ISSN 0023-1584, Kinetics and Catalysis, 2014, Vol. 55, No. 1, pp. 12–17. © Pleiades Publishing, Ltd., 2014.
Original Russian Text © V.A. Men'shchikov, L.Kh. Gol'dshtein, I.P. Semenov, 2014, published in Kinetika i Kataliz, 2014, Vol. 55, No. 1, pp. 14–19.

Kinetics of Ethanol Dehydrogenation into Ethyl Acetate

V. A. Men'shchikov, L. Kh. Gol'dshtein*, and I. P. Semenov
OOO Tekhnologii VNIIOS, Moscow, 105005 Russia
**e-mail: l_goldstein@hotmail.com*

Received November 27, 2012

Abstract—The kinetics of gas-phase dehydrogenation of ethanol into ethyl acetate over a copper–zinc–chromium catalyst has been investigated in a flow reactor at pressures of 10–20 atm and temperatures of 230–290°C. For the process occurring under kinetic control, the rate constants of two reactions and the adsorption constants of five components have been determined using the Langmuir–Hinshelwood model. A kinetic model has been developed for the process. This model provides means to design a reactor for dehydrogenation of ethanol into ethyl acetate in different regimes.

DOI: 10.1134/S0023158414010078

Ethyl acetate is a very popular solvent. It is used in the production of food colorings, printing inks, paintwork materials, medicines, etc. The manufacturers of food colorings consume up to 30% of the total amount of ethyl acetate produced. This is due to the very low toxicity of this product: its TLV for work zone air is 200 mg/m^3. The world output of ethyl acetate in 2010 was as high as ~2.6 million tons, including Russia's 30000 t [1].

The entire ethyl acetate in Russia is produced by acetic acid esterification with dry ethanol in the presence of sulfuric acid [1–3]. Most of the equipment employed in this process is made from stainless steel because of the high corrosiveness of acetic and sulfuric acids. In addition, the esterification reaction yields water, which is discharged into a sewage collector.

Ethyl acetate is alternatively produced by ethanol dehydrogenation [4], in which ethanol is the only reactant. This process is based on the following reversible reactions [5]:

$$C_2H_5OH \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} CH_3CHO + H_2, \quad \text{(I)}$$

$$C_2H_5OH + CH_3CHO \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} CH_3COOC_2H_5 + H_2. \quad \text{(II)}$$

The overall process is endothermic. The advantage of this technology is that ethanol is the only reactant. This process can also be carried out using bioethanol, a renewable raw material, thus falling under the category of green chemistry.

Ethanol dehydrogenation proceeds efficiently over copper–zinc catalysts [6, 7], and adding chromium to these catalysts enhances their selectivity [7, 8]. The optimum conditions for this reaction are the following: pressure, 10–15 atm; temperature, 230–290°C; volumetric flow rate of liquid ethanol, 0.6–1.5 L/h [9]. Under these conditions, the ethanol conversion is 30–55% at an ethyl acetate selectivity of 92–96%. The process is conducted in the gas phase.

In order to rightly choose the type of industrial reactor and to perform the corresponding design calculation, it is necessary to study the kinetics of the reaction. Experiments can be performed both in a differential reactor and in an integral one. In the latter case, for data processing it is necessary to have a special-purpose program taking into account the variation of component concentrations along the catalyst bed. In addition, the process should be conducted under kinetic control, when there are no internal and external diffusion limitations.

EXPERIMENTAL

Ethanol dehydrogenation was carried out over the commercial catalyst NTK-4 ($CuO–ZnO–Cr_2O_3–Al_2O_3$)) in a reactor 18 mm in diameter having an axial well intended for a movable thermocouple. This made it possible to record the temperature profile along the catalyst bed, whose height was 60 mm. The diameter of the catalyst particles was 3–4 mm, and the corresponding equivalent diameter was $d_{\text{equiv}} = 3.6$ mm. The reactor was placed in an electric furnace equipped with a temperature controller. An analysis of the temperature profile demonstrated that the catalyst operated at a constant temperature with a deviation of ±3°C.

