Investigation of the three-adsorber scheme used in the hybrid membrane-sorption system

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Abstract. Investigation of the three-adsorber scheme used in the hybrid membrane-sorption system was carried out. The three-adsorber scheme allows to obtain enriched with oxygen system’s product flow up to 70% without using additional devices and methods of sorbent regeneration on the PSA stage. It should be noticed, that it is impossible to reach similar oxygen concentration in the product flow without using proposed organization of the system’s flows. These conditions allow system to enter stationary mode much faster. The ways of system improvement for obtaining oxygen concentration higher than 90% are proposed in this work. Such systems will find a use in industrial air separation to the components, in development of mobile and compact energy-efficient gas separation systems based on hybrid membrane-sorption technologies, oxygen generators which are suitable for feed of artificial lung ventilation devices, oxygen concentrators for rehabilitation during post-surgery period and also for the prevention of various diseases including cardiovascular diseases. Furthermore, such hybrid systems have a potential of application in industrial gas drying as well as natural gas drying.

1. Introduction

Nowadays the main methods of oxygen and nitrogen industrial obtaining are: rectification, membrane and sorption. The choice of the method is usually determined by the required product purity and the required productivity. Operation principle of the low-temperature rectification method is in the difference between liquefaction temperatures of the air components. The method of low-temperature rectification provides a production of tons of pure air components: nitrogen, oxygen, argon, helium. The advantages of rectification are: the possibility of obtaining high-purity products, the reliability of equipment, the possibility of obtaining simultaneously several products of separation in the liquid and gas phases. However, the method has a number of significant drawbacks: high capital and operating costs, low profitability at small and medium production volumes, the mass and dimensions parameters of installations, the complexity of hardware and the long start-up period. The principle of the membrane separation method consists in the selective penetration of air mixture components through the membrane surface. Advantages of the membrane method are: small dimensions and time to start the operating mode, simplicity of design and maintenance, high selectivity, quick start and stop. The shortcomings include: the complexity of obtaining high purity oxygen (the maximum achievable concentration of oxygen in the product gas mixture is 50% of volume), low productivity, high energy costs when using recirculation schemes. A short-cycle, non-heated adsorption with variable pressure...
(PSA) is most often used as the sorption method for air separation. In this method the separation is carried out due to the difference in the sorption capacities of the sorbent at various pressures and the alternation of the stages of adsorption and desorption in special tanks - adsorbers. The main advantages of the PSA method are: low capital costs, a long period of non-stop operation, ease of operation, quick start-up, high productivity and enrichment level, and the main disadvantage is low extraction degree and also there is the need to remove sorbent abrasion products from the product flow. Developed membrane and sorption systems for the air separation are now widely used in the oil and gas industry, in the chemical, metallurgical and other industries, as well as in medicine.

Recently, special interest has been given to hybrid air separation systems. Systems possessing the advantages of several methods, as: membrane and adsorption, membrane and cryogenic, adsorption and cryogenic at the same time, due to mutual compensation of the shortcomings of each method separately, have a rather high potential in industry and medicine. With the example of membrane adsorption systems, hybridization allows one to get rid of the drawbacks of both membrane and adsorption methods due to the optimal combination of the advantages of each separation method: ease of implementation and high recovery for membrane and high enrichment for adsorption.

The use of hybrid membrane-adsorption gas separation systems allows to reduce significantly the energy consumption of the plants [1], and also to level off such disadvantages as contamination of the product flow by the products of abrasion of sorbents, through the use of a high-selective polymeric membrane, and the restriction on the oxygen concentration using a single membrane stage after the adsorption stage. Thus, the hybrid membrane-adsorption system is capable of solving effectively the problem of air separation into components.

In addition, it is possible to create mobile and compact gas separation systems on the basis of hybrid membrane-sorption systems, including oxygen generators suitable for feeding artificial respiration apparatus and oxygen concentrators for use during the post-surgery period, as well as for the prevention of various diseases as well as cardiovascular diseases. Hybrid systems also have the potential to be used in industrial gases drying, including natural gas.

