www.arpnjournals.com

THE THEORETICAL OPTIMIZATION OF THE PROCESS OF DEHYDROGENATION OF METHYLBUTENES WITH THE DEACTIVATION OF THE CATALYST

Dina Shaimukhametova[1], Svetlana Mustafina[1] and Denis Shaimukhametov[2]
[1]Department of Mathematics, Bashkir State University, Lenin Avenue, Postal Index, Sterlitamak City, Republic of Bashkortostan, Russian Federation
[2]Institute of Petrochemistry and Catalysis, Russian Academy of Sciences, October Avenue, Ufa City, Republic of Bashkortostan, Russian Federation
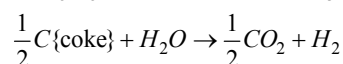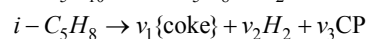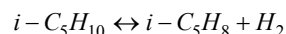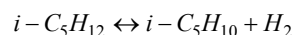E-Mail: Mustafina_SA@mail.ru

ABSTRACT

The paper presents the formulation and solution of the optimal control problem of the process of the dehydrogenation of methylbutenes with the deactivation of the catalyst. The results of computational experiments to analyze the influence of the deactivation parameter on the optimum temperature of the process of the methylbutene dehydrogenation are given. The solution of the problem of the optimal control of the process is based on the use of the Pontryagin maximum principle.

Keywords: deactivation, catalyst, the optimal control, the pontryagin maximum principle.

INTRODUCTION

The process of the dehydrogenation of hydrocarbons C_5H_{10} consists in the sequential conversion of isopentane into methylbutenes and a mixture of the latter - in isoprene. The process takes place in the presence of oxide ferric potassium catalysts. On the basis of the experimental data analysis and the literature [1] the four-stage scheme of transformation process of dehydrogenation of hydrocarbons C_5 has been proposed. The scheme and the corresponding rates of kinetic equations are as follows:

$$i-C_5H_{12} \leftrightarrow i-C_5H_{10} + H_2$$
$$i-C_5H_{10} \leftrightarrow i-C_5H_8 + H_2$$
$$i-C_5H_8 \rightarrow v_1\{\text{coke}\} + v_2 H_2 + v_3 CP$$
$$\frac{1}{2}C\{\text{coke}\} + H_2O \rightarrow \frac{1}{2}CO_2 + H_2$$

The deactivation of catalyst occurred for the industrial operation happened because of the presence of the catalyst poisons in the feedstock (chlorine and organic sulfur compounds), that are present in the methylbutenes mixture used in the synthesis of isoprene. Due to the dilution of raw steam during the reaction is partly self-regeneration of the catalyst [2]. In the work [3] was obtained by the kinetic model of the process of the dehydrogenation of methylbutenes into isoprene was obtained by in view of the deactivation of the catalyst, which is a system of equations:

$$r_1 = \frac{k_{+1}C_1 - k_{-1}C_2C_4}{(1 + b_{11}C_1 + b_{12}C_2 + b_{13}C_3)^2}a,$$

$$r_2 = \frac{k_{+2}C_2 - k_{-2}C_3C_4}{(1 + b_{21}C_2 + b_{22}C_3 + b_{23}C_4)^2}a,$$

$$r_3 = \frac{k_3C_3}{1 + b_3C_4}a, \quad r_4 = \frac{k_4}{1 + b_4C_4}a,$$

$$\frac{da}{dt} = -2a\frac{k_3b_{22}C_3^2}{(1 + b_{21}C_2 + b_{22}C_3 + b_{23}C_4)^2} + 2k_4(\sqrt{a} - a),$$

where r_j - the rate of the j-th stage (kmol/m³·h); C_i - component concentration (mol/l), components indexing by i: 1 - isopentane, 2 - methylbutene, 3 - isoprene, 4 - hydrogen, 5 - products of skeletal reaction (or products of cracking or - CP), 6 - carbon dioxide; k_i - the constants of rate reactions; b_i - absorption coefficients (m³/kmol); τ - contact time; t - astronomical time, a - the relative activity of the catalyst.

The mathematical model of the process of dehydrogenation of methylbutenes with changes in the catalyst activity is a system of the differential equations in the partial derivatives:

$$\frac{\partial C_i}{\partial \tau} = \sum_{j=1}^{4} v_{ij}r_j, \, i = 1,...,6 \qquad (1)$$

$$\frac{\partial a}{\partial t} = -2a\frac{k_3b_{22}C_3^2}{(1 + b_{21}C_2 + b_{22}C_3 + b_{23}C_4)^2} + 2k_4(\sqrt{a} - a). \qquad (2)$$

where v_{ij} - the stoichiometric ratio of the i-th component in the j-th stage.

The initial conditions for the system (1) - (2) are given in the form: $C(0,t) = C_i^0$, $i = 1,..,6$, $a(\tau,0) = 1$. The values of the kinetic parameters of dehydrogenation of methylbutenes were obtained by the calculational program and presented in the work [5]. The values C_i^0 were obtained respectively: $i-C_5H_{12}$ - 7.11% mol; $i-C_5H_{10}$ -

90.59% mol; $i - C_5H_8$ - 0.99% mol; cracking products - 1.31% mol.

