Modeling of Adsorption and Desorption of Hydrocarbons in Nanoporous Catalyst Zeolite using Nonlinear Langmuir's Isotherm

Mykhaylo Petryk, Dmytro Mykhalyk, Maria Petryk, Igor Boyko, Ivan Mudryk

Department of Software Engineering ,
Ternopil Ivan Puluj National Technical University, UKRAINE, Ternopil, 56 Ruska str.,
email: mykhaylo_petryk@tu.edu.te.ua

Abstract: **The theoretical bases of mathematical modeling of nonisothermal adsorption and desorption in nanoporous Catalyst Zeolite for nonlinear Langmuir's isotherm are given. 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.**

Keywords: **mathematical modeling, adsorption desorption process, nanoporous catalyst zeolite, Langmuir's isotherm.**

I. Introduction

The quality of mathematical models for adsorption and desorption processes of hydrocarbons in nanoporous catalytic media determines the effectiveness of technological solutions for neutralizing and reducing exhaust emissions of internal combustion engines, the number of which is rapidly increasing, contributing to global warming crisis. [1, 2].

At present, many experimental and theoretical studies of such processes are conducted, especially studies on the improvement of mathematical models, taking into account the influence of various factors that limit the internal kinetics of adsorption and desorption in nanopores of catalytic media. A detailed analysis of these works was made in [3].

This paper describes the theoretical foundations for modeling non-isothermal adsorption and desorption in nanoporous catalysts for a nonlinear isotherm obtained by the American physicist, Nobel Prize winner Erwin Langmuir, who most fully determines the mechanism of adsorption equilibrium for micro- and nanoporous systems of ZSM-5 zeolites.

II. Description of Kinetic Processes and Mathematical Model

A general description of the interaction of a diffusing gas stream in a biporous pore system of a catalytic medium of nanoporous particles, taking into account the main limiting factors of internal kinetics of mass transfer, including the interaction of micro- and macro transfer, is given in [3].

The main hypothesis assumed for the model is adsorption interaction between adsorbent molecules and active adsorption centers on the phase separation surface in micro- and nanopores of crystallites is determined on the basis of Langmuir's non-linear adsorption equilibrium function taking into account the physical prerequisites [4- 6]:

1. Adsorption are localized and is caused by 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 [4].
2. Adsorption takes place in active centers on the surface of adsorbent distributed throughout the internal surface of the micro- and nanopores.
3. Each active center adsorbs only one molecule of adsorbent and its molecular layer of adsorbate is formed on the surface.
4. Adsorbed molecules are retained by active centers during a certain time, depending on the temperature.

Proceeding from these, the adsorption equilibrium function (adsorption isotherm) of Lengmuir type, which describes the adsorbent phase transition from gas flow to the micro- and nanopores of catalytic medium, will be determined by a nonlinear dependence establishing relationship between equilibrium concentration and adsorption value [5]

$$a \equiv f\left(c_{eq}\right) = a_{full}\frac{bc_{eq}}{1+bc_{eq}}\,. \qquad (1)$$

Here a_{full}, $0<b<1$ are the empirical coefficients that depend on properties of nanoporous medium and diffused substance: a_{full} - the concentration (amount) of adsorbate in micro- and nanopores of zeolite with complete filling of the adsorption centers.

The refined kinetics of nonisothermal adsorption and desorption for exhaust gas neutralization systems in nanoporous catalysts, taking into account the nonlinear function of adsorption equilibrium and the given physical justifications, can be described by the following system of nonlinear partial differential equations [5, 6]:

$$\begin{gathered}
\frac{\partial c(t,z)}{\partial t}+\frac{\partial a(t,z)}{\partial t}+u\frac{\partial c}{\partial z}=D_{\text{inter}}\frac{\partial^2 c}{\partial z^2},\\
-H\frac{\partial T(t,z)}{\partial t}-uh_g\frac{\partial T}{\partial z}-Q\frac{\partial a}{\partial t}-\mathrm{X}^2T+\Lambda\frac{\partial^2 T}{\partial z^2}=0, \qquad (2)\\
\frac{\partial a}{\partial t}=\beta\left(c-\frac{1}{b}\frac{a}{a_{full}-a})\right).
\end{gathered}$$

with initial conditions:

a) adsorption b) desorption

$$c(t,z)|_{t=o}=0\,, \qquad c(t,z)|_{t=o}=c_0\,, \qquad (3)$$

$$T(t,z)|_{t=o}=T_0\,, \qquad T(t,z)|_{t=o}=T_0\,, \qquad (4)$$

and boundary condition:

a) adsorption b) desorption

$$c(t,z)|_{z=o}=c_{in}\,, \qquad c(t,z)|_{z=0}=c_{in}(t)\,, \qquad (5)$$

$$\frac{\partial}{\partial z}c(t,z)|_{z=\infty}=0\,, \qquad \frac{\partial}{\partial z}c(t,z)|_{z=\infty}=0\,, \qquad (6)$$

$$T(t,z)|_{z=0}=T_{in}\,, \qquad \frac{\partial}{\partial z}T(t,z)|_{z=\infty}=0\,, \qquad (7)$$

$$T(t,z)|_{z=0}=T_{in}(t)\,, \qquad \frac{\partial}{\partial z}T(t,z)|_{z=\infty}=0 \qquad (8)$$

Taking into account that $\frac{a}{a_{full}}<1$, the Maclaurin's series, we obtain:

$$c_{eq}(a)\equiv\varphi(a)=\frac{1}{b}\frac{a/a_{full}}{1-a/a_{full}}\approx\gamma a(t,z)+\varepsilon a^2(t,z), \quad (9)$$

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

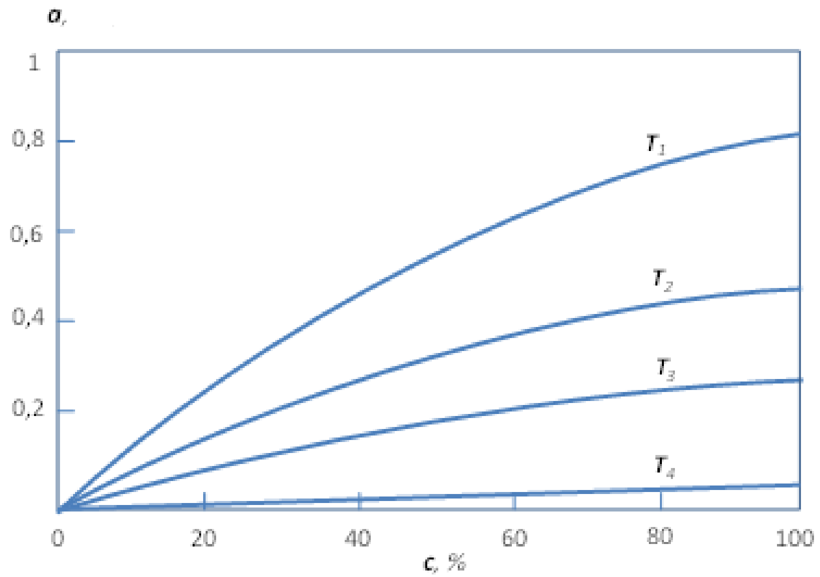

Fig.1 The ZSM-5 zeolite adsorption isotherm in the temperature range from 0 to 350 °C.

As can be seen from fig. 1, adsorption value increases according to the nonlinear law as the adsorbent concentration in the gas phase increases, accompanied by the "filling" of active adsorption centers on the surface of the micropores, and decreases with increasing medium temperature ($T_1<T_2<T_3<T_4$) [5].

Substituting the expanded expression (9) instead of the dependence in the third equation of system (3), we obtain

$$\frac{\partial a}{\partial t}=\beta(c-\gamma a(z,t)-\varepsilon a^2(z,t)) \qquad (10)$$

III. The linearization of a nonlinear model

The problem (2) - (8), taking into account the approximated kinetic equation of phase transformation (10) containing a small parameter ε, is a mixed boundary-value problem for a nonlinear system of second-order partial differential equations. The solution of problem (2) - (8) will be obtained using asymptotic expansions in small parameter ε in the form of following power series [7, 8]:

$$c(t,z)=c_0(t,z)+\varepsilon c_1(t,z)+\varepsilon^2c_2(t,z)+\ldots\,,$$

$$T(t,z)=T_0(t,z)+\varepsilon T_1(t,z)+\varepsilon^2T_2(t,z)+\ldots\,, \qquad (11)$$

$$a(t,z)=a_0(t,z)+\varepsilon a_1(t,z)+\varepsilon^2a_2(t,z)+\ldots\,.$$

As a result of the substitution of asymptotic sums (11) into equations (2) and taking into account (10), the initial nonlinear problem (2) - (8) is parallelized into two types of linear problems [8]:

The problem A_0 *(zero approximation)*: to find a solution for the system of partial differential equations:

$$\frac{\partial c_0(t,z)}{\partial t}+\frac{\partial a_0(t,z)}{\partial t}+u\frac{\partial c_0}{\partial x}=D_{inter}\frac{\partial^2c_0}{\partial z^2}\,, \qquad (12)$$

$$-H\frac{\partial T_0(t,z)}{\partial t}-uh_g\frac{\partial T_0}{\partial z}-Q\frac{\partial a_0}{\partial t}-\mathrm{X}^2T_0+\Lambda\frac{\partial^2T_0}{\partial z^2}=0, \quad (13)$$

$$\frac{\partial a_0}{\partial t}=\beta(c_0-\gamma a_0)\,, \qquad (14)$$

with initial and boundary conditions of initial problem.

The problem A_n *(n-th approximation with zero initial and boundary conditions)*: to find a solution for system of equations:

$$\frac{\partial c_n(t,z)}{\partial t}+\frac{\partial a_n(t,z)}{\partial t}+u\frac{\partial c_n}{\partial z}=D_{inter}\frac{\partial^2c_n}{\partial z^2}\,, \qquad (15)$$

$$-H\frac{\partial T_n(t,z)}{\partial t}-uh_g\frac{\partial T_n}{\partial z}-Q\frac{\partial a_n}{\partial t}-\mathrm{X}^2T_n+\Lambda\frac{\partial^2 T_n}{\partial z^2}=0, \quad (16)$$

$$\frac{\partial a_n}{\partial t}=\beta\left(c_n-\gamma a_n-\sum_{i=0}^{n-1}a_i(t,z)a_{n-1-i}(t,z)\right) \quad (17)$$

with zero initial and boundary conditions.

We construct analytic solutions of problems A_0 and $A_n; n=\overline{1,\infty}$ using the Heaviside's operation method [9, 10].

The problem A_0 is linear concerning to zero approximation a_0; The problem $A_n; n=\overline{1,\infty}$ is linear concerning to the nth approximation a_n and nonlinear concerning to all previous n-1 approximations. All equations of problems are obtained by linearizing the nonlinear differential equation of the internal adsorption kinetics with asymptotic sums (11), grouping the terms in the left and right sides of the equations and the conditions of the original boundary value problem for equal powers of a small parameter.

Having determined,

$$L\left[c(t,z)\right]\equiv c^*(p,z)=\int_0^\infty c(t,z)e^{-pt}dt,$$
$$L\left[T(t,z)\right]\equiv T^*(p,z)=\int_0^\infty T(t,z)e^{-pt}dt, \quad (18)$$
$$L\left[a(t,z)\right]\equiv a^*(p,z)=\int_0^\infty a(t,z)e^{-pt}dt$$

where p is a complex Laplace transform parameter, we obtain in the Laplace images A_0^* and A_n^* the above boundary value problems.

The problem A_0^*

$$\frac{d^2c_0^*(p,z)}{dz^2}-u_1\frac{dc_0^*}{dz}-q_1^2(p)c_0^*=-\mathcal{F}_{c_0}^*(p), \quad (19)$$

$$\frac{d^2}{dz^2}T_0^*-u_2\frac{d}{dz}T_0^*-q_2^2(p)T_0^*=-\mathcal{F}_{T_0}^*(p), \quad (20)$$

$$a_0^*(p,z)=\beta\frac{1}{p+\beta\gamma}c_0^*(p,z), \quad (21)$$

The problem A_n^*

$$\frac{d^2c_n^*}{dz^2}-u_1\frac{dc_n^*}{dz}-q_1^2(p)c_n^*=-\mathcal{F}_{c_n}^*(p,z), \quad (22)$$

$$\frac{d^2}{dz^2}T_n^*-u_2\frac{d}{dz}T_n^*-q_2^2(p)T_n^*=-\mathcal{F}_{T_n}^*(p,z), \quad (23)$$

$$a_n^*(p,z)=\beta\frac{1}{p+\beta\gamma}\left(c_n^*-\left(\sum_{i=0}^{n-1}a_ia_{n-1-i}\right)^*(p,z)\right), \quad (24)$$