2. Statement of the problem
Nowadays, the practical interest is in the creation of portable oxygen generator suitable for feeding of respiratory medical devices based on hybrid membrane-adsorption gas separation systems.

However, at the present time, the most complete and general model and methodology for calculating and constructing of hybrid membrane-adsorption systems does not exist. First of all, it’s connected to the complexity of the adsorption and membrane stages matching, as well as to the choice of sorbent and the method of operation of the adsorption stage. Requirements for sorbent are: high selectivity for pair nitrogen / oxygen, high durability and nitrogen sorption capacity. Researches [2, 3] have shown that zeolites of A and X groups, as well as their derivatives, are the most suitable sorbents for these parameters.

A scheme (Fig. 1) of a hybrid membrane-sorption system for effective air separation into components was proposed in [4]. The present work is devoted to experimental research of the separation characteristics of the developed hybrid scheme, its effective work area is shown, and experimental studies of air enrichment with oxygen are carried out. Experimental studies were carried out on a sample of a hybrid system, the pneumatic scheme of the system is shown in Fig. 1.

The work of the hybrid system is organized in a certain way. Compressor 1 supplies the compressed gas to one of the adsorbers 3-5, for example, to the adsorber A, through the filter system 7 and the mixing ejector 2. The solenoid valves 10 and 11 are closed, the valve 9 is open. The pressure in the adsorber 3 is kept constant, the gas injected by the compressor 1 through the valve 9 is pumped through the adsorber where the gas mixture is enriched with oxygen and through the valve 18 enters the membrane module 6 and filling adsorber B. The separation of the flow pumped through the adsorber A is realized by regulating valves 22 and 23, the valve 22 passes through itself a flow directed to fill the adsorber B through the open valve 16, while the valves 15 and 17 are closed, and the valve 23 serves to supply the oxygen-enriched gas in the membrane module 6, through the flowing
Surge vessel 25. Simultaneously, regeneration of the sorbent at atmospheric pressure occurs in the adsorber C, the valve 14 is opened and the gas is discharged into the atmosphere, while nitrogen desorption takes place on the sorbent. This operation of the PSA unit continues until the pressure in the adsorption unit B reaches the operating pressure of the system, then the adsorbers change in their functions: A - regeneration, B - pumping, C - filling. The gas which supplied to the membrane module 6 is also divided into the product gas that has passed through the membrane, which bypasses the second flowing surge vessel 26 through the control valve 8 and then supplied to the consumer, and into the waste gas low-enriched with oxygen which is fed through the valve 21 to the ejector where it mixes with the PSA flow of the stage. Thus, the system provides a stable product flow with a constant concentration at high pressure values up to 6-8 atm. The operating pressure of the PSA stage for switching of the adsorber functions is equal to 8 atm.

![Diagram](image)

**Figure 1.** Principal scheme of hybrid membrane-adsorption device.

Features of the developed hybrid system:

- A mixing ejector is used for the waste flow recycling of the membrane module, which allows mixing the oxygen-depleted flow on the membrane stage with the feed flow of the PSA stage;
- The filling of the adsorber up to the operating pressure is organized by a part of the product flow of the adsorber passing the displacement stage;
- The membrane module is fed by a part of the adsorbers product flow of the PSA stage.

Above mentioned features make it possible to increase the energy efficiency of the hybrid membrane-sorption system in comparison with hybrid analogs [3] and individual methods in common. The proposed hybrid system consists of two drying stages. At the first stage of the system, the three-
adsorption PSA system is used as the main drying block. The second stage used a closed-type membrane steam separator. The main feature of the proposed hybrid system is the use of the flow the dried by membrane steam separator to regenerate the sorbent on the PSA stage of the system. This scheme allows solving the problem of the return of the product flow of the PSA system for the regeneration of the sorbent.

3. Results and discussion
The main feature of the proposed hybrid membrane-sorption system is in the particular approach to the organization of the PSA system stage operation. The operation scheme of the stage is shown in Fig. 2.

