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Development of a mathematical model of molecular-selective gas transfer in a hybrid membrane-adsorption oxygen concentrator

A A Tishin¹ and V N Gurkin²

¹National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), Kashirskoe shosse 31, Moscow, Russia, 115409

²Dmitry Mendeleev University of Chemical Technology of Russia, Miusskaya sq. 9, Moscow, Russia, 125047

e-mail: alexzfrai@gmail.com

Abstract. Most modern oxygen concentrators use sorption air separation technology. The development of a hybrid membrane-sorption separation technology can improve the energy efficiency of the process. The paper considers a mathematical model of molecular-selective gas transfer in a hybrid oxygen concentrator consisting of adsorption and membrane units combined into a circulation loop. The considered hybrid model has based on a model of equilibrium isothermal sorption with linear isotherms without longitudinal mixing for numerical calculation of the adsorption unit of the system and a model of ideal displacement in the high-pressure cavity with perpendicular outflow in the low-pressure cavity to calculate the system membrane unit. In the course of the study, the high adequacy of the model was obtained with an experiment in the range of oxygen concentrations up to 90%, and a comparison was made with previously obtained results. A new model has been proposed that can take into account the equalization and countercurrent blowing stages.

1. Introduction

Currently, the development of a hybrid gas separation technology based on membrane and adsorption technologies is receiving considerable attention [1–4]. For the first time, the hybrid membrane-adsorption technology was applied at the beginning of the 21st century to release hydrogen, helium and carbon dioxide from gas mixtures of petrochemistry and biotechnology [1, 5]. Later, methods were developed for the separation of multicomponent gas mixtures containing these gases [6]. In addition to applications in petrochemistry, hybrid separation technologies have great prospects in the separation of air into components [7].

The current state of the air separation industry distinguishes three main methods for producing air components: membrane, adsorption and cryogenic [8]. Each of the methods has its field of application; a cryogenic method is used to produce large volumes of pure and high-purity components, which allows obtaining significant amounts of air separation products in liquid form. An adsorption separation method with low capital and operating costs are used to produce medium volumes of oxygen (from 15 to 1000 m³/h [8]) and nitrogen. To obtain small volumes of high-purity nitrogen and oxygen of medium concentrations (up to 50%), the membrane method is used, which is the most compact and mobile method [9, 10].



Based on hybrid technologies, oxygen concentrators are being actively developed and explored. Modern oxygen concentrators, most often, work on membrane or adsorption air separation technology. The first is used in portable and compact concentrators, used most often in rehabilitation outside hospitals, due to the low purity of the oxygen produced (35%). Based on the second developed many concentrators and systems suitable for obtaining oxygen from the air [11, 12]. Adsorption technology of air separation allows achieving oxygen purity up to 93 % [13]. The adsorption method is based on the Skarstrom's scheme PSA (pressure swing adsorption) [14], shown in Figure 1, consisting of two adsorbers cycling through the filling, adsorption and desorption stages (Figure 2). Modern oxygen concentrators often have three or more adsorbers [13].

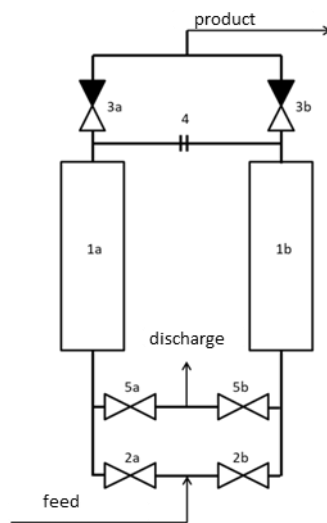


Figure 1. The scheme of the adsorption unit for air separation method Skarstrom [14].

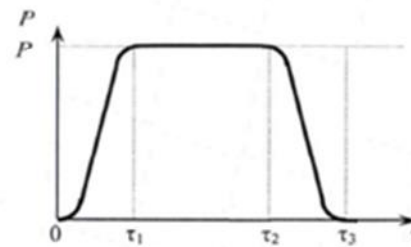


Figure 2. The cyclograms of the work of the adsorbers of the oxygen concentrator to the scheme: filling, displacement, desorption.

