

NUMERICAL RESEARCH TO DETERMINE THE DOMINANT MECHANISM OF MASS AND HEAT TRANSFER IN PRESSURE SWING ADSORPTION PROCESSES*O.O. Golubyatnikov¹, E.I. Akulinin¹, S.I. Dvoretzky¹*¹Tambov State Technical University, Russian Federation

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The existing mathematical models of pressure swing adsorption (PSA) apply various assumptions regarding the mass and heat transfer mechanisms in the “gas mixture-adsorbent” system. An increase in the number of assumptions leads to a simplification of the model, a decrease in the calculation time of one iteration in the model and, at the same time, a decrease in its accuracy. The simplification of the model is especially important in PSA processes, since the calculation of the model is carried out before the cyclic steady state and takes tens and even hundreds of cycles (iterations). Ensuring high accuracy of the PSA model and its minimum complexity is a contradictory requirement; therefore it is important to reasonably consider only those transfer mechanisms that are dominant in the model. The paper proposes a mathematical model of the PSA process, which takes into account the thermal effects of sorption, external and internal diffusion mechanisms of adsorptive transfer. A numerical research was carried out to determine the dominant transfer mechanism, and recommendations were proposed for using the preferred PSA model in terms of its accuracy and calculation time (for the processes of air oxygen enrichment and synthesis gas separation). It was found that to calculate PSA oxygen units with a capacity of less than 4 l/min at NTP, it is advisable to use an isothermal model, which saves at least 24,3% of the calculation time with a loss of accuracy of no more than 0,084 vol%. To calculate PSA hydrogen units, the use of an isothermal model is impractical even at the lowest productivity of 50 l/min at NTP. When the diameter of the adsorbent particles is less than 2 mm, it is advisable to use an external diffusion model, which saves at least 54,2% of the calculation time for oxygen units and at least 47,1% of the calculation time for hydrogen units with a slight loss of accuracy. At a gas flow velocity of more than 0,05 m/s, the model can ignore the diffusion in the gas. The research results can be used to calculate various PSA processes for separation of gas mixtures: rPSA, ultra rPSA, VSA, VPSA, and related processes.

Keywords: pressure swing adsorption; mathematical modelling; numerical research; hydrogen; oxygen.

Introduction

One of the most promising methods for producing gases from gas mixtures is pressure swing adsorption (PSA). This is a wide class of cyclic adsorption processes (PSA, VSA, VPSA, PTSA, rPSA, ultra-rPSA, etc.) allowing to extract target gases of high purity with the lowest cost and energy consumption in the range of productivity: for oxygen — up to 9000 m³/h at NTP [1]; for hydrogen — up to 50000 m³/h at NTP (according to JSC Grasy). The use of mathematical modelling and optimization methods in calculating the PSA processes and units allows to reduce the cost of extracting target gases from

mixtures up to 2 times by determining the best combinations of operating and design unit parameters [2].

In general, mathematical models of the PSA process represent a set of second-order partial differential equations describing the material and heat balance in the gas phase and the adsorbent, as well as the gas flow continuity and kinetics of mass and heat transfer at the gas mixture-adsorbent interface in the unit adsorber. The PSA process is cyclic when its modelling feature is the achievement of a cyclic steady state (CSS) [3–5]. CSS is achieved by multiple sequential solution of the system of model equations for each stage of the cyclic process (pressurization, adsorption, depressurization, desorption, etc.) until the product concentration at the adsorber outlet in the current cycle is very close to the concentration in the previous cycle. This procedure is a simulation of the stationary operation mode. The number of iterations (cycles) that needs to be calculated reaches several dozen, so the calculations are time-consuming (expensive), which is especially critical when solving the optimal design problems for PSA units [4]. In this regard, the calculation time of one iteration in the model is an important aspect, to reduce which it is advisable to simplify the model [4].

Obviously, the simplification of the model leads to a loss of its accuracy, however, PSA models must be sufficiently accurate (for example, the accuracy of the model must be at least 1 vol% for oxygen extraction and not less than 0,1 vol% for hydrogen extraction [6, 7]). Ensuring high accuracy of the PSA model and its minimum complexity is a contradictory requirement. Therefore, it is important to reasonably consider only those mechanisms of mass and heat transfer that are dominant in the adsorption–desorption process in the model.

In the existing PSA models, various assumptions are applied regarding the mass and heat transfer mechanisms in the gas mixture–adsorbent system:

- non-isothermal models [3, 8–15], where the heat effects of adsorption-desorption and temperature changes in the adsorbent and the gas phase are taken into account, and isothermal models [16, 17], where these effects are not considered;
- models with a dominant external diffusion transfer mechanism for the gas phase components in the adsorbent [3, 8–13, 16, 17], where adsorption and desorption are limited by the process of external mass transfer, and models with a mixed diffusion transfer mechanism [14, 15, 17], where adsorption and desorption are also limited by the process of internal diffusion in the adsorbent granule;
- models without taking into account the longitudinal mixing in the gas phase [11].

The considered studies do not sufficiently substantiate the assumptions regarding certain mass and heat transfer mechanisms for an adsorptive from the gas phase to the adsorbent. Moreover, there is no comparative analysis of the accuracy and calculation time of various PSA models.