The feed and product compositions were determined on a Carlo Erba Strumentozione 4200 (Italy) chromatograph (50-mm-long quartz capillary column with supported OV-101 phase, flame-ionization detector). Chromatograms were recorded and processed using a Spectrophysics 4270 (Carlo Erba Strumentazione, Italy) integrator.

The water concentration in the product stream was measured on an LKhM-80 (Russia) chromatograph fitted with a Polisorb-packed column. The carrier gas was helium.

The specific surface area and pore size distribution of the catalyst were estimated from nitrogen adsorption data.

RESULTS AND DISCUSSION

The catalyst had the following parameters: apparent density, $\rho_{app} = 1.0$ g/cm^3; specific surface area, $S_{BET} = 77.4$ m^2/g; mean pore diameter, $d_{pore} = 1.3 \times 10^{-8}$ m. The porosity of the catalyst calculated as

$$\varphi = S_{BET} d_{pore}/4, \qquad (1)$$

was 0.25 cm^3/g. The maximum ethanol dehydrogenation rate (r) was 0.43 g $\text{cm}_{\text{Cat}}^{-3}\text{h}^{-1}$.

We preliminarily estimated the effect of external and internal diffusion on the ethanol dehydrogenation rate. The intensity of mass transfer between the flow and the catalyst can be determined from the following relationship [11]:

$$\text{Nu}_{\text{equiv}} = \text{B} \times \text{Re}_{\text{equiv}}^{x} \times \text{Pr}_{\text{d}}^{y}, \qquad (2)$$

where $\text{Re}_{\text{equiv}} = \dfrac{w_{\text{ef}} d_{\text{equiv}} \gamma}{\mu}$, $\text{Pr}_{\text{d}} = \dfrac{\mu}{\gamma D_{\text{g}}}$,

$\text{Nu}_{\text{equiv}} = \dfrac{\beta d_{\text{equiv}}}{D_{\text{g}}}$, β is the mass transfer coefficient (m/s), d_{equiv} is the equivalent diameter of a catalyst particle (m), D_{g} is the molecular diffusion coefficient of ethanol (m^2/s), w_{ef} is the flow velocity in the empty space of the catalyst (m/s), γ is the flow density (kg/m^3), μ is the flow viscosity (kg s m^{-2}), and **B** is a constant.

The parameters of Eq. (2) depend on the Reynolds number. Since the composition of the flow varies along the catalyst bed, thermal properties were calculated from mean values.

Under the experimental conditions, the reaction system had the following parameters: $d_{\text{equiv}} = 3.6 \times 10^{-3}$ m, $D_{\text{g}} = 1.8 \times 10^{-6}$ m^2/s, $w_{\text{ef}} = 0.0031$ m/s, $\gamma = 11.3$ kg/m^3, $\mu = 1.7 \times 10^{-5}$ kg s m^{-2}, $\text{Re}_{\text{equiv}} = 0.59$, and $\text{Pr}_{\text{d}} = 0.845$.

For $\text{Re}_{\text{equiv}} = 0.1$–$2.0$ and $\text{Pr}_{\text{d}} = 0.6$–$10$, the coefficient of mass transfer from the flow to the catalyst surface can be determined via the following formula [11]:

$$\beta_{\text{g}} = \frac{D_{\text{g}}}{d_{\text{equiv}}} 0.515 \text{Re}_{\text{equiv}}^{0.85} \text{Pr}_{\text{d}}^{0.33}. \qquad (3)$$

Under our experimental conditions, $\beta_{\text{g}} = 1.55 \times 10^{-4}$ m/s. The specific outer surface area of the catalysts (a) can be taken to be 1800 m^2/m^3. The maximum amount of ethanol that can reach the catalyst surface is

$$G_{\max} = \beta_{\text{g}} a (C_{\text{g}} - C_{\text{eq.}}),$$

where C_{g} is the average ethanol concentration in the flow (kg/m^3) and C_{eq} is the equilibrium ethanol concentration, which is ~0.2 C_{g}.

