УДК 517.956

©2018 p. M. Petryk[a], I. Boyko[a], O. Petryk[a], J. Fraissard[b]

[a]Modelisation du Transfert de Masse, Ternopil Ivan Puluj National Technical University
[b]Sorbonne Universites, Paris

MODELING OF ADSORPTION AND DESORPTION OF HYDROCARBONS IN NANOPOROUS CATALYTIC ZELITE MEDIA USING NONLINEAR LANGMUIR ISOTERM

Подано теоретичні основи математичного моделювання неізотермічної адсорбції і десорбції в нанопористих каталітичних цеолітних середовищах з використанням нелінійної ізотерми Ленгмюра. Тримані результати найбільш повно визначають механізм адсорбційної рівноваги для нанопористих систем цеоліту ZSM-5. Реалізується ефективна схема лінеаризації нелінійної моделі. Високошвидкісні аналітичні розв'язки системи лінеаризованих граничних задач адсорбції і десорбції в нанопористих середовищах обгрунтовані і отримані з використанням операційного методу Хевісайда.

Ключові слова: операційний метод Хевісайда, інтегральні перетворення Лапласа.

The theoretical bases of mathematical modeling of nonisothermal adsorbtion and desorbtion in nanoporous catalytic zeolite media for the Langmuir's nonlinear isotherm are given. They most fully determine the mechanism of adsorption equilibrium for nanoporous systems of ZSM-5 zeolite. The effective scheme of linearization of a nonlinear model is implemented. High-speed analytical solutions of the system of linearized boundary problems of adsorption and desorption in nanoporous media are justified and obtained using the Heviside's operational method.

Keywords: Heaviside's operational method, Laplace integral transform.

1. Introduction

The main anthropogenic sources of atmospheric pollutants are the processes by which energy is generated for transport and industry. It has been demonstrated that the transport sector is the emission source that contributes the most to global warming at present, and it will probably remain so in the immediate future [1]. The quality of mathematical models of processes of adsorption and desorption of hydrocarbons in nanoporous catalytic media determines the effectiveness of technological solutions for neutralizing and reducing exhaust emissions which is rapidly increasing, contributing to global warming [2, 3].

At present, many experimental and theoretical studies of such processes are carried out, especially studies on the improvement of their mathematical models, taking into account the influence of various factors that limit the internal kinetics of adsorption and desorption in nanopores of catalytic media [3-7]. For the first time, it has been possible to specify all the processes along the columns during non-isothermal adsorption and desorption. The proposed work outlines the theoretical foundations for modeling nonisothermal adsorption and desorption in nanoporous catalysts for a nonlinear isotherm obtained by the Nobel laureate E.Langmuir, which most fully determines the mechanism of adsorption equilibrium for nanopore systems of the zeolite. For the modeling we have used the Heaviside operational method and the Laplace transform, but the development of calculations is quite original. This methodology allows you to get high-speed analytical solutions that improve the quality of computational paralleling and the simulation of real process.

Mathematical model of nonisothermal adsorption and desorption in a microporous medium

The general hypothesis adopted in the model development is that the adsorption interaction between adsorption molecules and active adsorption centers on the phase separation surface in crystallites nanopores

is determined on the basis of the nonlinear adsorption equilibrium Langmuir function with allowance of the following physical assumptions [5-7]:

1. Adsorption is localized and is caused by forces close to chemical forces: dispersion forces, the interaction of which is established by Lenard and the electrostatic forces of attraction and repulsion, the mechanism of which is described by Van- Der-Waals [6].

2. Adsorption takes place in active centers on the adsorbent surface e distributed throughout the internal surface of the micro- and nanopores.

3. Each active center adsorbs only one molecule of adsorbate and its molecular layer of adsorbate is formed on the surface.

4. Adsorbed molecules are retained by active centers duringa certain time, depending on the temperature.

Proceeding from this, the function of adsorption equilibrium (adsorption isotherm) of the Langmuir type describing the phase adoptive transition from the medium of the propagating gas stream to the nanopores of the adsorbent layer and she will be determined by a nonlinear relationship establishing the relation between the equilibrium concentration A_{eq} and the adsorption value a (concentration of adsorbate in nanoopores of the adsorbent) [6, 7]

$$a\left(c_{eq}\right)=a_{full}\frac{b\left(T\right)c_{eq}}{1+c_{eq}}. \tag{1}$$

Here ΔH- energy of activation, kJ/mole; R-gaze constant, kJ.mole/(m3.K); $a_{full}, 0 < b_0 < 1$, b_0– are the empirical coefficients that depend on the properties of the microporous adsorbent and the diffused substance: a_{full}- the concentration (amount) of adsorbate in the micropores of the zeolite with complete filling of the adsorption centers, mol/g, b_0 - is the coefficient equal to the ratio of the rate constants of desorption and adsorption.

The activation energy, having a physical meaning in this problem as the heat of adsorption, is defined as:

$$\Delta H=\bar{\varphi}-\left(U_g-U_s\right)-RT, \tag{2}$$

where U_g-U_s is the difference between the kinetic energies of the adsorbat molecule in the gaseous and adsorbed states depending therefore on the nature of the adsorbed phase, $\bar{\varphi}$ - is the value of the Lennard-Jones potential averaged over the pore volume of the adsorbent [8], which is a characteristic of the zeolite.

In addition, since, $U_g=\frac{i_g}{2}RT$; $U_s=\frac{i_s}{2}RT$, where i_g, i_s is the number of degrees of freedom of adsorbate molecules in the corresponding phase.

Then, using the principle of the uniform distribution of energy in degrees of freedom, we have

$$U_g-U_S=\frac{\left(i_g-i_s\right)}{2}RT, \tag{2}$$

Taking into account (2), the activation energy of the zeolite will be determined $\Delta H=\bar{\varphi}-\frac{2+i_g-i_s}{2}RT$. (4) The Lennard-Jones potential is defined as [8]:

$\varphi(r)=4\varepsilon\left[\left(\frac{r_0}{r}\right)^{12}-\left(\frac{r_0}{r}\right)^{6}\right]$,where the parameters ε and $r$depend on the nature of the ascorbate molecules.