IV. SOLUTIONS FOR ZERO AND N-TH APPROXIMATIONS

The distributions of adsorption concentration in gas phase $c_0(t,z)$, the temperature of the layer $T_0(t,z)$ and the concentration of the adsorbate (absorbed substance) in the nanopores of the adsorbent $a_0(t,z)$ are looks like:

$$c_0(t,z)=c_{in}(0)e^{\frac{u}{2D_{\text{inter}}}z}\Phi_c^0(t,z)+e^{\frac{u}{2D_{\text{inter}}}z}\int_0^t\frac{d}{d\tau}c_{in}(\tau)\Phi_c^0(t-\tau,z)d\tau$$
$$+c_0^0\frac{\gamma}{1+\gamma}\left(1+\frac{1}{\gamma}e^{-\beta(\gamma+1)t}-\frac{\gamma+1}{\gamma}e^{\frac{u}{2D_{\text{inter}}}z}\Phi_c^0(t,z)\right)$$
$$+\beta c_0^0e^{\frac{u}{2D_{\text{inter}}}z}\int_0^t e^{-\beta(\gamma+1)(t-s)}\Phi_c^0(\tau,z)d\tau \quad (25)$$

$$T_0(t,z)=T_{in}(0)\Phi_T^0(t,z)+\int_0^t\frac{d}{d\tau}T_{in}(\tau)\Phi_T^0(t-\tau,z)+$$
$$+\frac{1}{\Lambda}\int_0^t\int_0^\infty\left[\begin{matrix}HT_0^0\mathcal{H}_T(t-\tau;z,\xi)-\\ Q\beta\left(\begin{matrix}\mathcal{H}_T(t-\tau;z,\xi)-\\ \beta\gamma\int_0^{t-\tau}e^{-\beta\gamma(t-\tau-s)}\mathcal{H}_T(\tau-s;z,\xi)ds\end{matrix}\right)c_0^*(p,\xi)\end{matrix}\right]d\xi d\tau \quad (26)$$

$$a_0(t,z)=\beta\int_0^t e^{-\gamma\beta(t-\tau)}c_0(\tau,z)d\tau \quad (27)$$

The solutions $c_n(t,z)$, $T_n(t,z)$, $a_n(t,z)$ for problems (15)-(17) are the functions describing the temporal spatial distributions of adsorbent concentration in gas phase, temperature and adsorption concentration in micro and nanopores of the adsorbent particles [10, 11]:

$$c_n(t,z)=\frac{\beta}{D_{\text{inter}}}\times$$
$$\int_0^\tau\int_0^\infty\left[\begin{matrix}\mathcal{H}_c(t-\tau,z,\xi)-\\ \beta\gamma\int_0^{t-\tau}e^{-\beta\gamma(\tau-s)}\mathcal{H}_c(s,z,\xi)ds\end{matrix}\right]\left(\sum_{i=0}^{n-1}a_ia_{n-1-i}\right)(\tau,\xi)d\xi d\tau \quad (28)$$

$$T_n(t,z)=\frac{Q\beta}{\Lambda}\int_0^t\left[\begin{matrix}\int_0^\infty\left(\begin{matrix}\mathcal{H}_T(t-\tau;z,\xi)-\\ \beta\gamma\int^{t-\tau}e^{-\beta\gamma(t-\tau-s)}\mathcal{H}_T(s;z,\xi)ds\end{matrix}\right)\\ \left[\sum_{i=0}^{n-1}a_i(s,\xi)a_{n-1-i}(s,\xi)-c_n(\tau,\xi)\right]\end{matrix}\right]d\xi d\tau \quad (29)$$

$$a_n(t,z)=\beta\int_0^t e^{-\beta\gamma(t-\tau)}\left(c_n(\tau,z)-\sum_{i=0}^{n-1}a_i(\tau,z)a_{n-1-i}(\tau,z)\right)d\tau \quad (30)$$