If $C_{\text{g}} = 5$ kg/m^3, then $G_{\max} = 1.1$ kg m^{-3} s. For a catalyst bed volume of 15 mL, the maximum flow rate in the reactor can reach 60 g/h, but it did not exceed 6.5 g/h in our experiments. Thus, there were no external diffusion limitations.

Now we will estimate the internal diffusion limitations in the catalyst. The pore tortuosity coefficient for the catalyst with above-specified properties can be accepted to be $\sigma \approx 3$ [10]. Ethanol transport in the catalyst pores can occur via conventional molecular ("bulk") diffusion and Knudsen diffusion. The slowest one should be involved in further calculations. The conventional diffusion coefficient ($D_{\text{ef,con}}$) is determined via the following formula [12]:

$$D_{\text{ef,con}} = \frac{D_{\text{g}} \varphi}{\sigma}, \qquad (4)$$

and its value is 0.15×10^{-6} m^2/s.

The Knudsen diffusion coefficient determined via the formula [12]

$$D_{\text{ef,Kn}} = 19400 \frac{\varphi^2}{\sigma S_{\text{BET}} \rho_{\text{app}}} \sqrt{\frac{T}{M}}, \qquad (5)$$

where M is molar mass and T is temperature (K), is 0.181×10^{-6} m^2/s.

The formula for the effective diffusion coefficient has the following form [12]:

$$D_{\text{ef}} = \left(\frac{1}{D_{\text{ef,con}}} + \frac{1}{D_{\text{ef,Kn}}} \right)^{-1},$$

and $D_{\text{ef}} = 0.082 \times 10^{-6}$ m^2/s.

From the maximum rate of the reaction over the catalyst and the average ethanol concentration in the flow between the bed inlet and outlet, it is possible to derive the parameter Φ, which is defined as follows for spherical particles [10]:

$$\Phi = \left(\frac{d_{\text{equiv}}}{2} \right)^2 \frac{r}{D_{\text{ef}} C_{\text{g}}}. \qquad (6)$$

This parameter is 0.79×10^{-3}, and the corresponding operating efficiency of the catalyst granule bulk is ~1. Therefore, the entire catalyst volume operates and there are no external diffusion limitations.

These estimates were verified experimentally. Table 1 lists the data obtained for one catalyst sample at $T = 270$°C and $P = 10$ atm. The first three experiments were made on particles with different diameters. Reducing the particle diameter by a factor of 10 did increase the ethanol conversion or the reaction rate; therefore, there were no internal diffusion limitations. Experiments 1 and 4 were preformed at the same reaction time, but the liners flow velocity in experiment 4 was set to be 3 times higher than in experiment 1. This exerted no effect on the rate of the process; there, there were no external diffusion limitations.

Developing a kinetic model of the process, we proceeded from Langmuir and Hinshelwood's hypothesis that the components of the reaction mixture adsorb on

Table 1. Data for assessing the possibility of external and internal diffusion limitation taking place

Experiment no.	Ethanol flow rate, mL/h	Catalyst particle size, mm	Bed height, cm	Ethanol conversion, %
1	8	3–4	5	37.3
2	8	0.63–1.0	5	34.0
3	8	0.25–0.4	5	35.7
4	24	3–4	15	36.1

the catalyst. It was assumed that all components adsorb on the same active sites. For reactions (I) and (II), the time variation of the amounts of the reaction components is described by the following system of ordinary differential equations:

$$\frac{1}{V}\frac{dN_1}{d\tau} = k_1\theta_2 - k_{-1}\theta_1\theta_3 - k_2\theta_1\theta_2 + k_{-2}\theta_4\theta_3, \qquad (7)$$

$$\frac{1}{V}\frac{dN_2}{d\tau} = -k_1\theta_2 + k_{-1}\theta_1\theta_3 - k_2\theta_1\theta_2 + k_{-2}\theta_4\theta_3, \qquad (8)$$

$$\frac{1}{V}\frac{dN_3}{d\tau} = k_1\theta_2 - k_{-1}\theta_1\theta_3 + k_2\theta_1\theta_2 - k_{-2}\theta_4\theta_3, \qquad (9)$$