Expressing from (1) the equilibrium concentration function A_{eq} with respect to the adsorption concentration a at the interface, we obtain

$$c_{eq}(a)=\frac{1}{b\left(T\right)}\frac{a}{a_{full}-a}. \tag{5}$$

The refined kinetics of non-isothermal adsorption and desorption in nanoporous zeolites, taking into account the nonlinear function of adsorption equilibrium and the given physical justifications, is described by the following system of nonlinear partial differential equations [6]:

$$\frac{\partial c(t,z)}{\partial t}+\frac{\partial a(t,z)}{\partial t}+u\frac{\partial c}{\partial z}=D_{inter}\frac{\partial^2 c}{\partial z^2}, \tag{6}$$

$$-H\frac{\partial T(t,z)}{\partial t}-uh_g\frac{\partial T}{\partial z}-Q\frac{\partial a}{\partial t}-\mathrm{X}^2T+\Lambda\frac{\partial^2 T}{\partial z^2}=0, \tag{7}$$

$$\frac{\partial a}{\partial t}=\beta\left(c-\frac{1}{b_0\exp\left(-\frac{\Delta H}{RT}\right)}\frac{a}{a_{full}-a})\right). \tag{8}$$

Initial conditions:

a) adsorption: b) desorption:

$$c(t,z)|_{t=o}=0, c(t,z)|_{t=o}=c_0^0, \quad (9)$$

$$T(t,z)|_{t=o}=T_0^0, T(t,z)|_{t=o}=T_0^0, \quad (10)$$

Boundary conditions:
a) adsorption: b) desorption:

$$c(t,z)|_{z=o}=c_{in}, c(t,z)|_{z=0}=c_{in}(t), \quad (11)$$

$$\frac{\partial}{\partial z}c(t,z)|_{z=\infty}=0, \frac{\partial}{\partial z}c(t,z)|_{z=\infty}=0, \quad (12)$$

$$T(t,z)|_{z=0}=T_{in}\ , \frac{\partial}{\partial z}T(t,z)|_{z=\infty}=0,$$

$$T(t,z)|_{z=0}=T_{in}(t), \frac{\partial}{\partial z}T(t,z)|_{z=\infty}=0. \quad (13)$$

The meaning of the terms is given in the Nomenclature.

We use the same symbol c_0^0 for the adsorption and desorption because the methodology of calculation is the same for both.

First of all we obtain the analytical solution of the eq. (6)-(13), assuming conditions $c(t,z)|_{z=0}=c_{in}\equiv const$ (adsorption). At the end we generalize this solution to the conditions $c(t,z)|_{z=0}=c_{in}(t)$ (desorption).

The scheme of nonlinear model linearization and construction of a linearized problems system solution

We perform some expansions in the series of elements of the nonlinear component $\frac{1}{\exp\left(-\frac{\Delta H}{RT}\right)}\frac{a}{a_{full}-a}$ of the differential equation (8).

Given that the value $\frac{a}{a_{full}}<1$, taking into account the expansion

$$\exp\left(-\frac{\Delta H}{RT}\right)=1-\frac{R}{\Delta H}T+\left(\frac{R}{\Delta H}\right)^2T^2+...+$$

$$+\left(-\frac{R}{\Delta H}\right)^nT^n+..., \quad (14)$$

the expression (2) is represented by the series of Maclaurin, neglecting members of less than the second order [9]:

$$c_{eq}(a)=\frac{1}{b\left(T\right)}\frac{a/a_{full}}{1-a/a_{full}}\approx\frac{1-\frac{R}{\Delta H}T}{b_0a_{full}}a+$$
$$+\frac{1-\frac{R}{\Delta H}T}{b_0(a_{full})^2}a^2=\frac{1}{b_0a_{full}}a+\frac{1}{b_0(a_{full})^2}a^2-$$
$$\frac{R}{\Delta H}\frac{1}{b_0a_{full}}aT-\frac{R}{\Delta H}\frac{T}{b_0(a_{full})^2}a^2\varepsilon\approx$$
$$\approx\gamma a\left(t,z\right)+\varepsilon a^2\left(t,z\right)-\frac{R}{\Delta H}\varepsilon a\left(t,z\right)T\left(t,z\right), \quad (15)$$

where $\gamma=\frac{1}{b_0a_{full}}$ is the adsorption constant, which describes the linear component of the adsorption equilibrium function $c_{eq}(a)$ (according to Henry's law), $\varepsilon=\frac{1}{b_0(a_{full})^2}$ is a small parameter that takes into account the nonlinear component of the adsorption isotherm, $Q=\frac{\Delta H}{M_{ads}}$ - specific heat of adsorption.

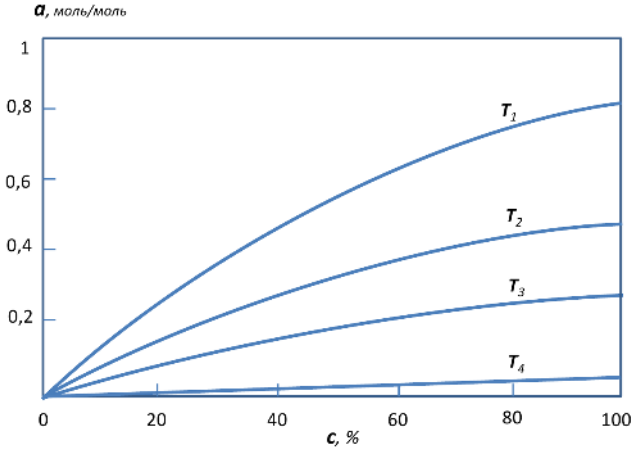

Fig. 1: ZSM-5 nanoporous zeolite curves for adsorption equilibrium

Figure 1 shows typical ZSM-5 nanoporous zeolite curves for adsorption equilibrium («convex» adsorption isotherms) in the temperature range of the adsorption medium from 0 to 350 0C [5 , 6]. It can be seen from Fig. 1 that the value of adsorption a increases according to the nonlinear law of the species $\frac{a/a_{full}}{1-a/a_{full}}$as the concentration of adsorbent increases in the gas phase c, accompanied by the "filling"of active adsorption centers on the surface of micropores and decreases with increasing temperature of the medium T

$(T_! < T_2 < T_3 < T_4)$ [5].

Substituting the expanded expression (9) instead of the dependence $c_{eq}(a)$in the third equation of system (6)-(8), we obtain

$$\frac{\partial a}{\partial t} = \beta(c - \gamma a(z,t) - \varepsilon a(z,t) \times \times \left(a\left(t,z\right) - \frac{R}{\Delta H} T\left(t,z\right) \right). \quad (16)$$

Scheme of linearization of a nonlinear model and construction of a solution of a linearized system of problems

Linearized system of problems with small parameter. Problem (6)-(13), taking into account the approximated kinetic equation of phase transformation (16) containing a small parameter ε, is a mixed boundary problem for a nonlinear system of second-order partial differential equations. The solution of problem (6) - (13) will be sought with the help of asymptotic expansions in the small parameter ε in the form of the following power series [10, 11]:

$$\begin{gathered} c\left(t,z\right) = c_0\left(t,z\right) + \varepsilon c_1\left(t,z\right) + \varepsilon^2 c_2\left(t,z\right) + ..., \\ T\left(t,z\right) = T_0\left(t,z\right) + \varepsilon T_1\left(t,z\right) + \varepsilon^2 T_2\left(t,z\right) + ..., \\ a\left(t,z\right) = a_0\left(t,z\right) + \varepsilon a_1\left(t,z\right) + \varepsilon^2 a_2\left(t,z\right) + ... \end{gathered} \quad (17)$$