The purpose of this work is to determine the combination of input parameters (productivity, diameter of adsorbent particles, flow rate), which is necessary to take into account the mass and heat transfer mechanism in the PSA model (using the example of the PSA process for air oxygen enrichment and hydrogen extraction from synthesis gas). This allows to reasonably use simpler and less expensive PSA models in terms of processor time (CPU time), which is especially important when solving the optimal design problems of units.

1. Mathematical Model of PSA Process for Gas Mixture Separation

The technological process of gas mixture separation by the PSA method is carried out in a two-adsorber unit with a 13X granular adsorbent [9, 14]. The principle of its operation lies in the cyclic alternation of the adsorption processes of the components from a continuous gas mixture flow and their desorption from the adsorbent in parallel working adsorbers. At the same time, a continuous flow of the target product is provided at the PSA unit outlet. One complete cycle of the unit operation includes two steps of adsorption and desorption which are equal in time.

The mathematical model of the PSA process describes the mass and heat transfer processes occurring in the unit adsorber and represents a system of 1-D second-order partial differential equations:

component-wise material balance in the gas phase flow along the height of the adsorbent bed, $0 \leq x \leq L$, $0 \leq \tau \leq \tau_{ads}$, $\tau_{ads} \leq \tau \leq \tau_{des}$,

$$\frac{\partial c_k(x, \tau)}{\partial \tau} + \frac{1 - \varepsilon}{\varepsilon} \frac{\partial \bar{a}_k}{\partial \tau} + \frac{\partial(\nu_g c_k(x, \tau))}{\partial x} = \frac{\partial}{\partial x} \left(D_g \frac{\partial c_k(x, \tau)}{\partial x} \right), \quad (1)$$

sorption kinetics (Gluckauf formula)

$$\frac{\partial \bar{a}_k(x, \tau)}{\partial \tau} = \beta_k (a_k^* - \bar{a}_k(x, \tau)), \quad (2)$$

saturation of adsorbent granules with adsorptive, $0 \leq r \leq r_p$, $i = 1, 2, \dots, \frac{L}{2r_p}$,

$$\frac{\partial a_k(r, \tau)}{\partial \tau} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(D_{a,k} r^2 \frac{\partial a_k(r, \tau)}{\partial r} \right), \quad \bar{a}_k(x_i, \tau) = \frac{3}{r^3} \int_0^{r_p} a_k(r, \tau) r^2 dr, \quad (3)$$

heat propagation in the gas mixture flow along the height of the adsorbent

$$c_{pg} \rho_g \frac{\partial T_g(x, \tau)}{\partial \tau} + c_{pg} \rho_g \nu_g \frac{\partial T_g(x, \tau)}{\partial x} - \frac{\alpha}{\varepsilon} S_{sp} (T_a - T_g(x, \tau)) = \lambda_g \frac{\partial^2 T_g(x, \tau)}{\partial x^2}, \quad (4)$$

heat propagation in the adsorbent

$$c_{pa} \rho_a \frac{\partial T_a(x, \tau)}{\partial \tau} + \alpha S_{sp} (T_a(x, \tau) - T_g) - \sum_k h_k \frac{\bar{a}_k}{\partial \tau} = \lambda_a \frac{\partial^2 T_a(x, \tau)}{\partial x^2}, \quad (5)$$

continuity of the flow

$$\sum_k c_k \frac{\partial \nu_g(x, \tau)}{\partial x} = \nu_g(x, \tau) \frac{\left(\partial \sum_k c_k \right)}{\partial x}, \quad (6)$$

Ergun's equation

$$\frac{\partial P(x, \tau)}{\partial x} = - \left(\frac{150(1 - \varepsilon)^2}{(d_p \varsigma)^2 \varepsilon} \mu_g \nu_g + 1, 75 M_g \rho_g \frac{1 - \varepsilon}{d_p \varsigma \varepsilon^3} \nu_g^2 \right), \quad (7)$$

where τ is a time, s; x is a spatial coordinate along the length (height) of the adsorbent bed, m; r is a spatial coordinate along the radius of the adsorbent granule, m; c_k is a molar concentration of the k -th component in the gas mixture, mol/m³; a_k is a concentration of the k -th component in the adsorbent granule, mol/m³; \bar{a}_k is an average concentration of the k -th component in the adsorbent, mol/m³; a_k^* is an equilibrium k -th component in the adsorbent, mol/m³; ν_g is a velocity of the gas mixture, m/s; T_g is a temperature in the gas phase, K; T_a is a temperature in the adsorbent, K; P is a pressure, Pa; L is a height of the adsorbent bed, m; τ_c is a duration of the adsorption–desorption cycle, s; $\tau_c = \tau_{ads} + \tau_{des}$.

The mechanism of matter transfer includes diffusion and convection in gas (1), external mass transfer (2), and diffusion in the adsorbent granule (3). The heat transfer mechanism includes convection, heat conduction, external heat transfer (4), and heat propagation in the adsorbent (5). Equation (6) reflects the change in the flow rate as a result of sorption of the components, while equation (7) describes the pressure drop in the adsorbent bed.

