MATHEMATICAL MODELING. MATHEMATICS

МАТЕМАТИЧНЕ МОДЕЛЮВАННЯ. МАТЕМАТИКА

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MATHEMATICAL MODELING OF PROCESSES OF NONISOTHERMAL ADSORPTION, DESORPTION AND HEAT TRANSFER OF HYDROCARBONS IN NANOPOROUS CATALYSTS BASED ON ZEOLITE ZSM-5 OF EXHAUST GAS NEUTRALIZATION SYSTEMS

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Summary. *An experimental and theoretical study of the non-isothermal adsorption and desorption of gas using microporous silica beds for motor fuel technology is described. Analytical solutions to the problem of non-isothermal adsorption and desorption and heat transfer are based on Heaviside's operational method and Laplace integral transformation. Modeling distributions of propane ant others hydrocarbon components at the inlet and outlet of the silica beds for each adsorption - desorption phase at different times are presented.*

Key words: *Natural gas dehydration, diffusion of adsorbed gas, adsorption and desorption of gases, modeling, Heaviside's operational method, Laplace integral transformation.*

Nomenclature

c – concentration of moisture in the gas phase in the column;

a – concentration of moisture adsorbed in the solid phase;

T – temperature of gas phase flow, °C;

u – velocity of gas phase flow, m/s^2;

D_{inter} – effective longitudinal diffusion coefficient;

Λ – coefficient of thermal diffusion along the columns;

h_g – gas heat capacity;

Q – heat sorption effect;

H – total heat capacity of the adsorbent and gas;

$\varphi(t, z)$ – function of adsorption equilibrium ($\varphi(t, z) \approx \gamma a(t, z)$);

$X^2 = 2\alpha_n / R$ – coefficient of heat loss through the wall of the adsorbent;

R – radius of adsorbent of solid particles, m ;

α_h – heat transfer coefficient;

γ – Henry's constant;

β – mass transfert coefficient;

z – distance from the top of the bed for mathematical simulation, m;

Z – dimensionless coordinate = abscissa z/height of the column;

in – index of parameter names (concentration, temperature) in the inlet of the column.

Statement of the problem. 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].

Analysis of the available investigations. Emissions of motor vehicles, especially products of incomplete combustion for gasoline engines, the number of which is rapidly increasing with frequent on-offs (idle and cold starts) are the greatest threat to the environment and human health, bringing the process of global warming closer [2]. Based on the analysis of international experience, one of the effective solutions to this problem is technology of incorporating various "carbon traps" on the basis of nanopores of zeolite adsorbents before the engine neutralizer, having a relatively low cost and compactness [3,4]. Optimum design of such objects is determined by experimental and theoretical studies of kinetics for complex heat and mass transfer processes, adsorption and desorption of hydrocarbons, that occur in the micro- and macropores of zeolite catalysts [4-6].

In work [7], authors emphases on the need for activation of adsorption-desorption studies of hydrocarbons in zeolites under cold start conditions. A set of experimental studies and numerical simulations of HC traps in conditions close to the real were carried out in [4].

The Objective of the work is mathematical modeling of adsorption and desorption processes for propane and other components of emissions of incomplete combustion products in ZSM-5 zeolite in cold-start conditions, using efficient analytical solutions based on Heaviside's operational calculus method [8].