In the result of substituting the asymptotic sum (17) into equation (6), considering (10), the initial nonlinear boundary value problem (6)-(13) is parallelized into two types of linearized boundary problems [11]:

The problem A_0 (*zero approximation with initial and boundary conditions of the initial problem*): to find a solution in the domain $D = \{(t,z) : t > 0, _z \in (0,\infty)\}$of a system of partial differential equations : A_0

$$\frac{\partial c_0(t,z)}{\partial t} + \frac{\partial a_0(t,z)}{\partial t} + u\frac{\partial c_0}{\partial x} = = D_{inter}\frac{\partial^2 c_0}{\partial z^2}, \quad (18)$$

$$-H\frac{\partial T_0(t,z)}{\partial t} - uh_g\frac{\partial T_0}{\partial z} - Q\frac{\partial a_0}{\partial t} - \mathrm{X}^2 T_0 + +\Lambda\frac{\partial^2 T_0}{\partial z^2} = 0, \quad (19)$$

$$\frac{\partial a_0}{\partial t} = \beta\left(c_0 - \gamma a_0\right). \quad (20)$$

Initial conditions:
a) adsorption: b) desorption:

$$c_0(t,z)|_{t=o} = 0, c_0(t,z)|_{t=o} = c_0^0, \quad (21)$$

$$T_0(t,z)|_{t=o} = T_0^0, T_0(t,z)|_{t=o} = T_0^0, \quad (22)$$

Boundary conditions:
a) adsorption: b) desorption:

$$c_0(t,z)|_{z=o} = c_{_{in}}, c_0(t,z)|_{z=0} = c_{_{in}}(t), \quad (23)$$

$$\frac{\partial}{\partial z}c_0(t,z)|_{z=\infty} = 0, \frac{\partial}{\partial z}c_0(t,z)|_{z=\infty} = 0, \quad (24)$$

$$T_0(t,z)|_{z=0} = T_{in}\ , \frac{\partial}{\partial z}T_0(t,z)|_{z=\infty} = 0,$$

$$T_0(t,z)|_{z=0} = T_{in}(t), \frac{\partial}{\partial z}T_0(t,z)|_{z=\infty} = 0. \quad (25)$$

The problem$A_n; n = \overline{1,\infty}$ (n-th *approximation with zero initial and boundary conditions*): to construct in the domain D a bounded solution of a system of equations

$$\frac{\partial c_n(t,z)}{\partial t} + \frac{\partial a_n(t,z)}{\partial t} + u\frac{\partial c_n}{\partial z} = D_{inter}\frac{\partial^2 c_n}{\partial z^2}, \quad (26)$$

$$-H\frac{\partial T_n(t,z)}{\partial t} - uh_g\frac{\partial T_n}{\partial z} - Q\frac{\partial a_n}{\partial t} - \mathrm{X}^2 T_n + +\Lambda\frac{\partial^2 T_n}{\partial z^2} = 0, \quad (27)$$

$$\frac{\partial a_n}{\partial t} = \beta\Big(c_n - \gamma a_n - \sum_{i=0}^{n-1}\Big(a_i(t,z)\times \times \left(a_{n-1-i}(t,z) - \frac{R}{\Delta H}T_{n-1-i}(t,z)\right)\Big)\Big) \quad (28)$$

with zero initial boundary conditions.

The problem $A_0$is linear with respect to zero approximation a_0; The problem $A_n; n = \overline{1,\infty}$ is linear with respect to the n-th approximation $a_n$and nonlinear with respect to all previous n-*1* approximations $a_0, ..., a_{n-1}$.

We build the analytic solutions of problems A_0 and $A_n; n = \overline{1,\infty}$ using the Heveside operationel method on the time variable t [12, 13].

Having determined $L\left[c(t,z)\right] \equiv c^*\left(p,z\right) = \int\limits_0^\infty c\left(t,z\right)e^{-pt}dt$,

$L\left[T(t,z)\right] \equiv T^*\left(p,z\right) = \int\limits_0^\infty T\left(t,z\right)e^{-pt}dt$, $L\left[a(t,z)\right] \equiv a^*\left(p,z\right) = \int\limits_0^\infty a\left(t,z\right)e^{-pt}dt$, where p is the complex parameter of the Laplace transform, we obtain the following boundary problems in Laplace imagesA_0^* and A_n^*:

The problem A_0^*: to construct in the area $D^* = \{z \in (0,\infty)\}$a limited solution of equations system

$$\frac{d^2A_0^*(p,z)}{dz^2} - u_1\frac{dA_0^*}{dz} - q_1^2\left(p\right)c_0^* = -\mathrm{F}_{c_0}^*\left(p\right), \tag{29}$$

$$\frac{d^2}{dz^2}T_0^* - u_2\frac{d}{dz}T_0^* - q_2^2(p)T_0^* = -\mathrm{F}_{T_0}{}^*\left(p\right), \tag{30}$$

$$a_0^*\left(p,z\right) = \beta\frac{1}{p+\beta\gamma}c_0^*\left(p,z\right), \tag{31}$$

Boundary conditions:
a) adsorption: b) desorption:

$$c^*(p,z)|_{z=o} = c_{in}^*\left(p\right), \frac{d}{dz}c^*(p,z)|_{z=\infty} = 0, \tag{32}$$

$$\frac{\partial}{\partial z}c^*(p,z)|_{z=\infty} = 0, c^*(p,z)|_{z=o} = \frac{1}{p}c_{in}, \tag{33}$$

$$T^*(p,z)|_{z=0} = \frac{1}{p}T_{in}, \frac{\partial}{\partial z}T^*(p,z)|_{z=\infty} = 0,$$

$$\frac{\partial}{\partial z}T^*(p,z)|_{z=\infty} = 0, T^*(p,z)|_{z=0} = T_{in}^*(p). \tag{34}$$