Within development of the model, we assume the following: 1) the initial gas mixtures are considered as an ideal gas, which is quite acceptable at a pressure in the adsorber up to 200×10^5 Pa [18, 19]; 2) the diffusion of the adsorptive and the spread of heat in the gas and solid phases are carried out only in the axial direction of the gas mixture flow in the adsorber (along the length of the adsorbent bed, $0 \leq x \leq L$) [3–17]; 3) the adsorption equilibrium (adsorption isotherms of components) on a microporous adsorbent are described by the Dubinin–Radushkevich equation [17, 18]; 4) the desorption branches of the adsorption isotherms of the gas phase components on the 13X zeolite coincide with the adsorption ones [18]; 5) the temperature distribution in the adsorbent granule is considered uniform due to its high thermal conductivity [20].

We determine the equilibrium concentration a_k^* of the adsorptive in the adsorbent by the Dubinin–Radushkevich equation [17, 18], the diffusion coefficient in the gas phase D_g by the Fuller–Schletter–Giddings formula [19], the heat of sorption h_k by the formula [20], the coefficients of mass transfer β and heat transfer α by the criterion equations [7, 14], the diffusion coefficient in the adsorbent $D_{a,k}$ by the Dubinin–Yavich formula [21], the specific surface of adsorbent granules S_{sp} by the formula [18], and the partial pressure $P_{p,k}$ by the formula [19]:

$$a_k^* = \rho_a \frac{W_0}{v_k^*} \exp \left[-B \frac{T_g^2}{\varphi_k^2} \lg^2 \left(\frac{P_{s,k}}{P_{p,k}} \right) \right], D_g = \frac{10^{-3} T_g^{1,75} \sqrt{\sum_k M_{g,k} \prod_k M_{g,k}}}{P \left(\sum_k v_k^{1/3} \right)^2},$$

$$h_{ads,k} = \gamma_k + E \left(\left[\ln \left(\frac{a_k^*}{a_k} \right) \right]^{\frac{1}{n}} + \frac{\chi_k T_a}{n} \left[\ln \left(\frac{a_k^*}{a_k} \right) \right]^{\frac{1}{n}-1} \right),$$

$$h_{des,k} = \gamma_k + E \left(1 + \left[\ln \left(\frac{a_k^*}{a_k} \right) \right]^{\frac{1}{n}} + \frac{\chi_k T_a}{n} \left[\ln \left(\frac{a_k^*}{a_k} \right) \right]^{\frac{1}{n}-1} \right),$$

$$\alpha = \frac{0,24 \text{Re}^{0,83} \lambda_g}{d_p}, \beta = \frac{15 D_e}{r_p}, S_{sp} = \frac{6}{d_p},$$

$$D_{a,k} = \frac{E^2 \tau_0 T_a^{0,7}}{M_{g,k} (1 - (1/2) \ln \varepsilon_1) (1 - \varepsilon_2) n R} \left[\ln \left(\frac{a_k^*}{a_k} \right) \right]^{\frac{1}{n}-1} \exp \left(-\frac{h_k}{2 R T_a} \right),$$

$$P_{p,k} = P c_k 0,0224 \times 1,013 \times 10^{-5}.$$

Table 1 presents the values of the remaining coefficients in the model.

Table 1

Values of coefficients and parameters in the PSA model

Initial data	Air	Synthesis gas
<i>Adsorbent characteristics:</i>		
Zeolite adsorbent	13X	13X
Density of the adsorbent, kg/m ³	$\rho_a = 2140$	$\rho_a = 2140$
Porosity coefficient of the adsorbent, m ³ /m ³	$\varepsilon = 0,39$	$\varepsilon = 0,39$
Thermal conductivity coefficient of the adsorbent, W/(m K)	$\lambda_a = 0,139$	$\lambda_a = 0,139$
Sphericity coefficient of adsorbent particles	$\varsigma = 1$	$\varsigma = 1$
Specific heat of the adsorbent, J/(kg K)	$c_{pa} = 830$	$c_{pa} = 830$
Input temperature in the adsorbent, K	$T_a^{in} = 298$	$T_a^{in} = 298$
Characteristic energy of adsorption, J/mol	$E = 13420$	$E = 13420$
Average lifetime of an adsorbate molecule in the adsorbate state, s	$\tau_0 = 10^{-13}$	$\tau_0 = 10^{-13}$
Relative volume of adsorbent macropores, m ³ /m ³	$\varepsilon_1 = 0,7$	$\varepsilon_1 = 0,7$
Relative volume of adsorbent micropores, m ³ /m ³	$\varepsilon_2 = 0,25$	$\varepsilon_2 = 0,25$
<i>Gas mixture characteristics:</i>		
Component concentration, vol%	$c_{O_2}^{in} = 22$ $c_{N_2}^{in} = 78$	$c_{H_2}^{in} = 68$ $c_{CO_2}^{in} = 27$ $c_{CO}^{in} = 5$
Temperature, K	$T_g^{in} = 298$	$T_g^{in} = 298$
Specific heat capacity, J/(mol K)	$c_{pg} = 1005$	$c_{pg} = 9971$
Thermal conductivity coefficient, W/(m K)	$\lambda_g = 0,023$	$\lambda_g = 0,129$
Latent heat of vaporization, J/mol	$\gamma_{O_2} = 6819,9$ $\gamma_{N_2} = 5577,3$	$\gamma_{H_2} = 903,7$ $\gamma_{CO_2} = 17154,4$ $\gamma_{CO} = 6041,7$
Dynamic viscosity, 10 ⁻⁵ Pa s	$\mu_g = 1,89$	$\mu_g = 1,07$
Coefficients of the Fuller–Schletter–Giddings equation	$\nu_{O_2} = 16,6$ $\nu_{N_2} = 17,9$	$\nu_{H_2} = 7,07$ $\nu_{CO_2} = 26,9$ $\nu_{CO} = 18,9$
<i>Adsorber design parameters:</i>		
Inner diameter of the adsorber, m	$D = 0,04$	$D = 0,1$
Adsorbent bed length, m	$L = 0,2$	$L = 1,0$
<i>Mode parameters:</i>		
Cycle duration, s	$\tau_c = 40$	$\tau_c = 120$
Desorption input pressure, atm	$P_{des}^{in} = 1$	$P_{des}^{in} = 0,75$