The developed air separation technology by the membrane-adsorption method includes two units, adsorption, and membrane. The use of two methods of separation allows you to achieve increased energy efficiency of air separation, by leveling the shortcomings of each of the methods by advantages of the second method. Since modern adsorption systems are technically complex devices, to develop and design a hybrid system that includes the adsorption part, it is necessary to carry out a numerical calculation of the system to determine the main performance characteristics of the adsorption unit. For this, it is necessary to develop a mathematical model of molecular-selective gas transfer in a hybrid membrane-adsorption system.

2. Theoretical analysis

To calculate the adsorption stage of the system, it is supposed to use a mathematical model of equilibrium isothermal sorption with linear isotherms without longitudinal mixing [2]. In the framework of the mathematical model used, we will assume the following [15]: 1) isotherms are linear without hysteresis, there are no nonlinear effects (volumetric sorption), the adsorption branch coincides with the desorption; 2) adsorption and desorption are fast, their durations can be neglected; 3) the pressure and temperature of the gas in the adsorber, the temperature of the adsorbent, and the concentration of nitrogen in the gas phase and the solid phase change only in the longitudinal direction of the adsorber; 4) the volume of the adsorbent consists of elementary layers within which the concentration of nitrogen and oxygen and the temperature are constant; 5) gaseous nitrogen and oxygen have the properties of ideal gases; 6) the components are sorbed independently, with

probabilities proportional to Henry's constants; 7) adsorption proceeds with the formation of a sharp stationary front.

2.1. Model of adsorption unit of the system

Consider the scheme [14] as an adsorption unit for an oxygen concentrator, with a cyclogram (Figure 2) consisting of the filling, displacement, and discharge stages. At the first moment, desorption takes place in the adsorber by reducing the pressure from the adsorption pressure P_{ads} to the desorption pressure P_{des} . Upon reaching the desorption pressure in the adsorber, the filling with the stream supplied to the inlet from the compressor begins. For an oxygen concentrator, the feed stream – atmospheric air can be considered as a binary mixture of nitrogen and oxygen, since the properties of argon, situated in the air in small quantities, are close to those of oxygen [16]. Thus, air with molar concentrations of the feed stream components C_{Fi}^{psa} (1 – oxygen, 2 – nitrogen) is supplied to the input of the adsorption unit. When the adsorption pressure is reached in the adsorber, the stage of production begins – the gas enriched in oxygen is displaced from the adsorber by the feed flow at a constant pressure. The processes occurring in the adsorbers at each stage of the cyclogram can be represented as follows.

Desorption. At the initial time, the adsorber is filled with a mixture of feed under adsorption pressure p_{ads} . The final state of the adsorber is the discharge of the mixture to the desorption pressure p_{des} into the external volume. Imagine the gas content of the adsorber as [15]:

$$k_i = \varepsilon + \sigma_i(1 - \varepsilon), \quad (1)$$

where ε is the porosity of the adsorber, σ_i is the constants of the linear adsorption isotherm (Henry).

Then the material balances of the substance in the adsorber at the stage of desorption and the balance of molar concentrations in equilibrium with the external volume will take the form [2]:

$$k_i C_{Fi}^p V = k_i C_{Wi}^p V + C_{Wi}^p W_p, \quad (2)$$

$$\frac{C_{F1}^p + C_{F2}^p}{C_{W1}^p + C_{W2}^p} = \frac{p_{ads}}{p_{des}}. \quad (3)$$

Using equations (2) and (3), it is easy to obtain the concentration values of the gas components at the end of the desorption stage (C_{Wi}^p) and the flow of the gas released in the process (W_p).

Filling. The filling is carried out by the feed flow F'_p from the compressor from the pressure p_{des} to the pressure p_{ads} , then the material balance of the substance at the stage and the ratio of concentrations are as follows:

$$k_i C_{Wi}^p V + C_{Fi}^p F'_p = k_i C_{Pi}^p V, \quad (4)$$

$$\frac{C_{W1}^p + C_{W2}^p}{C_{P1}^p + C_{P2}^p} = \frac{p_{des}}{p_{ads}}. \quad (5)$$

Equations (4) and (5) allow us to calculate the values of the concentrations of the components at the end of the filling stage (C_{Pi}^p) and the part of the feed flow of the adsorption unit going to filling the adsorber (F'_p).