$$\frac{1}{V}\frac{dN_4}{d\tau} = k_2\theta_1\theta_2 - k_{-2}\theta_4\theta_3, \qquad (10)$$

$$\frac{1}{V}\frac{dN_5}{d\tau} = 0. \qquad (11)$$

Here, k_1, k_{-1}, k_2, and k_{-2} are the rate constants of forward and reverse reactions occurring according to chemical equations (I) and (II), τ is time, MN is the number of components (five), N_i is the number of moles of the ith components ($i = 1$, acetaldehyde; $i = 2$, ethanol; $i = 3$, hydrogen; $i = 4$, ethyl acetate; $i = 5$, water), V is the flow volume occupied by all components of the reaction mixture in the gas phase, and θ_i is the active catalyst surface occupied by the ith component.

The initial conditions are the following: at $\tau = 0$, for components $i = 1, ..., 5$ $N_i = N_{i0}$.

The rate constants of the reverse reaction, k_{-1} and k_{-2}, can be eliminated from Eqs. (7)–(10) by involving the equilibrium constants of reactions (I) and (II). The k_1/k_{-1} and k_2/k_{-2} ratios can be determined via Nernst's approximate formula [5] using the heats of reactions (I) and (II), which are 16360 and −9980 cal/mol, respectively:

$$\log\frac{k_i}{k_{-i}} = \frac{-Q_r}{4.573T} + \sum\gamma \times 1.75\log T + \sum i^*, \qquad (12)$$

where Q_r is the heat of reaction (cal/mol), $\sum\gamma$ is the sum of stoichiometric coefficients, and i^* is a conventional chemical constant.

The $\sum\gamma$ values for reactions (I) and (II) are 1 and 0, respectively. The following values were accepted for the chemical constants i^*: hydrogen, 1.6; ethanol, 4.1; acetaldehyde and ethyl acetate, 3.5. From formula (12), we then obtain

$$\log\frac{k_1}{k_{-1}} = -\frac{3577.5}{T} + 1.75\log T + 1.0, \qquad (13)$$

$$\log\frac{k_2}{k_{-2}} = \frac{2182.4}{T} - 2.5. \qquad (14)$$

With the adsorption coefficients b_i [13] taken into account, the equilibrium constants will appears as

$$K_1 = \left(\frac{k_1}{k_{-1}}\right)\frac{b_2}{b_1 b_3},$$

$$K_2 = \left(\frac{k_2}{k_{-2}}\right)\frac{b_1 b_2}{b_3 b_4}.$$

The surface fraction that is active toward the ith component is determined via the formula

$$\theta_i = b_i\frac{N_i}{V}\Bigg/\left(1 + \sum_{i=1}^{5} b_i\frac{N_i}{V}\right), \qquad (15)$$

where b_i is the adsorption coefficient of the ith component.

The rate constants of the reactions and adsorption obey the Arrhenius relationship:

$$k_i = A_{k_i}\exp\left[-\frac{E_{k_i}}{R(T + 273)}\right], \qquad (16)$$

$$b_i = A_{b_i}\exp\left[\frac{E_{b_i}}{R(T + 273)}\right], \qquad (17)$$

where the activation energies have dimensions of cal/mol, R is the gas constant (1.987 cal K^{-1} mol^{-1}), and T is temperature (°C).

The differential equations are integrated with respect to the residence time of the flow in the catalyst bed pf length l:

$$\frac{dl}{d\tau} = \frac{V}{S_r}, \qquad (18)$$

where S_r (m^2) is the cross-sectional area of the reactor with the dimensions of the thermocouple well taken into account (m^2).

Since the overall reactions change the volume of the system, the system of equations (7)–(11) is supplemented by the equation

$$\frac{dV}{d\tau} = 22.4\frac{(T + 273)}{273P}\sum_{1}^{MN}\left(\frac{dN_i}{d\tau}\right), \qquad (19)$$

where P is the absolute pressure in the reactor (atm).