The mathematical model (1) – (7) is endowed with the initial conditions for each step of the cycle (adsorption and desorption):

$$\text{adsorption, first cycle } \tau = 0, i = 1, 0 \leq x \leq L, c_k(x, 0) = c_k^{in}, \bar{a}_k(x, 0) = 0, a_k(r, 0) = 0, T_g(x, 0) = T_g^{in}, T_a(x, 0) = T_a^{in}, \nu_g(x, 0) = \nu_g^{in}, P(x, 0) = P_{ads}^{in};$$

$$\text{desorption } \tau = i \times \tau_{des}, i = 1, 2, \dots, 0 \leq x \leq L, c_k(x, \tau) = c_k^{ads}(x, \tau_{ads}), \bar{a}_k(x, \tau) = \bar{a}_k^{ads}(x, \tau_{ads}), a_k(r, \tau) = a_k^{ads}(r, \tau_{ads}), T_g(x, \tau) = T_g^{ads}(x, \tau_{ads}), T_a(x, \tau) = T_a^{ads}(x, \tau_{ads}), \nu_g(x, \tau) = \nu_g^{ads}(x, \tau_{ads}), P(x, \tau) = P^{ads}(x, \tau_{ads});$$

adsorption, subsequent cycles $\tau = i \times \tau_{ads}, i = 2, 3, \dots, 0 \leq x \leq L, c_k(x, \tau) = c_k^{des}(x, \tau_{des}), \bar{a}_k(x, \tau) = \bar{a}_k^{des}(x, \tau_{des}), a_k(r, \tau) = a_k^{des}(r, \tau_{des}), T_g(x, \tau) = T_g^{des}(x, \tau_{des}), T_a(x, \tau) = T_a^{des}(x, \tau_{des}), \nu_g(x, \tau) = \nu_g^{des}(x, \tau_{des}), P(x, \tau) = P^{des}(x, \tau_{des});$

boundary conditions for each step of the cycle (adsorption and desorption):

adsorption $x = 0 c_k(0, \tau) = c_k^{in}(\tau), a_k(0, \tau) = a_k^*(\tau), T_g(0, \tau) = T_g^{in}(\tau), \frac{\partial T_a}{\partial x}(0, \tau) = \alpha S_{sp}(T_a(0, \tau) - T_g^{in}(\tau)), \nu_g(0, \tau) = \nu_g^{in}(\tau), P(0, \tau) = P_{ads}^{in}(\tau);$

adsorption $x = L \frac{\partial c_k}{\partial x}(L, \tau) = 0, \frac{\partial a_k}{\partial r}(r_p, \tau) = 0, \frac{\partial T_g}{\partial x}(L, \tau) = 0, \frac{\partial T_a}{\partial x}(L, \tau) = 0, \frac{\partial \nu_g}{\partial x}(L, \tau) = 0, \frac{\partial P}{\partial x}(L, \tau) = 0;$

desorption $x = 0 \frac{\partial c_k}{\partial x}(0, \tau) = 0, \frac{\partial a_k}{\partial r}(0, \tau) = 0, \frac{\partial T_g}{\partial x}(0, \tau) = 0, \frac{\partial T_a}{\partial x}(0, \tau) = 0, \frac{\partial \nu_g}{\partial x}(0, \tau) = 0, \frac{\partial P}{\partial x}(0, \tau) = P_{des}^{in}(\tau);$

desorption $x = L c_k(L, \tau) = c_k^{ads}(L, \tau), a_k(r_p, \tau) = a_k^*(r_p, \tau), T_g(L, \tau) = T_g^{ads}(L, \tau), \frac{\partial T_a}{\partial x}(L, \tau) = \alpha S_{sp}(T_a(L, \tau) - T_g^{ads}), \nu_g(L, \tau) = \nu_g^{ads}(L, \tau), P(L, \tau) = P_{ads}^{in}(\tau).$

The system of equations (1) – (7) was solved by the method of lines in the MatLab software environment using a Van Leer flux limiter to prevent physically unrealistic oscillations [4].