Displacement. The displacement step takes place at a constant adsorption pressure p_{ads} . For concentrations, the equality is true:

$$C_{P1}^p + C_{P2}^p = C_{F1}^p + C_{F2}^p. \quad (6)$$

The material balance of the substance entering and leaving the adsorber can be represented as:

$$k_i C_{pi}^p V + C_{Fi}^p F_p'' = C_{pi}^p P_p + k_i C_{Fi}^p V. \quad (7)$$

The displacement occurs by the flow of the compressor F_p'' supplied to the input of the adsorber, while at the outlet of the adsorber the production of the target flow P_p occurs, with concentrations of components C_{p1}^p and C_{p2}^p . The total feed flow of an adsorption unit of a system is defined as the sum of the flows supplied at the filling and displacement stages:

$$F_p = F_p'' + F_p'. \quad (8)$$

The system of equations (1) - (8) allows to calculate fully the adsorption block of the hybrid membrane adsorption system and to determine the efficiency of its energy consumption defined as the value of the relative selection (ψ_p) and the degree of extraction (φ):

$$\psi_p = \frac{P_p}{F_p}, \quad (9)$$

$$\varphi = 1 - \frac{x_{W1}^p W_p}{x_{F1}^p F_p}. \quad (10)$$

In [2, 15], a hybrid system for air separation using recirculation and two-stage filling with refilling was considered. The cyclogram of the process includes the following stages (Fig. 3): desorption, initial filling, refilling, and displacement. The peculiarity of this scheme is the use of a part of the product flow of the adsorption unit for the initial filling of the adsorber (G_p) to the intermediate pressure p_{int} . An alternative way to organize the initial filling is to use part of the retentate flow of the membrane unit of the system (G_m).

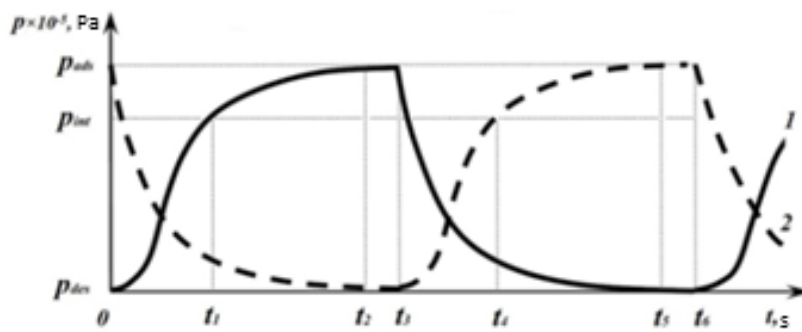


Figure 3. Cyclogram of adsorption unit: desorption, initial filling, filling, displacement [15].

Material balance of the initial filling stage using part of the product flow:

$$k_i C_{Wi}^p V + C_{Pi}^p G_p = k_i C_{Ni}^p V, \quad (11)$$

$$\frac{C_{W1}^p + C_{W2}^p}{C_{N1}^p + C_{N2}^p} = \frac{p_{des}}{p_{int}}, \quad (12)$$

where C_{Ni}^p is the concentration of components after the initial filling of the adsorbers to the intermediate pressure p_{int} with the product stream of the adsorption unit G_p .

The combination of equations (1) - (12) makes it possible to calculate the hybrid system [15] taking into account the bypass of the product flow of the system and allows to achieve higher concentrations of the product flow than the Skarstrom system [14].

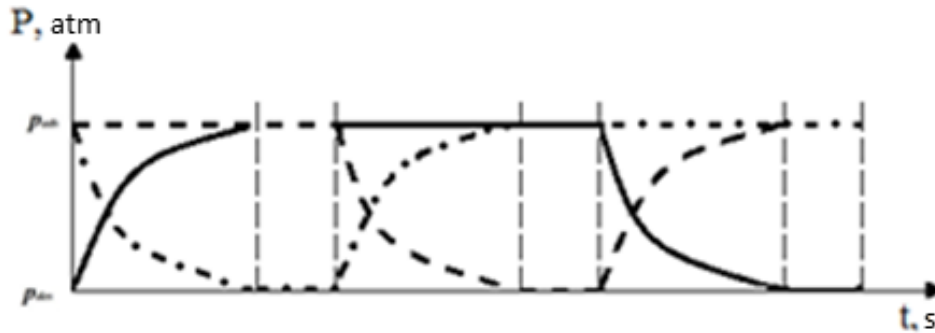


Figure 4. Cyclogram: equalization filling, filling, displacement, equalization discharge, discharge into the atmosphere, countercurrent blowdown [4].