The problem $A_n^*; n = \overline{1,\infty}$: to construct in the area $D^* = \{z \in (0,\infty)\}$a solution of equations systems

$$\frac{d^2c_n^*}{dz^2} - u_1\frac{dc_n^*}{dz} - q_1^2\left(p\right)c_n^* = -\mathrm{F}_{c_n}{}^*\left(p,z\right), \tag{35}$$

$$\frac{d^2}{dz^2}T_n^* - u_2\frac{d}{dz}T_n^* - q_2^2(p)T_n^* = -\mathrm{F}_{T_n}{}^*\left(p,z\right), \tag{36}$$

$$a_n^*(p,z) = \beta\frac{1}{p+\beta\gamma}\Big(c_n^* - \Big(\sum_{i=0}^{n-1}a_ia_{n-1-i}\Big)^*(p,z)\Big), \tag{37}$$

where $u_1 = \frac{u}{D_{inter}}$, $q_1^2\left(p\right) = \frac{p(p+\beta(\gamma+1))}{D_{inter}(p+\beta\gamma)}$, $q_2^2\left(p\right) = \frac{Hp+\mathrm{X}^2}{\Lambda}$,

$$\mathrm{F}_{c_0}^* = \frac{c_0^0}{D_{inter}}, \mathrm{F}_{T_0}{}^*\left(p,z\right) =$$

$$= \frac{1}{\Lambda}\left(HT_0^0 - Q\beta\left(1 - \frac{\beta\gamma}{p+\beta\gamma}\right)c_0^*(p,z)\right),$$

$$\mathrm{F}_{c_n}{}^*\left(p,z\right) = \frac{\beta}{D_{inter}}\left(1 - \frac{\beta\gamma}{p+\beta\gamma}\right)\times$$

$$\times\left(\sum_{i=0}^{n-1}a_i\left(a_{n-1-i} - \frac{R}{\Delta H}T_{n-1-i}\right)\right)^*\left(p,z\right),$$

$$\mathrm{F}_{T_n}{}^*\left(p,z\right) = -\frac{Q\beta}{\Lambda}\left(1 - \frac{\beta\gamma}{p+\beta\gamma}\right)\times$$

$$\times\Big(c_n^*(p,z) - \Big(\sum_{i=0}^{n-1}a_i\Big(a_{n-1-i} - \frac{R}{\Delta H}T_{n-1-i}\Big)\Big)^*(p,z)\Big).$$

The solution of the non-homogeneous boundary problem of zero - approximationA_0^*

We construct a solution of the heterogeneous boundary problem A_0^* (using the Cauchy method) [11, 14, 15]:

$$c_0^*\left(p,z\right) = c_{in}^*(p)e^{\left(\frac{u_1}{2}-\omega_1(p)\right)z} + \frac{c_0^0}{D_{inter}}\times$$

$$\times\int\limits_0^\infty e^{\frac{u_1}{2}(z-\xi)}\left(\frac{e^{-\omega_1(p)|z-\xi|}}{2\omega_1\left(p\right)} - \frac{e^{-\omega_1(p)(z+\xi)}}{2\omega_1\left(p\right)}\right)d\xi, \tag{38}$$

$$T_0^*(p,z) = pT_{in}^*(p)\frac{e^{\left(\frac{u_2}{2}-\omega_2(p)\right)z}}{p} + \int\limits_0^\infty e^{\frac{u_2}{2}(z-\xi)}\times$$

$$\times\left(\frac{e^{-\omega_2(p)|z-\xi|}}{2\omega_2(p)} - \frac{e^{-\omega_2(p)(z+\xi)}}{2\omega_2(p)}\right)\mathrm{F}_{T_0}^*\left(p,z,\xi\right)d\xi, \tag{39}$$

After integrating the second term in (38), we obtain:

$$c_0^*(p,z) = (pc_{in}^*(p))e^{\frac{u_1}{2}z}\frac{e^{-\omega_1(p)z}}{p} + c_0^0\frac{\gamma}{\gamma+1}\times$$

$$\times\left(\frac{1}{p} + \frac{1}{p+\beta\left(\gamma+1\right)} - \frac{\gamma+1}{\gamma}e^{\frac{u_1}{2}z}\frac{e^{-\omega_1(p)z}}{p}\right) +$$

$$+c_0^0\frac{\beta}{(p+\beta(\gamma+1))}\frac{e^{-\omega_1(p)z}}{p}e^{\frac{u_1}{2}z}. \qquad (40)$$

Here $\omega_1(p) = \left(\frac{u_1^2}{4}+q_1^2(p)\right)^{1/2}$, $\omega_2(p) = \left(\frac{u_2^2}{4}+q_2^2(p)\right)^{1/2}$, $Re\omega_1>0, Re\omega_2>0$.

Applying the integral operator of the inverse Laplace transform $L^{-1}\left[...^*(p,z)\right] = \frac{1}{2\pi i}\int\limits_{\sigma_0-i\infty}^{\sigma_0+i\infty}...^*(p,z)\,e^{pt}$ to formulas (38), (39), we obtain turning formulas for determining the distributions of the adsorbtive concentration in the gas phase $c_0(t,z)$, the temperature of the layer $T_0(t,z)$ and the adsorbate concentration in the nanopores of the zeolite $a_0(t,z)$:

$$c_0(t,z) = e^{\frac{u_1}{2}z}L^{-1}[pc_{in}^*(p)] * L^{-1}\left[\frac{e^{-\omega_1(p)z}}{p}\right]+$$
$$+c_0^0\frac{\gamma}{\gamma+1}\Big(L^{-1}\left[\frac{1}{p}\right]+L^{-1}\left[\frac{1}{p+\beta(1+\gamma)}\right]-$$
$$-\frac{\gamma+1}{\gamma}e^{\frac{u_1}{2}z}L^{-1}\Big[\frac{e^{-\omega_1(p)z}}{p}\Big]\Big)+$$
$$+c_0^0\beta L^{-1}\left[\frac{1}{p+\beta(\gamma+1)}\right]*L^{-1}\left[\frac{e^{-\omega_1(p)z}}{p}\right]e^{\frac{u_1}{2}z}, \qquad (41)$$

$$T_0(t,z) = e^{\frac{u_2}{2}z}L^{-1}\left[pT_{in}^*(p)\right]*L^{-1}\left[\frac{e^{-\omega_2(p)z}}{p}\right]+$$
$$+\int\limits_0^\infty e^{\frac{u_2}{2}(z-\xi)}\Big(L^{-1}\left[\frac{e^{-\omega_2(p)|z-\xi|}}{2\omega_2(p)}\right]-$$
$$-L^{-1}\left[\frac{e^{-\omega_2(p)(z+\xi)}}{2\omega_2(p)}\right]\Big)*L^{-1}\left[\mathrm{F}_{T_0}^*(p,z,\xi)\right]d\xi, \qquad (42)$$

$$a_0(t,z) = L^{-1}\left[\frac{\beta}{p+\gamma\beta}\right]*c_0(t,z)\ . \qquad (43)$$

Here L^{-1} - the symbol of the integral operator of the inverse Laplace transformation, i - the imaginary unit, * - the symbol of the convolution operator of the two functions.