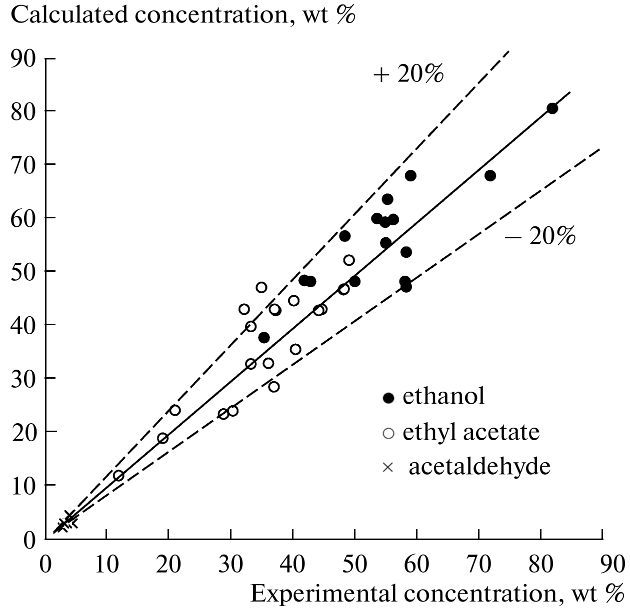

Fig. 1. Calculated (solid line) versus experimental (points) component concentrations in the reaction mixture at the outlet of the catalyst bed.

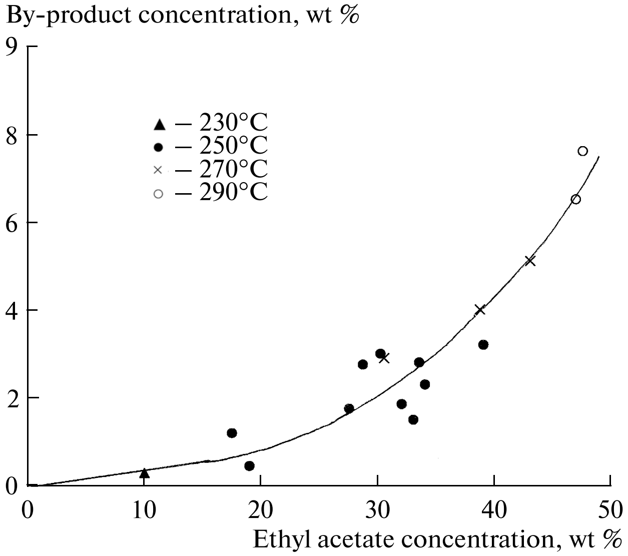

Fig. 2. Total by-product concentration versus the concentration of the resulting ethyl acetate in the reaction mixture at different temperatures.

Because of the low flow resistance of the catalyst bed, the pressure variation along its length can be neglected.

The kinetic model has 14 unknown parameters, namely, the preexponential factors of the rate constants and the activation energies of the two forward reactions and the preexponential factors and activation energies of adsorption of the five reaction components—ethanol, ethyl acetate, acetaldehyde, hydrogen, and water.

In each experiment, the concentrations of ethyl acetate, unreacted ethanol, and hydrogen and the total concentration of by-products (butanol, hemiacetal, butyl acetate, and acetic acid traces) were determined at the reactor outlet.

Table 2 presents the experimental data used in the determination of the kinetic parameters. The results of 18 experiments were processed. The amount of the resulting hydrogen was measured in each experiment, but this variable was not used in the calculations, because it is directly correlated with the amount of the resulting ethyl acetate and, therefore, is mot an independent variable. The discrepancy between the amounts of water at the reactor inlet and outlet, which was due to ethyl acetate hydrolysis, was within the error of the analysis; for this treason, the inlet value was involved in the calculations. The concentrations of ethanol, and acetaldehyde, ethyl acetate and the total concentration of by-products in each experiment were used in the calculations.

Since the by-products were different types of compounds and their yield was as low as 0.5–4.0%, their chemical reactions and, accordingly, the corresponding differential equations were not considered. Below, it will be demonstrated that their yield is unambiguously related with the ethyl acetate yield.