The most promising for the introduction of additional stages of the cyclogram of the adsorption unit of the system are countercurrent blowing and equalization stage [7]. The cyclogram of the work of the adsorption unit of the hybrid system will take the form [4], shown in figure 4 and consists of the stages: discharge by equalization, discharge into the atmosphere, regeneration by counter-current blowing, filling by equalization, refilling by feed flow, displacement. Then the processes occurring inside the adsorbers at the stage of equalization can be described by the following equations:

$$k_i C_{Fi}^p V = k_i C_{Gi}^p V + C_{Gi}^p G_p, \quad (13)$$

$$\frac{C_{F1}^p + C_{F2}^p}{C_{G1}^p + C_{G2}^p} = \frac{p_{ads}}{p_{int}}, \quad (14)$$

$$k_i C_{Ni}^p V + C_{Gi}^p G_p = k_i C_{Gi}^p V, \quad (15)$$

$$\frac{C_{N1}^p + C_{N2}^p}{C_{G1}^p + C_{G2}^p} = \frac{p_{des}}{p_{int}}. \quad (16)$$

The pressure p_{int} is the equilibrium pressure reached in the adsorber passing through the discharge stage by pressure equalization p_{ads} of equation (13), (14) and pressure in the adsorber passing through the pressure equalization stage p_{des} of equation (15), (16). The flow G_p corresponds to the gas flow that has passed from one adsorber to another and the concentrations C_{Gi}^p to steady-state equilibrium concentrations. The initial concentration of components at the stage of equalization C_{Ni}^p in equations (15), (16) corresponds to the concentration obtained as a result of the countercurrent blow described by the following equations:

$$k_i C_{Wi}^p V + C_{Pi}^p P_p^p = C_{Wi}^p W_p^p + k_i C_{Pi}^p V, \quad (17)$$

$$C_{W1}^p + C_{W2}^p = C_{P1}^p + C_{P2}^p, \quad (18)$$

where the countercurrent blow is carried out by part of the product stream P_p^p of the adsorption unit of the system, and the stream W_p^p is released into the atmosphere.

System of equations (1)-(8), (13)-(18) allows you to fully calculate the adsorption unit of a hybrid oxygen concentrator. In this case, by analogy with the initial filling of the adsorber with a part of the retentate of membrane unit proposed in [15], countercurrent blowing can also be carried out with the retentate of membrane unit.

2.2. Model of membrane unit of the system

To calculate the membrane unit, we use the equations describing the separation of a gas mixture with a perpendicular outflow in a low-pressure cavity and the assumption of ideal displacement in a high-pressure cavity [2]:

$$\frac{dZ_i}{ds} = Q_i \left(x_{hi}^m - \frac{p_l}{p_h} x_{li}^m \right), 0 \leq s \leq S \quad (19)$$

$$x_{hi}^m = \frac{Z_i}{q_{hi}}, \quad (20)$$

$$q_{hi} = \sum_{j=1}^2 Z_j, \quad (21)$$

$$x_{li}^m = \frac{Q_i \left(x_{hi}^m - \frac{p_l}{p_h} x_{li}^m \right)}{\sum_{j=1}^2 Q_j \left(x_{hj}^m - \frac{p_l}{p_h} x_{lj}^m \right)}. \quad (22)$$

The boundary conditions for the integration along the length of the module:

$$Z_i(0) = F_m x_{Fi}^m. \quad (23)$$

By integrating equation (19), it is possible to obtain the concentration in the retentate stream x_{Ri}^m and the separation ratio of the flow θ required to determine to permeate P_m and retentate R_m of the membrane unit:

$$P_m = \theta F_m, \quad (24)$$

$$R_m = (1 - \theta) F_m, \quad (25)$$

Thus, using equations (1) - (8), (11) - (25) with allowance for simplifications and approximations, it is possible to carry out a numerical calculation of the membrane-adsorption oxygen concentrator suitable for designing a concentrator.