Statement of the task. The input flow of gas mixture diffuses in the macropores (interparticle space) of catalytic medium and in the micro- and nanopores particles (crystals) of zeolite. Basic hypotheses and assumptions: the system achieves a state of dynamic equilibrium (saturation), which is determined by the appropriate gradient of concentrations for adsorbed substance (propane); the law of dynamic equilibrium is determined by Langmuir's dependence [9]. Processes of adsorption and desorption are considered in form of successively alternating phases, determined by the duration of saturation of working layer of adsorbent, and also by the duration of its regeneration (desorption of absorbed substance from the micropores of adsorbent) (figure 1). Due to changes in temperature operating modes of system and input streams, influence of the temperature on internal kinetics of mass transfer was taken into account.
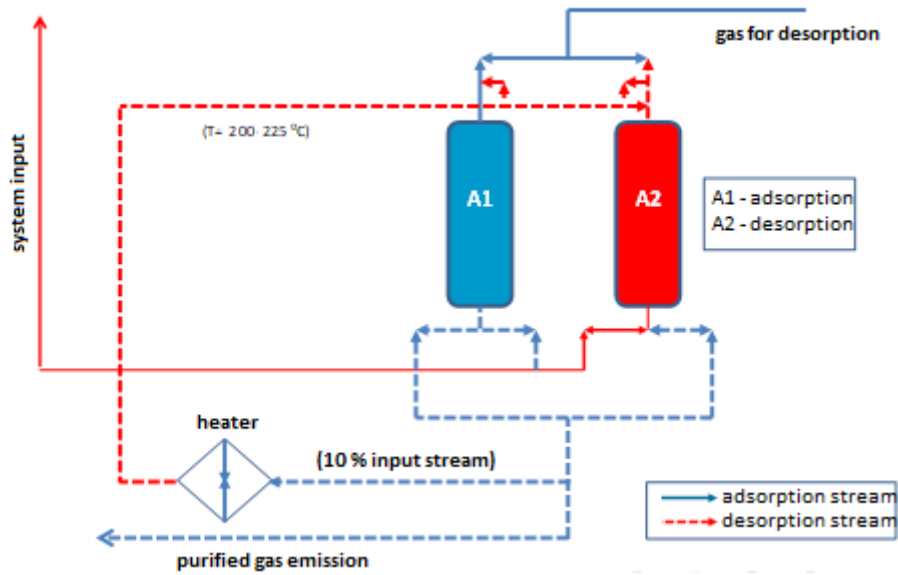
Figure 1. Scheme of experimental block of cyclic adsorption and desorption for processes of mass transfer in hydrocarbon nitrogen trap emissions simulations

The modeling of kinetics of gas dehydration processes on a microporous adsorbent and the corresponding regeneration is based on our approach [10] using a mathematical model that includes mass balance and heat in [11, 9]. The meaning of all terms is given in the Nomenclature section.

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

$$-H\frac{\partial T(t,z)}{\partial t} - uh_g\frac{\partial T}{\partial z} - Q\frac{\partial a}{\partial t} - X^2 T + \Lambda\frac{\partial^2 T}{\partial z^2} = 0, \tag{1}$$

$$\frac{\partial a}{\partial t} = \beta(c - \gamma a(z,t)),$$

with initial conditions:

a) adsorption:

b) desorption:

$$c(t,z)\big|_{t=o} = 0, \tag{2}$$

$$c(t,z)\big|_{t=o} = c_0, \tag{2}$$

$$T(t,z)\big|_{t=o} = T_0, \tag{3}$$

and boundary conditions:

a) adsorption:

b) desorption:

$$c(t,z)\big|_{z=o} = c_{in}, \tag{4}$$

$$c(t,z)\big|_{z=0} = c_{in}(t), \tag{4}$$

$$\frac{\partial}{\partial z}c(t,z)\big|_{z=\infty} = 0, \tag{5}$$

$$\frac{\partial}{\partial z}c(t,z)\big|_{z=\infty} = 0, \tag{5}$$

$$T(t,z)\big|_{z=0} = T_{in}(t), \quad \frac{\partial}{\partial z}T(t,z)\big|_{z=\infty} = 0. \tag{6}$$

To find the analytical solution of the problem (1)-(6) where the functions c and T depend on the concentration, the time and coordinate z, we use Heaviside's operational method [8, 12]. Solutions c and T are obtained according to the following procedure:

a) first the Laplace transforms of the functions c and T are determined:

$$c^*(p,z) = \int_0^\infty c(t,z)\,e^{-p}\,dp \equiv L[c], \quad a^*(p,Z) = \int_0^\infty a(t,z)\,e^{-p}\,dp \equiv L[a],$$

$$T^*(p,z) = \int_0^\infty T(t,z)\,e^{-p}\,dp \equiv L[T],$$

(7)

where p is a complex-value parameter of the Laplace transformation.

b) then the solutions, c and T, are obtained by using the Laplace inverse transform of the functions c^* and T^* with respect to the variable p.

Applying the Laplace transformation to eq. (1)-(6) one obtains:

$$\frac{d^2 c^*}{dz^2} - u_1 \frac{dc^*}{dz} - q^2 c^* = -\mathsf{F}^*,$$

(8)

$$\frac{d^2}{dz^2} T^* - u_2 \frac{d}{dz} T^* - q_2^2(p) T^* = -\mathsf{F}_2^*(p),$$

(9)

with boundary conditions:

a) adsorption:

$$c^*(p,z)\big|_{z=o} = \frac{1}{p} c_{in},$$

(10)

$$\frac{\partial}{\partial z} c^*(p,z)\big|_{z=\infty} = 0,$$

(11)