In each of the 18 experiments, three product concentrations were measured. Therefore, 14 unknowns had to be determined from 54 data points. For this purpose, it was necessary to carry out statistical processing of the results by minimizing a functional of an objective function (inverse problem). A possible objective function is the sum of the squares of the absolute or relative differences between the calculated and experimental concentrations (mean-square deviations):

$$F = \sqrt{\sum_{j=1}^{L}\sum_{i=1}^{MN}(N_{i\mathrm{calc}}^{j} - N_{i\mathrm{exp}}^{j})^2 \Big/ [MN(L-1)]}, \quad (20)$$

$$F = \sqrt{\sum_{j=1}^{L}\sum_{i=1}^{MN}\left(\frac{N_{i\mathrm{calc}}^{j} - N_{i\mathrm{exp}}^{j}}{N_{i\mathrm{exp}}^{j}}\right)^2 \Big/ [MN(L-1)]}, \quad (21)$$

where $i = 1, ..., 5$ is the compound number ($M = 5$), $j = 1, ..., L$ is the experiment number, L is the number of experiments ($L = 18$), and the subscripts calc and exp indicate calculated and experimental values.

Thus, in the calculations via formula (15), the contribution from acetaldehyde is insignificant; in the calculations using formula (16) its contribution is dominant. In order to equalize, as far as possible, the con-

Table 2. Experimental data on ethanol dehydrogenation

Entry	Process conditions			Feed composition, wt %					Reaction mixture composition, wt %				
	temperature, °C	absolute pressure, atm	liquid feed flow rate, kg/h	ethanol	water	acetaldehyde	ethyl acetate	hydrogen	ethanol	water	acetaldehyde	ethyl acetate	by-products
1	270	11	0.0098	0.01	8.0	–	–	–	41.54	8.0	1.98	43.28	5.20
2	250	11	0.0098	0.01	8.0	–	–	–	53.85	8.0	1.74	33.57	2.84
3	290	11	0.0098	0.01	8.0	–	–	–	33.95	8.0	2.70	47.69	7.66
4	250	11	0.0147	92.0	8.0	–	–	–	57.57	8.0	2.69	29.00	2.74
5	250	11	0.0065	92.0	8.0	–	–	–	53.53	8.0	1.56	34.68	2.23
6	250	6	0.0049	92.0	8.0	–	–	–	47.02	8.0	2.71	39.07	3.22
7	250	16	0.0147	92.0	8.0	–	–	–	70.37	8.0	1.45	19.7	0.48
8	250	11	0.010	92.0	16.3	–	–	–	52.18	16.3	2.46	27.46	1.78
9	270	16	0.0098	92.0	8.0	–	–	–	56.68	8.0	1.67	30.8	2.85
10	230	16	0.0147	92.0	8.0	–	–	–	80.33	8.0	0.70	10.63	0.29
11	290	11	0.0081	83.7	8.0	–	–	1.0	35.92	8.0	2.68	46.92	6.48
12	250	11	0.0098	92.0	25.0	–	–	–	53.64	25.0	2.39	17.7	1.27
13	250	11	0.0098	92.0	7.6	5.0	–	–	54.67	7.6	2.34	31.94	3.05
14	270	11	0.0080	91.0	8.0	–	–	–	46.85	8.0	2.25	38.84	4.06
15	270	11	0.0098	75.0	8.0	–	–	–	48.63	8.0	3.18	35.72	4.39
16	250	11	0.0098	87.4	6.8	–	15.0	–	56.88	6.8	2.56	31.92	1.84
17	250	11	0.0098	92.0	6.0	–	25.0	–	56.87	5.94	1.96	33.63	1.53
18	270	11	0.0098	92.0	8.0	–	–	–	40.52	8.0	1.81	42.76	6.91

tributions from all components to the functional F, formula (16) was transformed to

$$F = \sqrt{\sum_{j=1}^{L}\sum_{i=1}^{MN}\delta_i\left(\frac{N^j_{i\mathrm{calc}} - N^j_{i\mathrm{exp}}}{N^j_{i\mathrm{exp}}}\right)^2 \Big/ [MN(L-1)]}. \qquad (22)$$

