= \frac{k_4}{1+b_4C_4}, \end{aligned} \quad (2)$$

where C_i is the components concentration (mole/l), and the component *i*-indexation stands for: 1 - isopentane, 2 - methybutenes, 3 - isoprene, 4 - hydrogen, 5 - products of skeleton changes (or cracking products - CP), 6 - hydrogen dioxide; W_j - velocities of chemical reactions (kmole/m3·h)); k_i - constants of reactions velocities; and b_i - absorption coefficient (m3/kmole).

In the study at the kinetic level in paper [2, 3], the review calculations of the constant velocities for the given temperature value were made with reference temperature T_{rt}=620°C or T_{rt}= 893K according to Arrhenius relation:

$$k_i(T) = k_i(T_{on}) \cdot \exp\left[\frac{E_i}{RT_{on}}\left(1 - \frac{T_{on}}{T}\right)\right],$$
$$b_i(T) = b_i(T_{on}) \cdot \exp\left[\frac{Q_i}{RT_{on}}\left(\frac{T_{on}}{T} - 1\right)\right]. \quad (3)$$

where T_{rt} is the reference temperature for which the constant values of reaction velocities (k_i) and absorption coefficient (b_i) (°C) are experimentally specified, T is the current temperature reaction (°C), E_i is the activation energy (kcal/mole), Q is the reaction heat (kcal/mole), R is the common gas constant (kcal/mole·°C)) and i is the component index.

Currently, there are programs to work with neural networks. Among them, the following programs with a broad functioning include: Alinda Neurointelligence (Alyuda Research, США), Neurosolutions (Neuro Solutions, США), Statistica (StatSoft Inc, США) and others.

Let's construct and analyse neural networks with the use of the STATISTICA program (http://statsoft.ru/) for the process under study. In the laboratory, the experimental data for the dehydrogenation of methylbutenes into isoprene was determined: T_{rt}=620°C, weakening by heat vapour (mole/mole) 1/20 and velocity supply (h^{-1}) 1.0. In papers [4-6], the numerical values of reagent concentrations of the process under study were retrieved based on the kinetic model.

Let's make use of the data and hold the training of some 100 neural networks. We take X1 to be the process temperature (°C) and X2 to be the reaction period point (sec.) as input parameters of the neural network. The output parameters of the artificial neural network will be Y1, the concentration of i-C_5H_{10} (% mass) and Y2, the concentration of i-C_5H_8 (% mass).

RESULTS AND DISCUSSIONS

In the STATISTICA program, three adequate models were found for the artificial neural networks, making it possible to foresee regime parameters for the catalyst process of dehydrogenation of methylbutenes into isoprene (Table-1).

Table-1. Models of neural networks.

Software design	Algorithm	Function of covert neurons activation	Function of output neurons activation
MLP 2-95-2	BFGS 297	Tanh	Tanh
MLP 2-18-2	BFGS 118	Logistic	Logistic
MLP 2-67-2	BFGS 215	Tanh	Identity

The neural networks had a software design consisting of a multilayer perceptron with a covert layer. The algorithm of the second order by Broyden-Fletcher-Goldpharb-Shanno (BFGS) was used as the method of error minimization. The neural network model for the process of dehydrogenation of methylbutenes into isoprene showed a high accuracy of 99 % for the training, control and test samples. An additional analysis of the neural networks on other samples, and a qualitative analysis of the concentration changes according to the time of the source methylbutene material and target isoprene product, showed that the MLP 2-95-2 neural network model adequately displayed the character of the changes in the reagent concentrations (Figures 1, 2) within the temperature range of 570°C - 630°C.

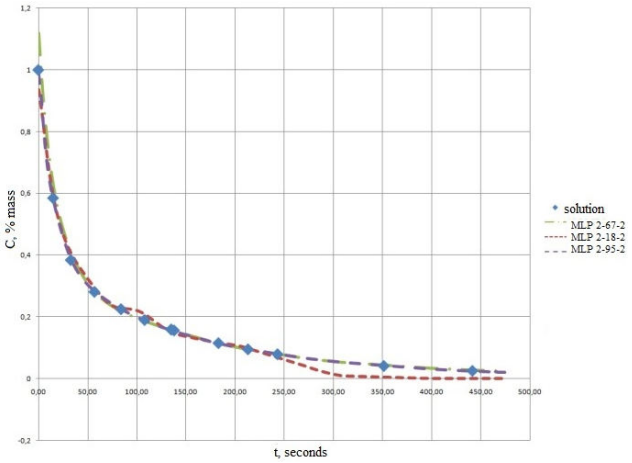

Figure-1. Changes in methylbutenes time concentration at 580 °C.