The calculation of the originals of the expression components (41)-(43)

$$\Phi_c^0(t,z)\equiv L^{-1}\left[\frac{e^{-\omega(p)z}}{p}\right] =$$
$$=\frac{1}{2\pi i}\int\limits_{\sigma_0-i\infty}^{\sigma_0+i\infty}\frac{e^{-\omega(p)z}}{p}e^{pt}dp = \frac{1}{\pi}\int\limits_0^\pi e^{-\varphi_1(\nu)z}\times$$
$$\times\frac{\sin\left(\nu t - z\varphi_2(\nu)^2\right)}{\nu}d\nu + e^{-\frac{u}{2D_{inter}}z}, \qquad (45)$$

$$\Phi_A(t,z)\equiv L^{-1}\left[\frac{e^{-\omega_1(p)z}}{2\omega_1(p)}\right] =$$
$$=\frac{1}{2\pi}\int\limits_0^\infty\Big(\frac{\varphi_1(\nu)cos\left(\nu t-\varphi_2(\nu)z\right)}{\left(\Gamma_1^2(\nu)+\nu^2\Gamma_2^2(\nu)\right)^{1/2}}+$$
$$+\frac{\varphi_2(\nu)\sin\left(\nu t-\varphi_2(\nu)z\right)}{\left(\Gamma_1^2(\nu)+\nu^2\Gamma_2^2(\nu)\right)^{1/2}}\Big)d\nu. \qquad (46)$$

$$\Phi_T^0(t,z)\equiv L^{-1}\left[\frac{e^{-\omega_2(p)z}}{p}\right] =$$
$$=\frac{1}{\pi}\int\limits_0^\infty e^{-\phi_1(\nu)z}\frac{\sin\left(\nu t-z\phi_2(\nu)^2\right)}{\nu}d\nu+e^{-\frac{u}{2D_{inter}}z}, \qquad (47)$$

$$\Phi_T(t,z)\equiv L^{-1}\left[\frac{e^{-\omega_2(p)z}}{2\omega_2(p)}\right] =$$
$$=\frac{1}{2\pi}\int\limits_0^\infty\Big(\frac{\phi_1(\nu)cos\left(\nu t-\phi_2(\nu)z\right)}{\left(\Gamma_{T_1}^2(\nu)+\nu^2\Gamma_{T_2}^2(\nu)\right)^{1/2}}+$$
$$+\frac{\varphi_2(\nu)\sin\left(\nu t-\phi_2(\nu)z\right)}{\left(\Gamma_{T_1}^2(\nu)+\nu^2\Gamma_{T_2}^2(\nu)\right)^{1/2}}\Big)d\nu, \qquad (48)$$

$$L^{-1}\left[\frac{e^{-\omega_2(p)|z-\xi|}}{2\omega_2(p)}\right] = \frac{1}{2\pi i}\int\limits_{\sigma_0-i\infty}^{\sigma_0+i\infty}\frac{e^{-\omega_2(p)|z-\xi|}}{2\omega_2(p)}e^{pt}dp \equiv$$
$$\equiv\Phi_T(t,|z-\xi|), L^{-1}\left[\frac{e^{-\omega_2(p)(z+\xi)}}{2\omega_2(p)}\right]\equiv$$
$$\equiv\Phi_T(t,z+\xi).$$

Here $\varphi_{1,2}(\nu) = \left[\frac{\left(\Gamma_1^2(\nu)+\nu^2\Gamma_2^2(\nu)\right)^{1/2}\pm\Gamma_1^2(\nu)}{2}\right]^{1/2}$, $\Gamma_1(\nu) = \frac{u^2}{4D_{inter}^2}+\frac{\nu^2\beta}{D_{inter}^2(\nu^2+\beta^2\gamma^2)}$, $\Gamma_2(\nu) = \frac{\nu^3+\nu\beta^2(\gamma+1)\gamma}{D_{inter}(\nu^2+\beta^2\gamma^2)}$, $\phi_{1,2}(\nu) = \left[\frac{\left(\Gamma_{T_1}^2(\nu)+\nu^2\Gamma_{T_2}^2(\nu)\right)^{1/2}\pm\Gamma_{T_1}^2(\nu)}{2}\right]^{1/2}$,

$$\Gamma_{T_1}(\nu) = \frac{u^2+4\Lambda X^2}{4\Lambda^2}, \Gamma_{T_2}(\nu) = \frac{H\nu}{\Lambda}.$$

Applying the expressions (45), (47), (48) into formulas (41) - (43), we obtain an analytic solution of the zero approximation problemA_0, which describes the dependence of the adsorptive concentration in the gas phase (interparticle space), of the temperature and of adsorbate concentration in nanoporous zeolite particles along the coordinate of the catalytic bed and in time for the adsorption $(c_0(t,z)|_{t=o}=0, c(t,z)|_{z=o}=c_{in}, T_0(t,z)|_{z=0}=T_{in})$ and desorption cycles $(c_0(t,z)|_{t=o}=c_0^0,\ c(t,z)|_{z=0}=c_{in}(t),\ T_0(t,z)|_{z=0}=T_{in}(t))$:

$$c_0(t,z)=c_{in}(0)\,e^{\frac{u}{2D_{inter}}z}\Phi_c^0(t,z)+$$

$$+e^{\frac{u}{2D_{inter}}z}\int_0^t\frac{d}{d\tau}c_{in}(\tau)\,\Phi_c^0(t-\tau,z)\,d\tau+$$

$$+c_0^0\frac{\gamma}{1+\gamma}\Big(1+\frac{1}{\gamma}e^{-\beta(\gamma+1)t}-$$

$$-\frac{\gamma+1}{\gamma}e^{\frac{u}{2D_{inter}}z}\Phi_c^0(t,z)\Big)+\beta c_0^0e^{\frac{u}{2D_{inter}}z}\times$$

$$\times\int_0^t e^{-\beta(\gamma+1)(t-s)}\Phi_c^0(\tau,z)d\tau \qquad (49)$$

$$T_0(t,z)=T_{in}(0)\,\Phi_T^0(t,z)+\int_0^t\frac{d}{d\tau}T_{in}(\tau)\times$$

$$\times\Phi_T^0(t-\tau,z)+\frac{1}{\Lambda}\int_0^t\int_0^\infty\Big[HT_0^0\mathrm{H}_T(t-\tau;z,\xi)-$$

$$-Q\beta\Big(\mathrm{H}_T(t-\tau;z,\xi)-\beta\gamma\int_0^{t-\tau}e^{-\beta\gamma(t-\tau-s)}\times$$

$$\times\mathrm{H}_T(\tau-s;z,\xi)ds\Big)c_0^*(p,\xi)\Big]d\xi d\tau, \qquad (50)$$

$$a_0(t,z)=\beta\int_0^t e^{-\gamma\beta(t-\tau)}c_0(\tau,z)\,d\tau. \qquad (51)$$

If $c_{in}=const$, the formula (49) well be the forme :

$$c_0(t,z)=c_{in}e^{\frac{u_1}{2}z}\Phi_c^0(t,z)+c_0^0\frac{\gamma}{\gamma+1}\Big(1+$$

$$+\frac{1}{\gamma}e^{-\beta(\gamma+1)t}-\frac{\gamma+1}{\gamma}e^{\frac{u_1}{2}z}\Phi_c^0(t,z)\Big)+$$

$$+\beta c_0^0e^{\frac{u_1}{2}z}\int_0^t e^{-\beta(\gamma+1)(t-\tau)}\Phi_c^0(\tau,z)\,ds\ .$$

In the transition to the original of Laplace in formula (41), the circulation of its first component was carried out with the using the Duamel integral [13].