Here, δ_i is the weighting factor of component i. The following conditions were accepted:

$$\text{at } N_{i\mathrm{exp}} < 5 \text{ wt \%}, \delta_i = 0.1;$$

$$\text{at } N_{i\mathrm{exp}} > 5 \text{ wt \%}, \delta_i = 1.$$

Accordingly, for ethanol and ethyl acetate, $\delta_i = 1$; for acetaldehyde, $\delta_i = 0.1$. For determining the parameters of the model, we developed a program for calculating the component concentrations as a function of time with checking the catalyst bed length and minimizing the functional F. The following results were obtained (A, s^{-1} or $cm^3\ mol^{-1}\ s^{-1}$; E, cal/mol):

$$A_{k_1} = 0.96 \times 10^{10}, \quad E_{k_1} = -29500,$$

$$A_{k_2} = 0.82 \times 10^{9}, \quad E_{k_2} = -21000,$$

$$A_{B_1} = 6.6, \quad E_{B_1} = 2400,$$

$$A_{B_2} = 17.9, \quad E_{B_2} = 320,$$

$$A_{B_3} = 12.0, \quad E_{B_3} = 3250,$$

$$A_{B_4} = 0.50, \quad E_{B_4} = 2360,$$

$$A_{B_5} = 102.5, \quad E_{B_5} = 830.$$

Figure 1 presents a comparison between the calculated and experimental component concentrations at the outlet of the catalyst bed. Clearly, the deviation does not exceed ±20%.

An analysis of the experimental data concerning by-product formation demonstrates that the by-product yield depends on the ethyl acetate yield and temperature (Fig. 2). The following relationship was obtained:

$$\frac{C_{\mathrm{by}}}{C_{\mathrm{EA}}} = 1.4\exp\left(-\frac{6860}{RT}\right), \qquad (23)$$

where C_{by} and C_{EA} are the by-product and ethyl acetate concentrations, respectively.

Thus, the kinetic relationships obtained here make is possible to design a reactor for ethanol dehydrogenation into ethyl acetate in different operating regimes.

REFERENCES

1. www.him-kurier.ru
2. Chashchin, A.M. and Glukhareva, M.I., *Atsetatnye rastvoriteli v lesokhimicheskoi promyshlennosti* (Acetate Solvents in the Wood Chemical Industry), Moscow: Lesnaya Promyshlennost', 1988.
3. Karrer, P., *Lehrbuch der organischen Chemie*, Stuttgart: Thieme, 1954.
4. *Chem. Eng.*, 2003, vol. 110, no. 11, p. 44.
5. Vvedenskii, A.A., *Termodinamicheskie raschety protsessov toplivnoi promyshlennosti* (Thermodynamic Calculations for Processes of the Fuel Industry), Leningrad: Gostopizdat, 1950.
6. Inui, K., Rurabayashi, T., and Sato, S., *J. Catal.*, 2002, vol. 212, no. 2, p. 125.
7. Elliott, D.L. and Pennella, F., *J. Catal.*, 1989, vol. 119, p. 359.
8. Bolder, F.M., *Ind. Eng. Chem. Res.*, 2008, vol. 47, no. 19, p. 4796.
9. Semenov, I.P. and Men'shchikov, V.A., Katal. *Prom—sti.*, 2012, no. 5, p. 32.
10. Satterfield, Ch.N., *Mass Transfer in Heterogeneous Catalysis*, Cambridge, Mass.: Massachusetts Inst. of Technology Press, 1970.
11. Aerov, M.E., Todes, O.M., and Narinskii, D.A., *Apparaty so statsionarnym zernistym sloem* (Fixed-Bed Apparatuses), Leningrad: Khimiya, 1979.
12. Sherwood, T., Pigford, R., and Wilke, Ch., *Mass Transfer*, New York: McGraw-Hill, 1975.
13. Kiperman, S.L., *Osnovy khimicheskoi kinetiki v geterogennom katalize* (Fundamentals of Chemical Kinetics in Heterogeneous Catalysis), Moscow: Khimiya, 1979.

Translated by D. Zvukov