The solution of the system (1) – (7) must be carried out sequentially for the adsorption and desorption steps before the onset of the CSS mode in the adsorber [3–5]:

$$|y_{p,i}^{out} - y_{p,i-1}^{out}| \leq 10^{-3}, \quad (8)$$

where $y_{p,i}^{out}$ is a purity of the product (oxygen or hydrogen) at the adsorber outlet on the i -th unit cycle

$$y_p^{out} = \frac{1}{\tau_{ads}} \frac{c_p^{out}(\tau, L)}{\sum_k c_k^{out}(\tau, L)} 100\%. \quad (9)$$

The adequacy of the model (1) – (7) was assessed using the root mean square error RMS:

$$RMS = \sqrt{\frac{1}{N} \sum_{j=1}^N (y_{p,j}^{out}(\tau) - y_{p,j}^{out,e}(\tau))^2}, \quad (10)$$

where $y_p^{out,e}$ is a gas purity at the adsorber outlet obtained at the PSA experimental unit; y_p^{out} is a gas purity at the adsorber outlet calculated according to the model (1) – (7).

To test the adequacy of the PSA models for air oxygen enrichment and synthesis gas separation, a set of experimental studies was carried out, including the study of equilibrium conditions (sorption isotherms) and the dynamics of the process. The following values of the sorption Dubinin–Radushkevich isotherm parameters were obtained: limiting adsorption volume $W_0 = 0,262 \text{ cm}^3/\text{g}$; parameter of the dominant micropore size $B = 2,2 \times 10^{-6} \text{ 1/K}^2$; affinity coefficients $\varphi_{O_2} = 0,65, \varphi_{H_2} = 0,15, \varphi_{N_2} = 1, \varphi_{CO_2} = 2,31, \varphi_{CO} = 0,84$; the exponent of the thermal Dubinin equation $n = 2$; molar volume $v_{O_2}^* = 0,04, v_{H_2}^* = 0,007, v_{N_2}^* = 0,06, v_{CO_2}^* = 0,04, v_{CO}^* = 0,05 \text{ cm}^3/\text{mmol}$; thermal coefficient of limiting adsorption (10^{-3}) $\chi_{O_2} = 1,7861, \chi_{H_2} = 5,1448, \chi_{N_2} = 2,1753, \chi_{CO_2} = 2,626, \chi_{CO} = 1,7372$; saturation pressure $P_{S,O_2} = 498,08, P_{S,H_2} = 620,78, P_{S,N_2} = 525,99, P_{S,CO_2} = 212,49, P_{S,CO} = 323,99 \text{ atm}$. The dynamics of the process was investigated on an experimental unit where the output curves of the gas purity at the adsorber outlet were determined depending on the input conditions: $\nu_g = 0,05 - 0,2 \text{ m/s}, P = 2 - 6 \text{ atm}$ (for air), $P = 5 - 30 \text{ atm}$ (for synthesis gas); adsorber parameters: $L = 0,2 \text{ m}, D = 0,04 \text{ m}$ (for air) and $L = 1 \text{ m}, D = 0,1 \text{ m}$ (for synthesis gas).

The *RMS* values were as follows: $RMS_{O_2} = 0,55$ vol% in the range of required purity for oxygen $y_p^{out} = 90 - 96$ vol% and $RMS_{H_2} = 0,021$ vol% in the range of required purity for hydrogen $y_p^{out} = 99,950 - 99,999$ vol%.

2. Numerical Research

The PSA model (1) – (7) is a non-isothermal mixed diffusion model (heat propagation in the gas and adsorbent, as well as internal diffusion transfer in the adsorbent is taken into account), which also considers the diffusion in the gas. Its use causes significant computational complexity when solving the optimization problem due to the need to achieve CSS [3-5]. In the case when additional assumptions are introduced into the model (1) – (7) with respect to a specific transfer mechanism, the model (1) – (7) is simplified to the options presented in Table 2 (Models 2 – 8). In this case, the model is simplified computationally, but its accuracy is reduced in comparison with Model 1.

Table 2

PSA models with various assumptions regarding the mass and heat transfer mechanisms

PSA model	Heat propagation in the gas and adsorbent	Internal diffusion transfer in the adsorbent	Diffusion in the gas
(1) – (7), model 1	yes	yes	yes
(1) – (7), model 2	yes	yes	no
(1), (2), (4) – (7) model 3	yes	no	yes
(1), (2), (4) – (7) model 4	yes	no	no
(1) – (3), (6), (7) model 5	no	yes	yes
(1) – (3), (6), (7) model 6	no	yes	no
(1) – (3), (6), (7) model 7	no	no	yes
(1) – (3), (6), (7) model 8	no	no	no

To determine the ranges of input variables, where the mass and heat transfer mechanism can be neglected, and to estimate the accuracy of simplified models, it is proposed to conduct a numerical research, which includes three computational experiments: the study of heat propagation in the gas and adsorbent, the internal diffusion transfer in the adsorbent, and the diffusion in the gas. In the course of computational experiments, the input variables P_{ads}^{in} , v_g^{in} , d_p are varied (Table 3) and calculations are carried out using Model 1.