Here $\mathrm{H}_T(\tau;z,\xi)=e^{-\frac{u_2}{2}(z-\xi)}\left(\Phi_T(\tau,|z-\xi|)-\Phi_T(\tau,z+\xi)\right)$.

The solution of the inhomogeneous boundary problem of the$n$-th approximationA_n^*, $n=\overline{1,\infty}$

The solutions $A_n(t,z)\,, T_n(t,z)\,, a_n(t,z)$ of the problems A_n^* (20)- (22) are the functions [11, 13]:

$$c_n^*(p,z)=\int_0^\infty e^{\frac{u_1}{2}(z-\xi)}\Big(\frac{e^{-\omega_1(p)|z-\xi|}}{2\omega_1(p)}-$$

$$-\frac{e^{-\omega_1(p)(z+\xi)}}{2\omega_1(p)}\Big)\mathrm{F}_{c_n}{}^*(p,\xi)d\xi, \qquad (52)$$

$$T_n^*(p,z)=\int_0^\infty e^{\frac{u_2}{2}(z-\xi)}\Big(\frac{e^{-|z-\xi|\omega_2(p)}}{2\omega_2(p)}-$$

$$-\frac{e^{-(z+\xi)\omega_2(p)}}{2\omega_2(p)}\Big)\mathrm{F}_{T_n}^*(p,\xi)d\xi, \qquad (53)$$

$$a_n^*(p,z)=\frac{\beta}{p+\gamma\beta}\Big[c_n^*(p,z)-\Big(\sum_{i=0}^{n-1}a_i\times$$

$$\times\left(a_{n-1-i}-\frac{R}{\Delta H}T_{n-1-i}\right)\Big)^*(p,z)\Big]. \qquad (54)$$

Substituting the values $\mathrm{F}_{c_n}{}^*(p,\xi)$ и $\mathrm{F}_{T_n}{}^*(p,\xi)$ accordingly in the eq. (52), (53) and applying the integral operator of the inverse Laplace transform $L^{-1}[...]$ to formulas (52)-(54), we obtain the turning formulas for determining the n-th approximations for the concentrations distributions $c_n(t,z)$, $a_n(t,z)$ and the temperature distribution $T_n(t,z)$ in the layer:

$$c_n(t,z)=\frac{\beta}{D_{inter}}\int_0^\infty e^{\frac{u_1}{2}(z-\xi)}L^{-1}\Big[\frac{e^{-\omega_1(p)|z-\xi|}}{2\omega(p)}-$$

$$-\frac{e^{-\omega_1(p)(z+\xi)}}{2\omega(p)}\Big]*\Big(\sum_{i=0}^{n-1}a_i\Big(a_{n-1-i}-$$

$$-\frac{R}{\Delta H}T_{n-1-i}\Big)\Big)(\tau,\xi)d\xi-\frac{\beta}{D_{inter}}\beta\gamma\int\limits_0^\infty e^{\frac{u_1}{2}(z-\xi)}\times$$

$$\times L^{-1}\left[\frac{1}{p+\beta\gamma}\left(\frac{e^{-\omega_1(p)|z-\xi|}}{2\omega_1(p)}-\frac{e^{-\omega_1(p)(z+\xi)}}{2\omega_1(p)}\right)\right]*$$

$$*\Big(\sum_{i=0}^{n-1}a_i\left(a_{n-1-i}-\frac{R}{\Delta H}T_{n-1-i}\right)\Big)(\tau,\xi)d\xi, \tag{55}$$

$$T_n(t,z)=\frac{Q\beta}{\Lambda}\int\limits_0^\infty e^{\frac{u_2}{2}(z-\xi)}\times$$

$$\times\left(L^{-1}\left[\frac{e^{-|z-\xi|\omega_2(p)}}{2\omega_2(p)}-\frac{e^{-(z+\xi)\omega_2(p)}}{2\omega_2(p)}\right]\right)*$$

$$*\Big(\left(\sum_{i=0}^{n-1}a_i\left(a_{n-1-i}-\frac{R}{\Delta H}T_{n-1-i}\right)\right)(t,\xi)-$$

$$-c_n(t,\xi)\Big)d\xi-\frac{Q\beta}{\Lambda}\beta\gamma\int\limits_0^\infty e^{\frac{u_2}{2}(z-\xi)}\times$$

$$\times L^{-1}\Big[\frac{1}{p+\beta\gamma}\Big(\frac{e^{-|z-\xi|\omega_2(p)}}{2\omega_2(p)}-$$

$$-\frac{e^{-(z+\xi)\omega_2(p)}}{2\omega_2(p)}\Big)\Big]*\Big(\Big(\sum_{i=0}^{n-1}a_i\Big(a_{n-1-i}-$$

$$-\frac{R}{\Delta H}T_{n-1-i}\Big)\Big)(t,\xi)-c_n(t,\xi)\Big)d\xi, \tag{56}$$

$$a_n(t,z)=\beta L^{-1}\left[\frac{1}{p+\beta\gamma}\right]*L^{-1}\Big[c_n^*(p,z)-$$

$$-\Big(\sum_{i=0}^{n-1}a_i\Big(a_{n-1-i}-\frac{R}{\Delta H}T_{n-1-i}\Big)\Big)^*(p,z)\Big]. \tag{57}$$

In the formulas (55) - (57), using the inverse Laplace transformation formulas (46), (48) for their components, we obtain an analytic solution of the problem $A_n^*, n=\overline{1,\infty}$ describing the temporal spatial distributions$n$-th approximations of adsorption condensations in the gas phase $A_n(t,z)$, of temperature $T_n(t,z)$and of adsorption (the adsorbate concentration in particle nanopores) $a_n(t,z)$ for desorption adsorption stages [11, 13]:

$$c_n(t,z)=\frac{\beta}{D_{inter}}\int\limits_0^\tau\int\limits_0^\infty\Big[\mathrm{H}_c(t-\tau;z,\xi)-$$

$$-\beta\gamma\int\limits_0^{t-\tau}e^{-\beta\gamma(\tau-s)}\mathrm{H}_c(s;z,\xi)ds\Big]\times$$

$$\times\left(\sum_{i=0}^{n-1}a_i\left(a_{n-1-i}-\frac{R}{\Delta H}T_{n-1-i}\right)\right)(\tau,\xi)d\xi d\tau, \tag{58}$$

$$T_n(t,z)=\frac{Q\beta}{\Lambda}\int\limits_0^t\int\limits_0^\infty\Big(\mathrm{H}_T(t-\tau;z,\xi)-$$

$$-\beta\gamma\int\limits_0^{t-\tau}e^{-\beta\gamma(t-\tau-s)}\mathrm{H}_T(s;z,\xi)\,ds\Big)\Big[\sum_{i=0}^{n-1}a_i\times$$

$$\times\left(a_{n-1-i}-\frac{R}{\Delta H}T_{n-1-i}\right)(s,\xi)-c_n(\tau,\xi)\Big]d\xi d\tau, \tag{59}$$

$$a_n(t,z)=\beta\int\limits_0^t e^{-\beta\gamma(t-\tau)}\Big(c_n(\tau,z)-\sum_{i=0}^{n-1}a_i\times$$

$$\times\left(a_{n-1-i}-\frac{R}{\Delta H}T_{n-1-i}\right)(\tau,z)\Big)d\tau. \tag{60}$$

Here $\mathrm{H}_c(\tau;z,\xi)=e^{-\frac{u_1}{2}(z-\xi)}\left(\Phi_c(\tau,|z-\xi|)-\Phi_c(\tau,z+\xi)\right)$.