3. The results of numerical simulation

Approbation of the mathematical model was carried out in two stages, at the first stage, the calculation of the adsorption unit of the system with different variants of the cyclogram was carried out. In the second stage, the hybrid membrane-adsorption system was calculated and compared with experimental data.

To transfer molar concentrations to the molar fractions and the flows to the molar flows use the formula:

$$C = \frac{xp}{RT'} \quad (26)$$

$$Y_F = F_p \frac{p_{ads}}{RT}, \quad (27)$$

where R is the universal gas constant, and T is the process temperature.

Table 1 presents the characteristics of the adsorption unit of a hybrid oxygen concentrator operating on the Skarstrom cyclogram [14] depending on the pressure p_{ads} for various pressures p_{des} . The following parameters are set as initial conditions for the process calculation: p_{ads} , p_{des} , V , C_{F1}^p , C_{F2}^p , σ_i , ε .

Table 1. The dependence of the flows and oxygen concentrations in them for the adsorption unit [14] of the system on the adsorption pressure p_{ads} for various desorption pressures p_{des} .

p_{ads} , atm	p_{des} , atm	Y_F , mol/s	Y_P , mol/s	ψ_p	φ	x_{P1}^p , mol.fr.	x_{W1}^p , mol.fr.
6	0.1	4.68	1.747	0.373	0.725	0.408	0.092
	1	4.198		0.416	0.716	0.361	0.102
	2	3.671		0.476	0.711	0.314	0.116
	3	3.157		0.553	0.718	0.273	0.132
	4	2.661		0.656	0.749	0.24	0.153
	5	2.189		0.798	0.828	0.218	0.179
4	0.1	3.102	1.165	0.375	0.724	0.405	0.093
	1	2.622		0.444	0.713	0.337	0.109
	2	2.105		0.553	0.718	0.273	0.132
	3	1.615		0.721	0.781	0.227	0.165
2	0.1	1.524	0.582	0.382	0.722	0.397	0.094
	1	1.052		0.553	0.718	0.273	0.132
1	0.1	0.735	0.291	0.396	0.719	0.381	0.098

Table 1 shows that the regeneration of the sorbent at atmospheric pressure by reducing the pressure from p_{ads} to p_{des} is insufficient to obtain oxygen concentrations above 36 %, which significantly limits its applicability and is consistent with the theory [13].

Table 2 presents the characteristics of the adsorption unit operating on a cyclogram [15], at a pressure of $p_{ads} = 6$ atm, depending on the desorption pressure p_{des} for different pressures p_{int} .

When using a combined filling, the oxygen concentration in the x_{P1}^p feed increases with the p_{int} filling pressure, while the relative selection ψ_p and the extraction coefficient φ decrease.

Figure 5 shows the dependence of the oxygen concentration in the product flow of the hybrid membrane-adsorption system on the pressure of the product flow and the oxygen concentration in the flow coming out of the adsorption unit, obtained as a result of the calculation.

It is seen that with increasing oxygen concentration in the flow of the product of the adsorption unit, the efficiency of the membrane decreases with a large pressure drop, and slightly increases with a small differential. The maximum concentration increase on the membrane unit of the system, about 17%, is observed at pressures of 2–3 atm and oxygen concentration in the unit's feed flow of 30–36%.

Table 2. The dependence of the flows and oxygen concentrations in them for the adsorption unit [15] of the system on the desorption pressure p_{des} for different pressures p_{int} at $p_{ads} = 6$ atm.

p_{des} , atm	p_{int} , atm	Y_F , mol/s	Y_P , mol/s	Y_G , mol/s	ψ_p	φ	x_{P1}^p , mol.fr.	x_{W1}^p , mol.fr.
1	1	4.198		0	0.416	0.716	0.361	
	2	3.852		0.115	0.424	0.69	0.399	
	3	3.541		0.328	0.401	0.663	0.452	
	4	3.279		0.612	0.346	0.636	0.529	0.102
	5	3.076		0.935	0.264	0.612	0.633	
	6	2.929		1.269	0.163	0.593	0.763	
2	2	3.671	1.747	0	0.476	0.711	0.314	
	3	3.304		0.183	0.473	0.679	0.341	
	4	2.969		0.468	0.431	0.643	0.384	0.116
	5	2.683		0.823	0.344	0.605	0.449	
	6	2.465		1.206	0.219	0.57	0.546	
4	4	2.661		0	0.656	0.749	0.24	
	5	2.255		0.338	0.625	0.704	0.249	0.153
	6	1.864		0.797	0.509	0.642	0.265	