Table 3

Manipulated variables for numerical research

Manipulated variables	Air		Synthesis gas	
	Nominal value	Variation range	Nominal value	Variation range
P^{in} , atm	4	2; 3; 4; 5; 6	15	5; 10; 15; 20; 30
v_g^{in} , m/s	0,1	0,05; 0,1; 0,2	0,1	0,05; 0,1; 0,2
d_p , 10^{-3} m	1,5	0,25; 0,5; 1; 1,5; 2; 3; 4	1,5	0,25; 0,5; 1; 1,5; 2; 3; 4

The study of heat propagation in the gas and adsorbent supposes obligatory estimation of the heating amount in the adsorbent bed for different unit productivity Gout.

When studying the internal diffusion transfer in the adsorbent, it is necessary to find the value of the adsorbent granule diameter d_p at which the main resistance to mass transfer from the external diffusion region to the internal diffusion region is shifted at different input flow rates ν_g^{in} .

When studying diffusion in the gas, it is necessary to estimate the contributions of the convective and diffusion components to the mass transfer in the gas phase.

After analyzing the obtained results and determining the ranges of the input variables, the loss of accuracy in the simplified models is calculated in comparison with Model 1:

$$\Delta = |y_{p,full}^{out}(P_{ads}^{in}, \nu_g^{in}, d_p) - y_{p,easy}^{out}(P_{ads}^{in}, \nu_g^{in}, d_p)|, \quad (11)$$

where $y_{p,full}^{out}$ is the gas purity at the adsorber outlet calculated using Model 1; $y_{p,easy}^{out}$ is the gas purity at the adsorber outlet calculated using a simplified model (Table 2, Models 2-8).

3. Results and Discussion

Based on the results of the numerical research to determine the dominant transfer mechanism in the PSA process, recommendations for calculating PSA units (the processes of air oxygen enrichment and synthesis gas separation) are presented (Table 4).

Table 4

Recommendations on the choice of the model for calculating the PSA process

No	G^{out} , l/min NTP	d_p , at mm	ν_g^{in} , m/s	Dominant transfer mechanism	Preferred model	CPU time, min	Δ , vol%	Opt time, min
Air oxygen enrichment								
1	≥ 4	≥ 2	$< 0,05$	NonIso, InDif	Model 1	10,7	0	535
2	≥ 4	≥ 2	$\geq 0,05$	NonIso, InDif	Model 2	10,6	0,024	530
3	≥ 4	< 2	$< 0,05$	NonIso, ExDif	Model 3	4,9	0,083	245
4	≥ 4	< 2	$\geq 0,05$	NonIso, ExDif	Model 4	4,8	0,095	240
5	< 4	≥ 2	$< 0,05$	Iso, InDif	Model 5	8,1	0,084	405
6	< 4	≥ 2	$\geq 0,05$	Iso, InDif	Model 6	8,0	0,097	400
7	< 4	< 2	$< 0,05$	Iso, ExDif	Model 7	3,5	0,199	175
8	< 4	< 2	$\geq 0,05$	Iso, ExDif	Model 8	3,4	0,211	170
Synthesis gas separation								
9	≥ 50	≥ 2	$< 0,05$	NonIso, InDif	Model 1	18,7	0	935
10	≥ 50	< 2	$\geq 0,05$	NonIso, InDif	Model 2	18,6	0,0012	930
11	≥ 50	≥ 2	$< 0,05$	NonIso, ExDif	Model 3	9,9	0,0072	495
12	≥ 50	< 2	$\geq 0,05$	NonIso, ExDif	Model 4	9,8	0,0086	490

G^{out} , d_p , ν_g^{in} are input variables of PSA process. NonIso means non-isothermal; Iso means isothermal; InDif means internal diffusion; ExDif means external diffusion; CPU time means time of the model calculation to the CSS mode; Opt time means approximate time for solving the problem of optimal design [22] in the case of using this model, which was obtained according to the practical calculation experience (the number of miscalculations of the PSA model to the CSS mode when solving the optimization problem is at least 50). Computer specifications are Intel Core i7-7700, DDR4 16Gb, NVIDIA GeForce GTX 1050 2Gb, Win7x64.

The study of heat propagation in the gas and adsorbent. The analysis of temperature changes in the gas and adsorbent (with the unit productivity $G^{out} = 2$ l/min at NTP) showed that the adsorbent bed heating is insignificant (less than ≈ 2 K). The calculations show that at a unit productivity $G^{out} = 4$ l/min at NTP, the adsorbent bed heating is $\approx 3, 4$ K, at $G^{out} = 10$ l/min at NTP, ≈ 5 K, and at $G^{out} = 20$ l/min at NTP, more than ≈ 8 K. It is known that when the bed is heated at 3 – 4 K, the allowance for the thermal effects of sorption in the PSA process can be neglected [8]. Therefore, when the productivity of the PSA oxygen unit is less than 4 l/min at NTP, it is expedient to use the isothermal Model 5. Note that the use of the isothermal model 5 in solving the optimal design problem of oxygen units saves at least 24,3% of the calculated time in comparison with the non-isothermal model (Table 4, cases 1, 5) with a loss of accuracy of no more than 0.084 vol%. To calculate PSA hydrogen units, the use of the isothermal Model 5 is impractical, since the heating of the adsorbent is 10 – 15 K even at the lowest unit productivity $G^{out} = 50$ l/min at NTP.