For the first approximation of the solution of the nonlinear boundary problem (3) - (8), formulas (58) - (60) have the form:

$$c_1(t,z)=\frac{\beta}{D_{inter}}\int\limits_0^\tau\int\limits_0^\infty\Big[\mathrm{H}_c(t-\tau;z,\xi)-$$

$$-\beta\gamma\int\limits_0^{t-\tau}e^{-\beta\gamma(\tau-s)}\mathrm{H}_c(s;z,\xi)\,ds\Big]\times$$

$$\times a_0(\tau,\xi)\left(a_0(\tau,z)-\frac{R}{\Delta H}T_0(\tau,z)\right)d\xi d\tau,$$

$$T_1(t,z)=\frac{Q\beta}{\Lambda}\int\limits_0^t\int\limits_0^\infty\Big(\mathrm{H}_T(t-\tau;z,\xi)-$$

$$-\beta\gamma\int\limits_0^{t-\tau}e^{-\beta\gamma(t-\tau-s)}\mathrm{H}_T(s;z,\xi)\,ds\Big)\Big[a_0(\tau,\xi)\times$$

$$\times\Big(a_0(\tau,z)-\frac{R}{\Delta H}T_0(\tau,z)\Big)-c_1(\tau,\xi)\Big]d\xi d\tau,$$

$$a_1(t,z) = \beta \int_0^t e^{-\beta\gamma(t-\tau)} \Big(c_1(\tau,z) - a_0(\tau,z) \times$$

$$\times \Big(a_0(\tau,z) - \frac{R}{\Delta H} T_0(\tau,z) \Big) \Big) d\tau.$$

Discussion of results

Ehe purpose final of our investigation is to study the possibilities of model proposed for its further use in purification technologies of the carbon emissions into the atmosphere by energy and transport objects (propane, CO2 and other products of combustion). It is today one of the key ways to solve global warming and create a safe energy strategy energy and transport systems [2].

As a model adsorbate, we have selected to start the propane, the volume of which covers about 30% of the total flow of gas emanating from the engine of the car during the first minute of its operation [3].

Using the developed theory, the modeling and calculation of the concentration dependences of non-isothermal adsorption and desorption curves in nanoporous catalytic beds was carried out. The calculations were performed for an experimentally nanoporous sample [8]. The physical parameters of the zeolite are known from the literature [5-7].

Fig. 2 shows the logarithmic dependence of the error $\sigma = |c_{n+1}(t,z) - c_n(t,z)| / c_n(t,z)$ in calculating the concentration $c(t,z)$as a function of the approximation number n.

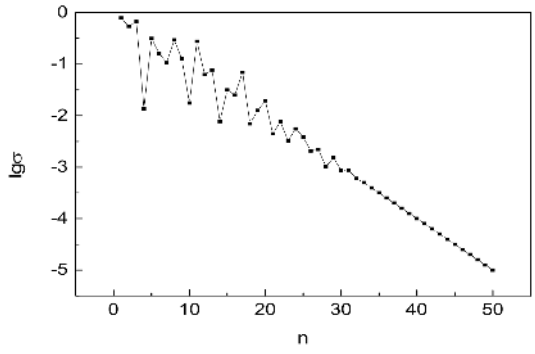

Fig. 2: logarithmic dependence of the error $\sigma = |c_{n+1}(t,z) - c_n(t,z)| / c_n(t,z)$ in calculating the concentration $c(t,z)$as a function of the approximation number n

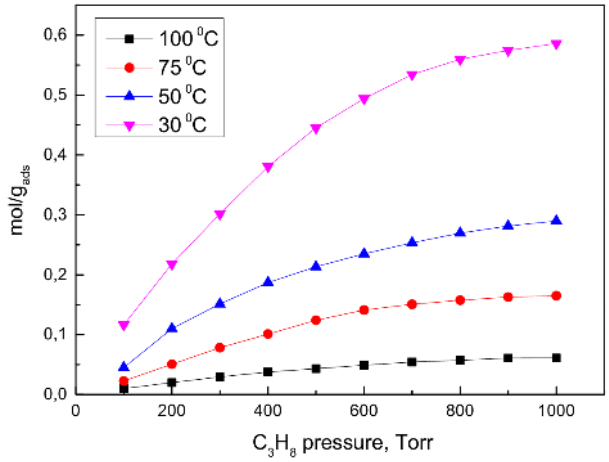

Fig. 3: The dependences of the adsorbate concentration in the gas phase$A = A(t,z)$ for fixed values z ($z/z_0 = 0,25;\ 0,5:\ 0,75$), calculated at the temperature 20^0C (a), 50 ^{0}C (b), 100 ^{0}C (c), 300 ^{0}C (d)

From Fig.1 it can be seen that the error, adopted in the subsequent calculations $\sigma = 10^{-5}$ is achieved by the approximation $n \approx 50$s. Fig. 2 shows the results of calculating the adsorption isotherms for propane at different temperatures: 30^0 !; 50^0 !; 75^0 !; 100^0 ! (using eq. (50), (59)).

Fig. 2. Isotherms of propane adsorption

From Fig. 2 it can be seen that for each the temperature values the adsorption isotherms are located lower with increasing temperature. In addition, with increasing propane pressure, each of the isotherms goes to saturation (equilibrium).

Conclusion

The theoretical foundations of mathematical modeling of nonisothermal adsorption and desorption in nanoporous catalysts for the nonlinear Langmuir isotherm that best describes the mechanism of adsorption equilibrium for micro- and nanopore systems of the ZSM-5 zeolite class are outlined. An effective linearization scheme for the nonlinear model is realized. High-speed analytical solutions of the system of linearized boundary-value problems of adsorption and desorption in nanoporous media are substantiated and obtained using the Heaviside operational method.