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

(12)

b) desorption:

$$\frac{d}{dz} c^*(p,z)\big|_{z=\infty} = 0,$$

(10)

$$c^*(p,z)\big|_{z=o} = \frac{1}{p} c_{in},$$

(11)

where:

$$u_1 = \frac{u}{D_{inter}}, \quad q^2(p) = \frac{p(p+\beta(\gamma+1))}{D_{inter}(p+\beta\gamma)}, \quad \mathsf{F}^* = \frac{c_0}{D_{inter}},$$

$$u_2 = \frac{uh_g}{\Lambda}, \quad q_2^2(p) = \frac{Hp+X^2}{\Delta}, \quad \mathsf{F}_2^*(p) = \frac{1}{\Lambda}\left(HT_0 - Q\beta \frac{p}{p+\beta\gamma} c^*(p,z)\right).$$

The solution of eq. (13) with conditions (10), (11) is [10, 11- 13]:

$$c^*\left(p,z\right) = \frac{c_{in}}{p} e^{\frac{u_1}{2}z} e^{-\omega(p)z} + c_0 \frac{1}{1+\gamma}\left[\frac{\gamma}{p} + \frac{1}{p+\beta\left(1+\gamma\right)}\right]\left(1 - e^{\frac{u_1}{2}z} e^{-\omega(p)z}\right), \tag{13}$$

where $\omega\left(p\right) = \left(\frac{1}{4}u_1^2 + q^2\left(p\right)\right)^{1/2}$, $\operatorname{Re}\omega > 0$.

Calculating the Laplace originals in eq. (13), we obtain the analytical solution of (1)-(6) which describe the consentatin distributions in the phase of gaze and of phase solid [11, 12]:

$$c\left(t,z\right) = \frac{\gamma c_0}{1+\gamma} + \frac{c_0}{1+\gamma} e^{-\beta(\gamma+1)t} + \left(c_{in} - c_0\right)e^{\frac{u_1}{2D_{inter}}z} \mathbb{W}_c\left(t,z\right) + \beta c_0 e^{\frac{u}{2D_{inter}}z} \int_0^t e^{-\beta(\gamma+1)(t-s)} \mathbb{W}_c\left(s,z\right)ds, \tag{14}$$

$$a\left(t,z\right) = \beta\int_0^t e^{-\gamma\beta(t-\tau)} c\left(\tau,z\right)d\tau. \tag{15}$$

Here

$$\mathbb{W}_c\left(t,z\right) = \frac{1}{\pi}\int_0^\pi e^{-\varphi_1(\nu)z} \frac{\sin\left(\nu t - z\varphi_2\left(\nu\right)^2\right)}{\nu}d\nu + e^{-\frac{u}{2D_{inter}}z},$$

$$\Gamma_1(\nu) = \frac{u^2}{4D_{inter}^2} + \frac{\nu^2\beta}{D_{inter}^2\left(\nu^2 + \beta^2\gamma^2\right)}, \qquad \Gamma_2(\nu) = \frac{\nu^3 + \nu\beta^2(\gamma+1)\gamma}{D_{inter}\left(\nu^2 + \beta^2\gamma^2\right)}.$$

Using the conditions $c(t,z)|_{z=0} = c_{in}(t)$ for the desorption phase, eq. (13) will be:

$$c\left(t,z\right) = \frac{\gamma c_0}{\gamma+1} + \frac{c_0}{\gamma+1} e^{-\beta(\gamma+1)t} + e^{\frac{u}{2D_{inter}}z}\int_0^t \mathbb{W}_c^{in}\left(t-\tau,z\right)c_{in}(\tau)d\tau - c_0 e^{\frac{u}{2D_{inter}}z} \mathbb{W}_c^0\left(t,z\right) +$$

$$+\beta c_0 e^{\frac{u}{2D_{inter}}z}\int_0^t e^{-\beta(\gamma+1)(t-\tau)} \mathbb{W}_c^0\left(\tau,z\right)d\tau, \tag{16}$$

where $\mathbb{W}_c^{in}\left(t,z\right) = \frac{1}{\pi}\int_0^\pi e^{-\varphi_1(\nu)z}\cos\left(\nu t - \varphi_2(\nu)\right)d\nu$.