The study of internal diffusion transfer in the adsorbent. The shift of the main resistance to mass transfer from the external diffusion region to the internal diffusion one is characterized by the curves of changes in the oxygen and hydrogen concentration y_p^{out} (Figs. 1, 2). All curves clearly show a bend at a particle diameter $d_p = 2 - 3$ mm. This suggests that, in the range of adsorbent particle sizes $d_p = 2 - 3$ mm, the effect of transfer mechanisms by external and internal mass transfer diffusion is comparable. At $d_p < 2$ mm, the value of the mass transfer coefficient β increases sharply, and the internal diffusion resistance decreases (characterized by the duration t_L of the granule saturation with the extracted component); the process of external mass transfer acquires the limiting influence, and the diffusion process in granules can be ignored. At $d_p > 3$ mm, the value of the mass transfer coefficient β decreases, and the internal diffusion resistance increases sharply; the diffusion process in the adsorbent granules acquires the limiting influence.

The intensification of the mass transfer process can be provided by reducing the size of the adsorbent granules d_p , however, at the same time, the pressure drop ΔP in the adsorbent bed increases (7), which significantly reduces the dynamic capacity of the adsorbent (calculated by the Dubinin–Radushkevich equation).

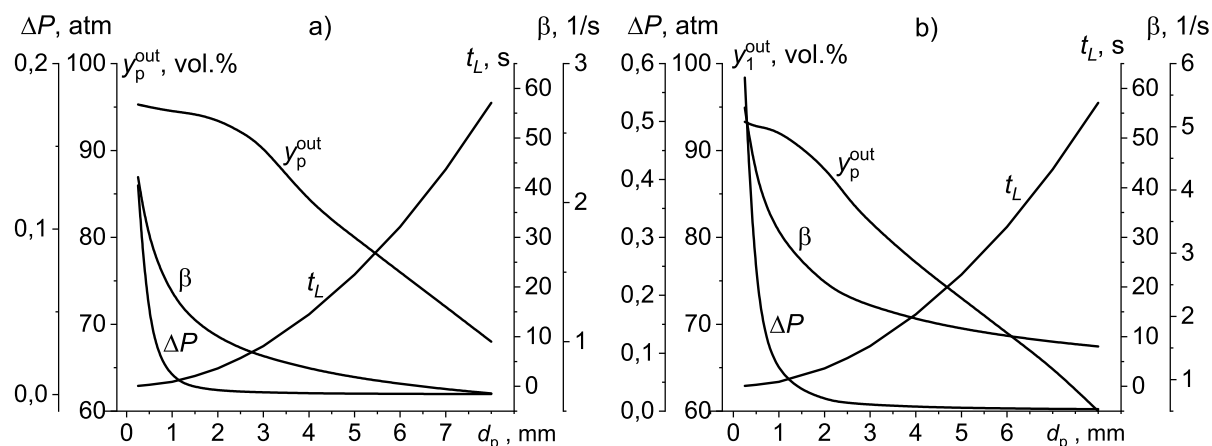


Fig 1. Dependence of oxygen purity y_p^{out} , pressure drop in the adsorbent bed ΔP , external mass transfer coefficient β and saturation time of the adsorbent granule t_L in its center on the granule diameter d_p at the input flow rate ν_g^{in} : a) 0,05 m/s; b) 0,2 m/s

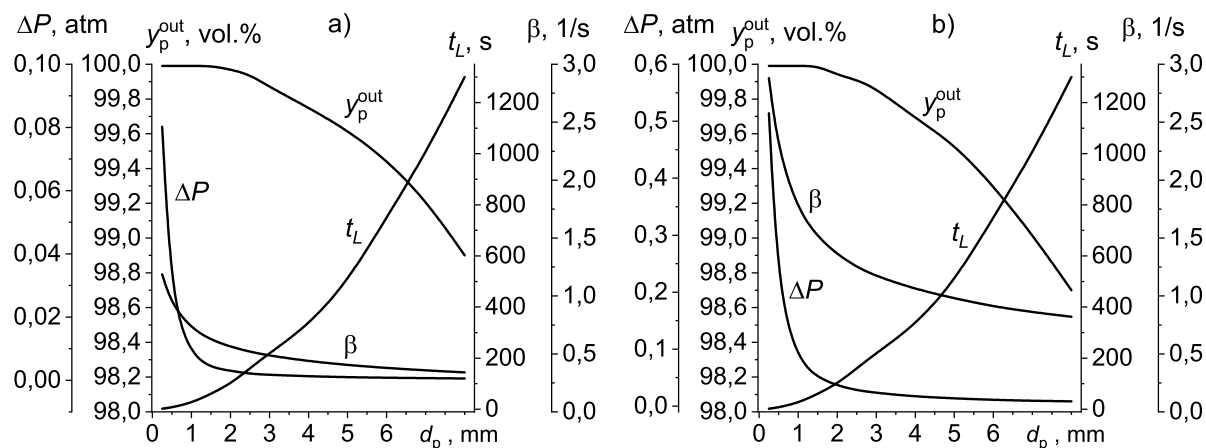


Fig 2. Dependence of hydrogen purity y_p^{out} , pressure drop in the adsorbent bed ΔP , external mass transfer coefficient β and saturation time of the adsorbent granule t_L in its center on the granule diameter d_p at the input flow rate v_g^{in} : a) 0,05 m/s; b) 0,2 m/s

Note that the use of the external diffusion Model 3 in solving the optimal design problem saves at least 54,2% of the calculation time for oxygen units and at least 47,1% of the calculation time for hydrogen units with a loss of accuracy of no more than 0,083 vol% and no more than 0,0072 vol% , respectively (Table 4, cases 1, 3 and Table 4, cases 9, 11).