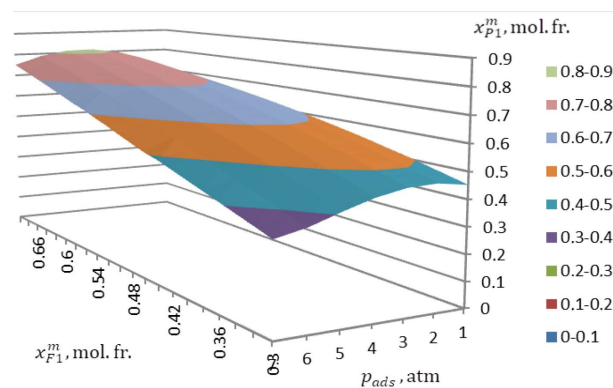


Figure 5. Three-dimensional plot of the oxygen concentration in the product stream of the hybrid system x_{P1}^m from pressure p_{ads} and oxygen concentration in the feed flow of membrane unit x_{F1}^m (numerical).

More accurate results can be achieved using other models of separation on the membrane module, but comparing the data obtained with the results of the calculation of the adsorption block in the assumptions [15] and experimental data obtained earlier [7], it is clear that the deviations are not more than 5 %. Figure 6 shows the dependences of oxygen concentrations in the product flow of the system for various values of filling pressure obtained as a result of experiments [7], numerical calculations using the model proposed in [15] for the adsorption unit of the hybrid system and numerical calculation of the hybrid system when the adsorbers are filled with a membrane retentate flow block.

Thus, since the calculation carried out according to the model based on equations (1) - (12), (19) - (25) with a cyclogram consisting of reset, initial filling, refilling and displacement, coincides with the experimental data obtained during operation hybrid system with this cyclogram and has a deviation of less than 5%, then the proposed model for calculating hybrid systems based on equations (1) - (8), (13) - (25) can be used to calculate and design hybrid systems with a more complex cyclogram, including equalization and countercurrent blowing stages.

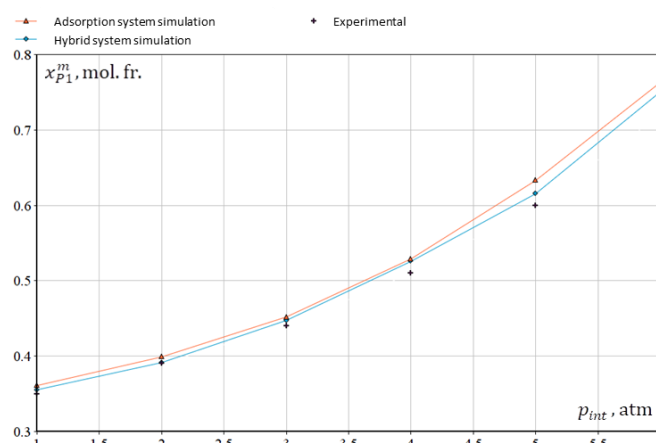


Figure 6. Dependencies of oxygen concentration x_{p1}^m in the product flow of the system on refilling pressure p_{int} for the adsorption system (numerical), hybrid system (numerical) and hybrid system (experimental).

4. Conclusion

The paper proposes a mathematical model of the hybrid membrane adsorption system. The model of equilibrium isothermal adsorption with linear isotherms without longitudinal mixing was used for the adsorption block of the system. For the membrane unit of the system, a model of ideal mixing in the high-pressure cavity with perpendicular outflow in the low-pressure cavity was used. The simulation of a system with a simplified sequence diagram of the work, consisting of the stages of discharge, initial filling, refilling, and displacement, has shown its effectiveness and high convergence with the results of experimental studies. The deviation of the numerical data from the experimental data was less than 5%. In the future, the proposed model can be used for the calculation and design of hybrid systems for oxygen enrichment of air, working on more complex cyclograms, including the stages of countercurrent blowing and equalization.

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