Here:

$$\Phi_c^0(t,z)=\frac{1}{\pi}\int_0^\pi e^{-\varphi_1(\nu)z}\frac{\sin\left(\nu t-z\varphi_2(\nu)^2\right)}{\nu}d\nu+e^{-\frac{u}{2D_{\text{inter}}}z}$$

$$\Phi_c(t,z)=$$
$$\frac{1}{2\pi}\int_0^\infty\frac{\varphi_1(\nu)\cos\left(\nu t-\varphi_2(\nu)z\right)+\phi_2(\nu)\sin\left(\nu t-\varphi_2(\nu)z\right)}{\left(\Gamma_1^2(\nu)+\nu^2\Gamma_2^2(\nu)\right)^{1/2}}d\nu$$

$$\Phi_T^0\left(t,z\right)=\frac{1}{\pi}\int_0^{\pi} e^{-\phi_1(\nu)z}\,\frac{\sin\left(\nu t - z\phi_2\left(\nu\right)^2\right)}{\nu}d\nu + e^{-\frac{u}{2D_{\text{inter}}}z},$$

$$\Phi_T\left(t,\mathrm{z}\right)=$$

$$\frac{1}{2\pi}\int_0^{\infty}\frac{\phi_1(\nu)\cos\left(\nu t-\phi_2(\nu)\mathrm{z}\right)+\phi_2(\nu)\sin\left(\nu t-\phi_2(\nu)\mathrm{z}\right)}{\left(\Gamma_{T_1}^2(\nu)+\nu^2\Gamma_{T_2}^2(\nu)\right)^{1/2}}d\nu,$$

$$\varphi_{1,2}(\nu)=\left[\frac{\left(\Gamma_1^2(\nu)+\nu^2\Gamma_2^2(\nu)\right)^{1/2}\pm\Gamma_1^2(\nu)}{2}\right]^{1/2},$$

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

$$,\;,\phi_{1,2}(\nu)=\left[\frac{\left(\Gamma_{T_1}^2(\nu)+\nu^2\Gamma_{T_2}^2(\nu)\right)^{1/2}\pm\Gamma_{T_1}^2(\nu)}{2}\right]^{1/2},$$

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

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

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

V. 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; $\mathrm{X}^2 = 2\alpha_n / R$ - 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;

VI. CONCLUSION

In paper proposed theoretical foundations of mathematical modeling of nonisothermal adsorption and desorption in nanoporous catalysts for exhaust gas neutralization systems for the nonlinear Langmuir isotherm. Such approach in our opinion most fully describes the mechanism of adsorption equilibrium for micro- and nanopore systems of the ZSM-5 zeolite. 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 was substantiated and obtained using Heaviside's operational method.

REFERENCES

[1] R.M. Barrer, "Diffusion and Flow in Porous Zeolite, Carbon or Ceramic Media, Characterization of Porous Solids", *Society of Chemical Industry*, London, 1979

[2] B. Puertolas, M.V. Navarro, J.M. Lopez, R.Murillo, A.M. Mastral, T.Garcia "Modelling the heat and mass transfers of propane onto a ZSM-5 zeolite" *Separation and Purification Technology.* vol.86., pp.127-136, 2012

[3] M.R.Petryk, A.M.Himich, M.M.Petryk, J.Fraissard "Modeling of heat-mass-transfer adsroption and desorption in nanoporous zeolit catalytic media of exhaust gases neutralization systems" *International scientific and technical journal "Problems of control and informatics"*, vol. 2, pp. 49-57, 2018

[4] J.Kärger and D.Ruthven "Diffusion in Zeolites and Other Microporous Solids" *New York, John Wiley & Sons*., 605p, 1992

[5] J.Kärger, D.Ruthven, D.Theodorou "Diffusion in Nanoporous Materials", *Hoboken, John Wiley & Sons.*, 660 p., 2012

[6] N.Y.Chen, T.F.Degnan and M.C.Smith "Molecular Transport and Reaction in Zeolites: Design and Application of Shape Selective Catalysis", *New York, Wiley-VCH.*, 510 p., 1994

[7]. A.Prudnikov, Y.Brychkov, O.Marychev "Integrals and series. Additional chapters" – M:Nauka, 736p, 1973

[8] I.Sergienko, M.Petryk, A.Khimith, D.Mykhalyk, S.Leclerc, J.Fraissard "Mathematical Modelling of Diffusion Process in Microporous Media (Numerical analysis and application)" *Kyiv: National Academy of Sciences of Ukraine*. 196 p., 2014

[9] O. Heaviside "Electromagnetic Theory", *London, The Electrician*. 1-3. – E.C., 1893

[10] M.A. Lavrentiev, B.V. Shabat "Methods of theory of functions of a complex variable", *M.:Nauka*, 736 p., 1973

[11] M. Petryk, S. Leclerc, D. Canet, I.V. Sergienko, V.S. Deineka, J. Fraissard 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 (USA).* 119 (47). – P. 26519-26525, 2015