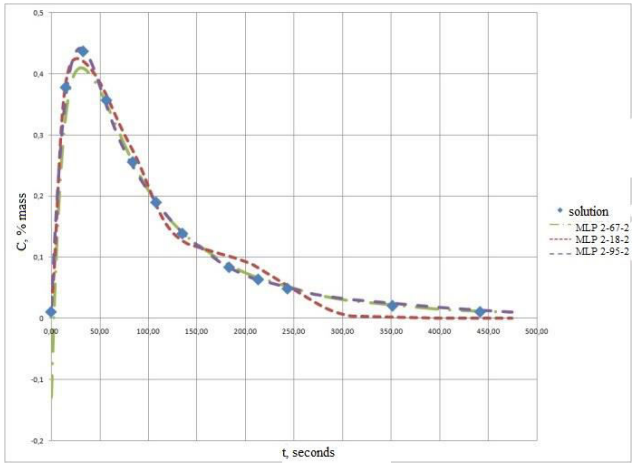

Figure-2. Changes in isoprene time concentration at 580 °C.

Value deviations for other samples with the MLP 2-95-2 artificial neural network model can be seen in Figures 3, 4.

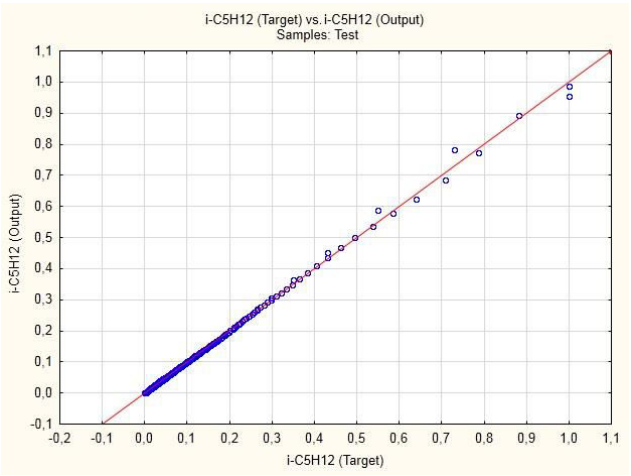

Figure-3. The graph of scattering of the foreseen values for the MLP 2-95-2 artificial neural network on methylbutenes.

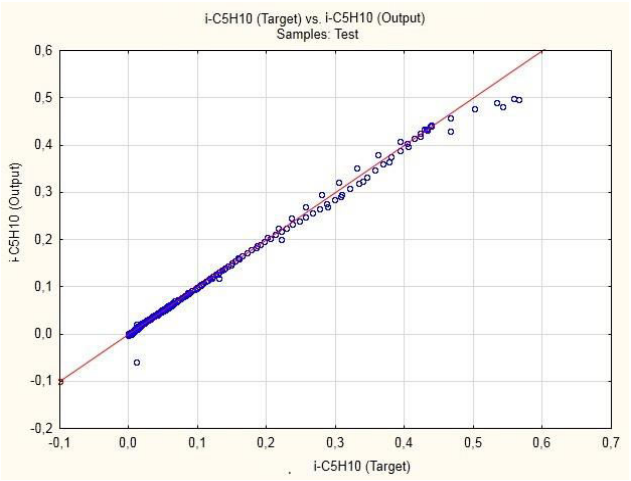

Figure-4. The graph of scattering of the foreseen values for the MLP 2-95-2 artificial neural network on isoprene.

Table-2 shows an average error deviation in the concentration (dots - computing results on the neural network, continuous line - quality line defining a full coincidence of the test value (target) with the output result of the neural network computing (output)).

In Table-2, it can be seen that the MLP 2-95-2 model is characterized by the least deviation in error within the limits of 13.89 % on methylbutene and 19.37 % on isoprene.

Table-2. Average error deviation.