The mathematical formulation of the problem of optimization is to find the optimum temperature, with restrictions $500°C \leq T^* \leq 640°C$, in which the maximum yield of the desired product (isoprene) is achieved:

$$\max J = \int_0^{t_k} C_3(\tau_k, t, T, a) dt.$$

The Pontryagin function for this process would be:

$$H(\tau, t, C_1, C_2, ..., C_6, T, a, \psi_1, .., \psi_6, \chi) = \sum_{i=1}^{6} \psi_i \frac{\partial C_i}{\partial \tau} + \chi \frac{\partial a}{\partial t},$$

where ψ_i и χ - the conjugate function.

$$\frac{\partial \psi_i}{\partial \tau} = \frac{\partial H(\tau, t, C_1, C_2, ..., C_6, T, a, \psi_1, .., \psi_6, \chi)}{\partial C_i}, i = 1, .., 6$$

$$\frac{\partial \chi}{\partial t} = \frac{\partial H(\tau, t, C_1, C_2, ..., C_6, T, a, \psi_1, .., \psi_6, \chi)}{\partial a}.$$

The boundary conditions are given as:

$$\psi_i(\tau_k, t) = 0, \ i = 1, .., 6, \ i \neq 3, \qquad \psi_3(\tau_k, t) = 1,$$
$$\chi(\tau, t_k) = 0,$$

RESULTS AND DISCUSSIONS

The computational experiment in solving the optimal control problem of the dehydrogenation reaction of methylbutenes to changing activity of the catalyst showed that the optimum temperature will be as follows (Figure-1). At the beginning of contact time the temperature reaches the maximum value and is held at this value for some time, and then the temperature sharply reduces to its minimum value. However, over time the deactivation of the catalyst influences the optimal temperature process conditions, and the contact time at which the temperature reaches its maximum value should be increased.
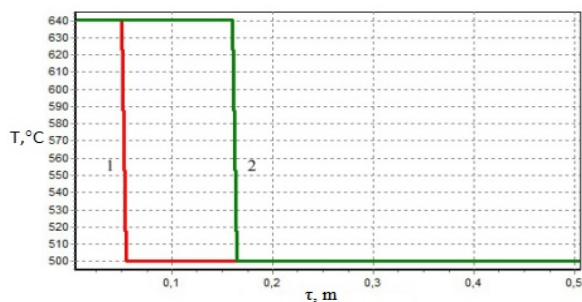
Figure-1. The optimum temperature conditions of the process of the dehydrogenation of metilbutenes: 1- in the fresh catalyst, 2 - in 2 hours work of the catalyst.

Changes in the relative concentrations of methylbutenes and isoprene are shown in Figure-2 in a slice through the contact time in 2 hours work of the catalyst. With the astronomical time the consumption of the starting material and the yield will decrease. However, due to the self-regeneration of the catalyst from the time when the activity reaches its steady-state value, a further influence on the basic parameters of the process will be negligible.
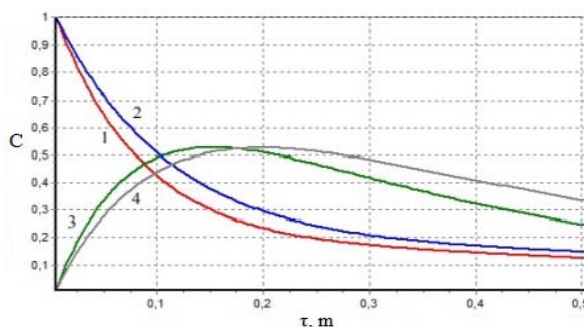
Figure-2. Changes in the concentrations of methylbutenes and isoprene and 1 - methylbutenes in the fresh catalyst; 2- methylbutenes in 2 hours work of the catalyst; 3-isoprene in the fresh catalyst; 4 - isoprene in 2 hours work of the catalyst.

The developed model of the process of the dehydrogenation of methylbutenes allows to predict the course of the process, the product yield, and to determine the optimal time of the catalyst work and to find the optimum temperature of the process, enabling you to get the maximum yield of isoprene with set limits on the temperature.

REFERENCES

[1] Mustafina S., Smirnov D., Balaev A., Spivak S. 2006. Control Systems and Information Technology. 1: 10-14.

[2] Berzina D.V., Mustafina S.A. 2014. Catalysis in Industry. 6(84): 549.

[3] Mustafina S.A., Valieva Yu.A., Davletshin R.S., Balaev A.V., Spivak S.I. 2005. Kinetics and Catalysis. 46(5): 705-711.

[4] Shaimukhametova Dina, Mustafina Svetlana. 2016. Bulletin of the Technological University. 19(15): 147-150.

[5] Mustafina Svetlana, Shaimukhametova Dina. 2015. International Journal of Applied Chemistry. 11(2): 163-166.