The study of diffusion in the gas phase. According to Equation (1), the transfer of components in the gas phase occurs due to longitudinal diffusion Dg and convection (term 3). The results of the performed numerical analysis showed that at a gas flow rate of more than 0,05 m/s, longitudinal mixing can be neglected (the contributions of longitudinal mixing and convective components differ by more than an order of magnitude).

Conclusions

We develop the mathematical model of the PSA process considering the heat effects of sorption, external and internal diffusion mechanisms of adsorptive transfer from the gas to the adsorbent (for air oxygen enrichment and synthesis gas separation) and providing high accuracy of calculations ($RMS_{O_2} = 0,55$ vol% in the range of required purity for oxygen $y_p^{out} = 90 - 96$ vol% and $RMS_{H_2} = 0,021$ vol% in the range of the required purity for hydrogen $y_p^{out} = 99,950 - 99,999$ vol%). The numerical research was carried out to calculate PSA oxygen units. It was found that with a capacity of less than 4 l/min at NTP, it is advisable to use an isothermal model, which saves at least 24,3% of the calculated time with a loss of accuracy of no more than 0,084 vol%. To calculate PSA hydrogen units, it is impractical to use the isothermal model even at the lowest productivity of 50 l/min at NTP. When the diameter of the adsorbent particles is less than 2 mm, it is advisable to use an external diffusion model, which saves at least 54,2% of the calculated time for oxygen units and at least 47,1% of the calculated time for hydrogen units with a loss of accuracy of no more than 0,083 vol% and no more than 0,0072 vol%, respectively. At a gas flow rate of more than 0,05 m/s, the model can ignore the diffusion in the gas.

Based on the research results, we give recommendations on the use of the preferred PSA model in terms of its accuracy and calculation time. The research results can be used to calculate various PSA and gas mixture processes: rPSA, ultra rPSA, VSA, VPSA, and related processes.

Acknowledgments. *This research was supported by the Ministry of Science and Higher Education of the Russian Federation within the President Grant MK-1604.2020.8.*

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Received February 2, 2021

УДК 661.935+519.633.2

DOI: 10.14529/mmp210204

**ЧИСЛЕННОЕ ИССЛЕДОВАНИЕ ДЛЯ ОПРЕДЕЛЕНИЯ
ПРЕОБЛАДАЮЩЕГО МЕХАНИЗМА МАССО- И ТЕПЛОПЕРЕНОСА
В ПРОЦЕССАХ КОРОТКОЦИКЛОВОЙ БЕЗНАГРЕВНОЙ
АДСОРБЦИИ**

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В существующих математических моделях короткоциклового безнагревной адсорбции (КБА) применяются различные допущения относительно учета механизмов массо-

и теплопереноса в системе «газовая смесь-адсорбент». Увеличение количества допущений приводит к упрощению модели, снижению времени просчета одной итерации модели и одновременно к снижению ее точности. Упрощение модели особенно важно в процессах КБА, поскольку расчет модели осуществляется до циклически устойчивого состояния и составляет десятки и даже сотни циклов (итераций). Обеспечение высокой точности модели КБА и ее минимальной сложности является противоречивым требованием, поэтому важно обоснованно учитывать в модели только те механизмы переноса, которые являются преобладающими. В работе предложена математическая модель процесса КБА, которая учитывает тепловые эффекты сорбции, внешнедиффузионный и внутридиффузионный механизмы переноса адсорбтива. Проведено численное исследование для определения преобладающего механизма переноса и предложены рекомендации по использованию предпочтительной модели КБА с точки зрения ее точности и времени просчета (для процессов обогащения воздуха кислородом и разделения синтез-газа). Установлено, что для расчетов кислородных установок КБА производительностью менее 4 нл/мин целесообразно использовать изотермическую модель, что позволит сэкономить не менее 24,3% расчетного времени при потере точности не более 0,084 об.%. Для расчетов водородных установок КБА использование изотермической модели является нецелесообразным даже при наименьшей производительности 50 нл/мин. При диаметре частиц адсорбента менее 2 мм целесообразно использовать внешнедиффузионную модель, что позволит сэкономить не менее 54,2% расчетного времени для кислородных установок и не менее 47,1% расчетного времени для водородных установок при незначительной потере точности. При скорости газового потока более 0,05 м/с диффузию в газе в модели можно не учитывать. Результаты исследований могут быть использованы для расчета различных процессов КБА разделения газовых смесей: rPSA, ultra rPSA, VSA, VPSA, а также смежных процессов.

Ключевые слова: короткоцикловая безнагревная адсорбция; математическое моделирование; численное исследование; водород; кислород.

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Поступила в редакцию 2 февраля 2021 г.