Nomenclature

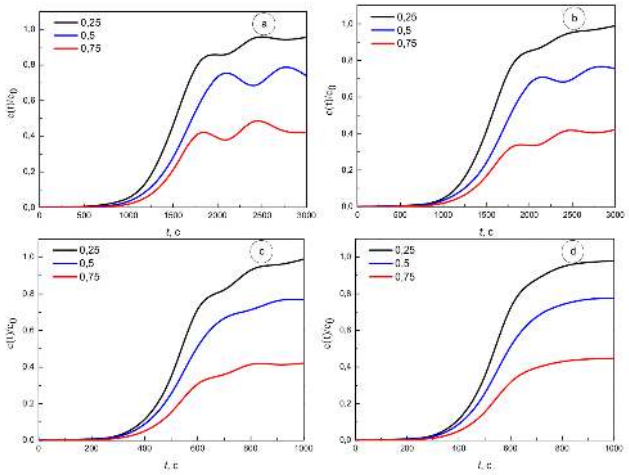

Fig. 4: Dependence of the concentration in the pores of the adsorbent $a = a(t, z)$ for fixed values$z$ $(z/z_0 = 0,25;\ 0,5:\ 0,75)$, calculated at a temperature of 200 C (a), 50 $C(b), 100C(c), 300$C (d).

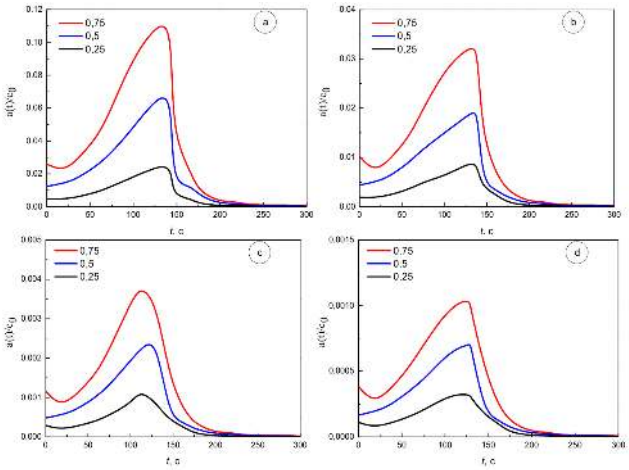

Fig. 5: Dependence of temperature inside the sample$T = T(t, z)$ on time for fixed values z $(z/z_0 = 0,25;\ 0,5:\ 0,75)$

c- concentration of moisture in the gas phase in the column, kg/kg (mol/m^{-3})
a- concentration of moisture adsorbed in the solid phase, kg/kg
T- temperature of gas phase flow, K;
u- velocity of gas phase flow, m/s;
ρ_{ads} - density of adsorbent, kg/km^3;
M_{ads} - molar mass of adsorbent, kg/mole;
D_{inter}- effective longitudinal diffusion coefficient, m^2/s
Λ - coefficient of thermal diffusion along the columns, kJ/kg.m^2/s.
h_g - gas heat capacity, kJ/kg·K
H- total heat capacity of the adsorbent and gas, kJ/kg·K
ΔH- energy of activity, kJ/mole;
$Q = \frac{1}{M_{ads}}\Delta H$- specific heat of sorption (adsorption heat capacity), kJ/kg;
R - gaze constant, kJ/(mol·K) ; radius of adsorbent of solid particles, m;
$\mathrm{X}^2 = 2\alpha_n/R$- coefficient of heat loss through the wall of the adsorbent, kJ/(kg·K.s)
α_h - heat transfer coefficient, kJ/(kg·K.m.s)
γ - Henry's constant;
β - mass transfer coefficient, m/s
z - distance from the top of the bed for mathematical simulation, m;
in - index of parameter names (concentration, temperature) in the inlet of the column.

REFERENCES

1. *Euro 5* and Euro 6 standards: reduction of pollutant emissions from light vehicles. Available at: europa.eu/legislation_summaries/environment/air_pollution/l28186_es.htm (May 5, 2010).
2. Horizon 2020 (LC-SC3-NZE 1-2018); https://ec.europa.eu/research/participants/portal/desktop/en/opportunities/h2020/topics/ict-01-2019.html
3. Puertolas B., Navarro M.V., Lopez J.M., Murillo R., Mastral A.M., Garcia T. Modelling the heat and mass transfers of propane onto a ZSM-5 zeolite. Separation and Purification Technology. 2012, 86,127-36.
4. Barrer, R.M., Diffusion and Flow in Porous Zeolite, Carbon or Ceramic Media, Characterization of Porous Solids, Society of Chemical Industry, London, 1979
5. Kärger J. and Ruthven D. Diffusion in Zeolites and Other Microporous Solids, John Wiley & Sons, New York, 1992, 605 p.
6. Kärger J., Ruthven D., Theodorou D. Diffusion in Nanoporous Materials, John Wiley & Sons, Hoboken, 2012, 660 p.
7. Chen, N.Y., Degnan T.F. and Smith M.C. Molecular Transport and Reaction in Zeolites: Design and Application of Shape Selective Catalysis, Wiley-VCH, New York, 1994, 510 p.
8. Mulero A., Cuadros F. Isosteric heat of adsorption for monolayers of Lennard-Jones fluids onto flat surfaces. Chemical Physics. 996, 205, 379-388.
9. Prudnikov A.P., Brichkov Yu.A. Marychev O.I. Integrals and series. Additional chapters, Nauka, Moscow, 1986, 800 p.

10. Petryk M. Mathematical Modeling of Nonlinear Non-isothermic Process of Diffusion and Adsorption in Compressed Layer of Adsorbent. Integral Transformations and Application in Boundary Problems. Bulletin of Institute of Mathematics. National Academy of Sciences of Ukraine. Kyiv, 1994, 6, 151-64.
11. Petryk M., Parafeinyk V., Kruchnevytch T., Zeria A. The gas dehydration block of NGV filling stations BCV 250. Chemical Technology. Naukova Dumka. 1988, 6, 59-61.
12. Sergienko I., Petryk M., Khimith O.N., Mykhalyk D., Leclerc S., Fraissard J. Mathematical Modelling of Diffusion Process in Microporous Media (Numerical analysis and application). National Academy of Sciences of Ukraine. Kyiv, 2014, 196 p.
13. Heaviside O. Electromagnetic Theory. The Electrician. Vo1. 1-3. London, E.C. 1893.
14. Lavrentiev M.A., Shabat B.V. Methods of theory of functions of a complex variable. M. Nauka, 1987, 736 p.
15. Petryk M., Leclerc S., D. Canet, Sergienko I.V., Deineka V.S., Fraissard J. The Competitive Diffusion of Gases in a zeolite bed: NMR and Slice Procedure, Modelling anmd Identification of Parameters. The Journal of Physical Chemistry C. ACS, 2015,**119** (47), 26519-26525.
16. Petryk M., Vorobiev E. Liquid Flowing from Porous particles During the Pressing of Biological Materials. Computer & Chem. Eng., 2007, 31, 1336-1345.