Neural network type	Average deviation on source material, %	Average deviation on isoprene product, %
MLP 2-95-2	13,89	19,37
MLP 2-18-2	62,12	61,59
MLP 2-67-2	49,42	29,12

Technological level

In commercial conditions, the dehydrogenation processes are held in an adiabatic reactor with a fixed bed of solid ferric potassium catalyst [2, 7]. To study the regularities of the process in commercial conditions, let's construct a mathematical model regarding material and heat balances of the reaction shown in Eq. (4).

The mass change of the responding reaction components in the reaction volume (ΔV) during the time (Δt) takes place with raw material supply to the reactor with velocity U_0:

$$U_0 C_i^0 \Delta t = N_0 x_i^0 \Delta t,$$

Raw material reactor output has a velocity U:

$$UC_i \Delta t = N x_i \Delta t,$$

The chemical reaction process is:

$$\left(\sum_j v_{ij} W_j \right) \Delta V \Delta t.$$

where u_{ij} is the stoichiometric coefficient of i component of j stage.

The system of differential equations for the material balance can be expressed in the following way:

$$\frac{\partial x_i}{\partial \tau} + \frac{\partial x_i}{\partial \xi} = \frac{F_i - x_i F_N}{N}, \quad i = 1,\ldots,6,$$
$$F_i = \sum_{j=1}^{4} v_{ij} \omega_j, \tag{4}$$

$$\frac{\partial N}{\partial \tau} + \frac{\partial N}{\partial \xi} = F_N = \sum_{j=1}^{4} \delta_j \omega_j,$$
$$\delta_j = \sum_{i=1}^{6} v_{ij} \tag{5}$$

with boundary conditions:

$$\xi = 0: \quad x_i = x_i^0, N = 1,$$
$$\tau = 0: \quad x_i = 0, N = 1.$$

where x_i is the mole shares of the reaction components, ξ is the non-dimensional reactor's length, τ is the non-dimensional time, N is the relative change of number of moles of the reaction environment, ω_j is the non-dimensional velocity of the reaction, v is the stoichiometric coefficient, i is the component index (i = 1,…,6) and j is the stage index (j = 1, …,4).

The heat balance of the process of methylbutenes dehydrogenation into isoprene is presented in the following differential equation:

$$\frac{\partial T}{\partial \tau} + \frac{\partial T}{\partial \xi} = \frac{1}{C_p} \sum_j Q_j \omega_j, \tag{6}$$

where C_p is the mole capacity of reaction substance (J/(mole·K)) and Q_j is the r reaction heat effects (кJ/mole). Non dimensionalizing V and N, we get the following equations for the reactions velocities:

$$\omega_1 = \frac{k_{+1}\tau_k z_1 - k_{-1}\tau_k z_2 z_4 C_0}{(1 + b_{11}C_0 z_1 + b_{12}C_0 z_3 + b_{13}C_0 z_4)^2},$$
$$\omega_2 = \frac{k_{+2}\tau_k z_2 - k_{-2}\tau_k z_3 z_4 C_0}{(1 + b_{21}C_0 z_1 + b_{22}C_0 z_3 + b_{23}C_0 z_4)^2}, \tag{7}$$
$$\omega_3 = \frac{k_3 \tau_k z_3}{1 + b_3 C_0 z_4},$$
$$\omega_4 = \frac{k_4 \tau_k}{C_0 (1 + b_4 C_0 z_4)},$$

where C_0 is the mole gas density, calculated on the equation of ideal gas law of Mendeleev-Cliperton (mole/м^3),

$$z_i = x_i N, \ (i = 1,\ldots 6),$$

$$\tau_k = \frac{V_P \rho_c \cdot 10^{-3}}{\rho_0 U_0 \left(1 + n \frac{18}{\sum x_i^0 M_i}\right)},$$

where V_p is the reaction volume (м^3), ρ_c is the density of the substance at the reactor input (kg/м^3), ρ_0 is the substance density (kg/м^3), U_0 is the velocity of substance supply (м^3/h), $1/n$ is the ratio of substance and water vapour in the substance and M_i is the molecular mass of i substance.

Thus, the system of differential equations (4) - (7) is a non-stationary non-isothermal mathematical model of the process of methylbutene dehydrogenation into isoprene in an adiabatic reactor with a non-fixed catalyst layer. The model makes it possible to note the changes of number of moles in the reaction gas substance. Let's give the boundary conditions for model (4) - (7) in the following way:

$$\xi = 0: \quad x_i = x_i^0, N = 1, T = T_0;$$
$$\tau = 0: \quad x_i = 0, N = 1, T = T_0.$$

We compared the results of computing experiments obtained on the basis of the solution of the primal problem according to model (4) - (7), and on the basis of the model of the artificial neural network. It is noteworthy that the model of the artificial neural network allowed one to not only obtains changes in time and length concentration of reagents. It also allowed one to foresee the concentration of the isoprene target product based on the changes of technological parameters of the setting, in addition to the composition of the source substances of the reaction compound.