The solution of eq. (14) with conditions (12) is [11, 12]:

$$T^*\left(p,z\right) = \frac{T_{in}}{p} e^{\frac{u_2}{2}z} e^{-\omega_2(p)z} + \frac{1}{Hp+X^2}\left(1 - e^{\frac{u_2}{2}z} e^{-\omega_2(p)}\right)\left(HT_0 - Q\beta\left(1 - \frac{\beta\gamma}{p+\beta\gamma}\right)c^*(p,z)\right), \tag{17}$$

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

Calculating the originals of Laplace in eq. (17), we obtain the analytical solution of (1)-(6) which describe the temperature distribution in the adsorbent [11, 12]:

$$T\left(t,z\right)=e^{\frac{uh_g}{2\Lambda}z}\int_0^t \mathbb{W}_T^{in}\left(t-\tau,z\right)T_{in}\left(\tau\right)d\tau+T_0 e^{-\frac{X^2}{H}t}-T_0 e^{\frac{u_2}{2}z}\int_0^t e^{-X^2/Ht(t-\tau)}\mathbb{W}_T^{HX^2}\left(\tau,z\right)d\tau-$$

$$-\frac{Q\beta}{H}e^{\frac{uh_g}{2\Lambda}z}\left(e^{-\frac{X^2}{H}t}-\frac{\beta\gamma}{\beta\gamma-X^2/H}\int_0^t\left(e^{-\frac{X^2}{H}(t-\tau)}-e^{-\beta\gamma(t-\tau)}\right)c(\tau,z)d\tau\right)+ \tag{18}$$

$$+\frac{Q\beta}{H}e^{\frac{uh_g}{2\Lambda}z}\int_0^t\left(\left(1-\frac{1}{\beta\gamma-X^2/H}\right)\mathbb{W}_T^{HX^2}\left(\tau,z\right)+\frac{1}{\beta\gamma-X^2/H}\mathbb{W}_T^{\beta\gamma}\left(\tau,z\right)\right)c(\tau,z)d\tau.$$

Here

$$\mathbb{W}_T^{in}\left(t,z\right)\equiv L^{-1}\left[e^{-\omega_2(p)z}\right]=\frac{1}{\pi}\int_0^\pi e^{-\phi_1(v)z}\cos\left(vt-z\phi_2\left(v\right)\right)dv,$$

$$\mathbb{W}_{T_{HX}}\left(t,z\right)\equiv L^{-1}\left[\frac{e^{-\omega_2(p)z}}{p+X^2/H}\right]=\frac{1}{\pi}\int_0^\pi e^{-\phi_1(v)z}\frac{\left(X^2/H\cos\left(\phi_2(v)z-vt\right)-v\sin\left(\phi_2(v)z-vt\right)\right)}{\left(X^2/H\right)^2+v^2}dv,$$

$$\mathbb{W}_{T_{\beta\gamma}}\left(t,z\right)=\frac{1}{\pi}\int_0^\pi e^{-\phi_1(v)z}\frac{\left(\beta\gamma\cos\left(\phi_2(v)z-vt\right)-v\sin\left(\phi_2(v)z-vt\right)\right)}{\left(\beta\gamma\right)^2+v^2}dv,$$

where:

$$\phi_{1,2}(v)=\left[\frac{\left(\Gamma_{T_1}^2(v)+v^2\Gamma_{T_2}^2(v)\right)^{1/2}\pm\Gamma_{T_1}^2(v)}{2}\right]^{1/2},\quad \Gamma_{T_1}(v)=\frac{u^2+4\Lambda X^2}{4\Lambda^2},\quad \Gamma_{T_2}(v)=\frac{Hv}{\Lambda}.$$

Analysis and simulation. In this section, presented simulations of hydrocarbon absorption isotherms, breakthrough curves, desorption cycles performed on the basis of proposed theoretical model. All calculations were made for the experimentally researched nanoporous ZSM-5 zeolite sample [4, 9] whose geometric dimensions are: length – $l=1,5\cdot10^{-2}$ м, radius $R=0,7\cdot10^{-2}$ м. Physical parameters of zeolite are known from [4, 9, 14, 15]. In figure 2. a, b, c are shown simulated results of adsorption capacity of ZSM-5 zeolite sample for various alkanes: methane (CH_4) (a), ethane (C_2H_6) (b), and propane (C_3H_8) (c). Calculations were performed for different environment temperatures of sample placement $25\,^0C$; $50\,^0C$; $75\,^0C$; $100\,^0C$. On the figure 2 can be seen that for all three gases, intensity of adsorption increases with increasing temperature, and it is most effective for the most volatile methane. It should be noted that since the mass fraction of propane and methane in the fuel mixture is greatest, the use of ZSM-5 zeolite as an adsorbent in engine catalysts working on this type of fuel is the best option.
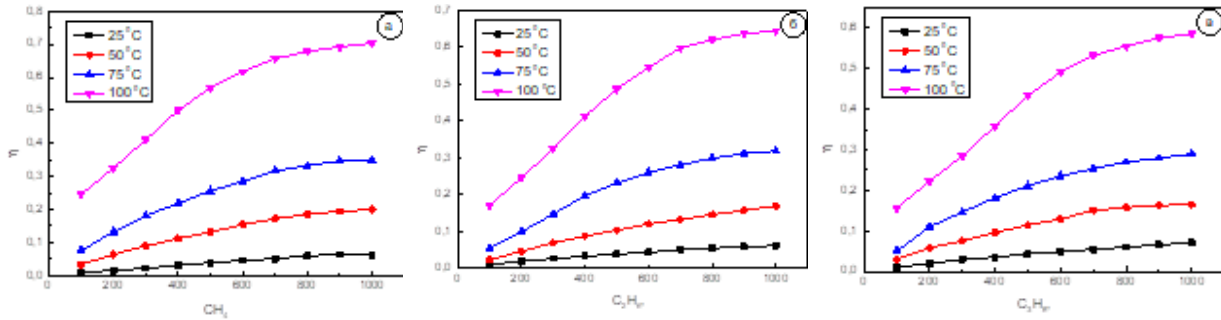
Figure 2. Adsorption isotherms of methane (a), ethane (b), propane (c) in zeolite ZSM-5