The following technological parameters of the process under study were varied: velocity of the source compound supply to the reactor from 0.6 till 2.0 h^{-1} and

weakening the substance with water vapour from 1/10 to 1/20.

The input parameters were chosen as: Z1 as the weakening with vapour, Z2 as the i-C_5H_{12} concentration (% mass), Z3 as the average molecular mass, Z4 as the i-C_5H_{10} concentration (% mass), Z5 as the H_2 concentration (% mass), Z6 as the cracking products, Z7 as the CO_2 concentration (% mass), Z8 as the temperature process procedure (°C) and Z9 as the velocity of source substance supply to the reactor (h^{-1}).

RESULTS AND DISCUSSIONS

Five hundred (500) artificial neural networks were analysed. The best among them was the model of perceptron with a covert layer of MLP 9-6-1 and logical activated function for the neurons of a covert layer and output neuron. As a method of error minimization, the same BFGS algorithm similar to the first experiment was used. Figure-3 shows the results of changes in isoprene concentration obtained by model (4) - (7), and on the basis of the artificial neural network.

In the process of the computing experiment with the neural network, the data was compared to the data of the direct modelling on the basis of the system of differential equations. The deviations of the foreseen values are given in Figure-5, where the values of the neural network are marked with dots. The full line marks the quality line, which defines the complete coincidence of the test value (target) with output of the neural network (output).

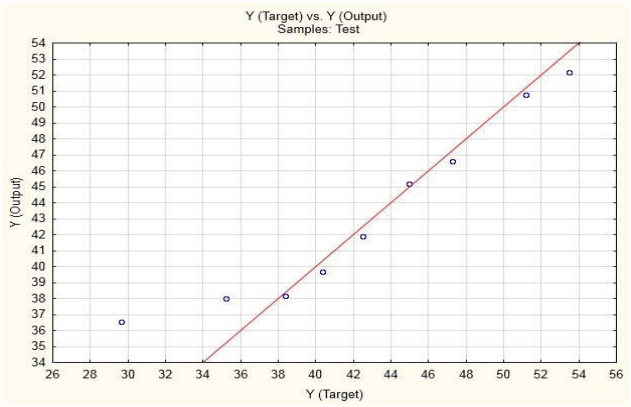

Figure-5. The scheme of diffusion of the foreseen values of the artificial neural network on the target product.

Figure-6 shows the comparison of the results of the experimental data obtained in laboratory conditions and calculation values on the basis of the neural network. Table-3 contains the basic data of the taught neural network.

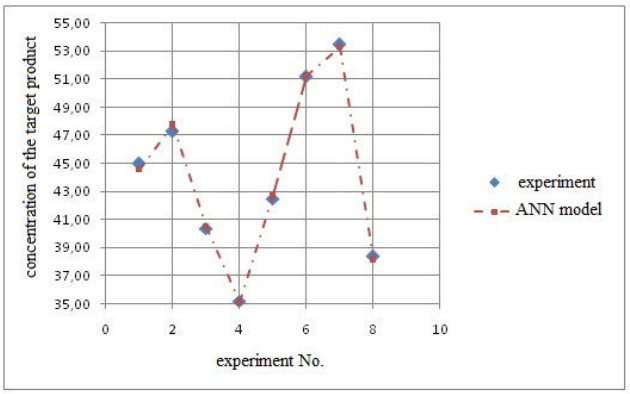

Figure-6. Comparative isoprene input results.

Table-3. Deviations in selection errors.

	Teaching selection	Test selection	Test values
Standard data deviations, %	3,85	4,23	4,37
Average errors, %	1,03	7,45	5,67

On the basis of the laboratory data and the calculation results, we can conclude that the constructed multifactorial model of the neural network of the process of methylbutene dehydrogenation into isoprene makes it possible to foresee the output of isoprene target product, depending on the changes in regime parameters of the setting and the composition of the source substances of reaction compound with a higher accuracy (no less than 95%).

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