Figure 3 shows the results of desorption curves (breakthrough) simulation at temperature of 100 ºC for methane, ethane and propane. It is seen that in the studied range of time dependence $\eta = C(t)/C_0$ for all gases are increasing, proceeding from saturation in the vicinity of the point $t_{CH_4} = 700$ s for methane, $t_{C_2H_6} = 800$ s for ethan, and $t_{C_3H_8} = 1000$ s for propane. It is also worth to note that the given results correlate well with the result of experiment given in [4, 7]. Thus, it can be concluded that zeolite ZSM-5 has the highest adsorption efficiency for volatile gases.
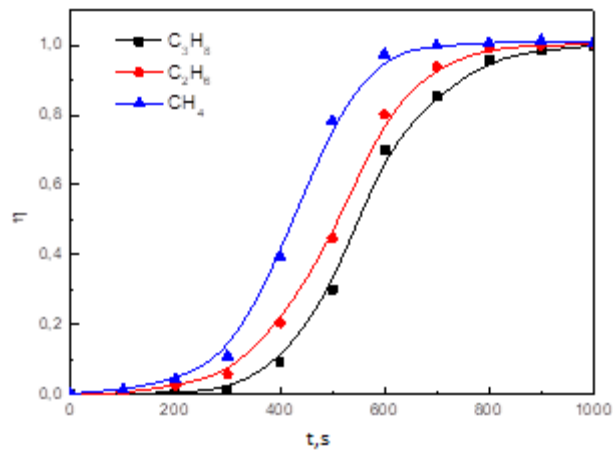
Figure 3. Simulation results of breakthrough curves at a temperature of 100 ºC
for methane, ethane and propane

Conclusions. The model of adsorption of volatile hydrocarbons in zeolite ZSM-5 was studied. The solution of the proposed mathematical model of adsorption and desorption cycle of gas process and adsorbent regeneration is based on the algorithm original using the Heaviside's operational method and Laplace transformation. The analytical solution of this model allows the analysis of the concentrations profiles in the gas phase in the column of microspores adsorbent and the adsorbats in the solid phase for the non-isothermic adsorption and desorption phases.

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МАТЕМАТИЧНЕ МОДЕЛЮВАННЯ ПРОЦЕСІВ НЕІЗОТЕРМІЧНОЇ АДСОРБЦІЇ, ДЕСОРБЦІЇ І ТЕПЛОПЕРЕНОСУ ВУГЛЕВОДНІВ У НАНОПОРИСТИХ КАТАЛІЗАТОРАХ НА ОСНОВІ ЦЕОЛІТУ ZSM-5 СИСТЕМ НЕЙТРАЛІЗАЦІЇ ВИХЛОПНИХ ГАЗІВ

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Резюме. Описано експериментальне й теоретичне дослідження неізотермічної адсорбції та десорбції газу з використанням мікропористих каталізаторів для технології паливних двигунів. Аналітичні розв'язки проблеми неізотермічної адсорбції, десорбції й теплообміну побудовано на основі операційного методу Хевісайда та інтегральних перетвореннях Лапласа. Представлено числове моделювання розподілів компонентів пропану та інших вуглеводнів на вході й виході цеолітного ложе для кожної адсорбційно-десорбційної фази в часі.

Ключові слова: дегідратація газу, дифузія адсорбції газів, адсорбція та десорбція газів, моделювання, метод Хевісайда, інтегральне перетворення Лапласа.