![Figure 2. Operation scheme of the PSA stage of the hybrid membrane-sorption system.](image1)

![Figure 3. Operation scheme of the PSA stage of the system with countercurrent expulsion and compensation stage.](image2)

The adsorbers and the valve system are presented on the scheme, the adsorber in position A always passes the expulsion stage, the adsorber in position B passes the filling stage, and the adsorber C – the stage of discharge. The valve marked 1 are opened, 2 – closed. Adsorbers imaginary move in a counterclockwise direction, changing its functions, while the valve opening scheme is maintained. The adsorber B is filled with a part of the product flow from adsorber A, the rest of the product flow is withdrawn from the PSA stage. The regeneration of the adsorber C is carried out at atmospheric pressure by venting of gas into the atmosphere. The balance equation for this PSA stage is:

\[ F' = P' + W', \]

where \( F' \) - feed flow, supplied by compressor to the PSA stage, \( P' \) is the product flow of the PSA stage, supplied to the membrane stage of the system, \( W' \) - the waste flow of the PSA stage, which excluded from the system in a whole.

On the model sample of a hybrid membrane-sorption system developed according to the scheme (Figure 1), the PSA stage of which operates according to the scheme presented in Fig. 2, experimental researches of the hybrid system were carried out.

During the experiments the following parameters were maintained in the system: working pressure of the PSA stage of the system was 8 atm., pressure of sorbent regeneration was 1 atm., full cycle duration – 60 seconds, cycle time of one adsorber work (N) – 20 seconds, which corresponds to a third of the cycle, the pressure of the product flow of the PSA stage – 8 atm., pressure of the membrane stage and hybrid system as a whole – 6 atm. System performance was maintained at 10 normal liters per minute. This performance was chosen, cause it corresponds to the average capacity level of the oxygen concentrators used for feeding the respiratory medical devices, introduced to the market.
Figure 4. Experimental dependence between the oxygen concentration in the product flow and the number of operating cycles of adsorbers of the PSA stage: the PSA stage of the hybrid system (1), the hybrid membrane-sorption system (2) and the hybrid system with the flowing surge vessel (3).

Figure 5. Experimental dependence between oscillation amplitude of oxygen concentration in the product flow and the number of operating cycles of adsorbers of the PSA stage: the PSA stage of the hybrid system (1), the hybrid membrane-sorption system (2) and the hybrid system with the flowing surge vessel (3).

Experimental research of the hybrid membrane-sorption system have shown its rather high efficiency. On the figure 4. the chart ratio of the oxygen concentration in the product flow of the PSA stage of the hybrid system (curve 1), the hybrid membrane-sorption system with the regeneration of the sorbent at atmospheric pressure (curve 2) and the hybrid membrane-sorption system with the flowing surge vessel (curve 3) in dependence to the number of operating cycles of adsorbers of the PSA stage was presented. It is shown on the plot, that the curve 1 has maximum oscillation amplitude of oxygen concentration while entering the stationary mode of the PSA stage operation, concentration is equal to 6 % of oxygen. The number of cycles required to enter the operating mode of the PSA stage is minimal and amounts to 10-20 cycles of adsorption operation or 3-6 cycles of the PSA. At the same time, the concentration of product oxygen in the stationary mode of the PSA stage is about 70-72%. A membrane unit addition to the system, as seen on curve 2, allows to reduce the oscillation amplitude of oxygen concentration, when entering the stationary mode, to 2%, however, the number of cycles which is necessary to reach the stationary mode increases to 8-10 cycles. Compared to the PSA stage, the oxygen concentration in the product flow of the hybrid system increases slowly, due to the fact that the pressure fall on the membrane module during the operation of the hybrid system decreases rapidly and the membrane begins to function as a filter. Adding flowing surge vessels to the system, as seen in curve 3, virtually eliminated fluctuations in the product oxygen concentration, which now amount to 0.1%. but the output to the stationary mode of such a system amounted to about 13 cycles. The experimental dependences of the oscillation amplitude of the oxygen concentration as a function of the number of operating cycles of adsorbers of the step are shown in Fig. 5. The data on the amplitudes of the oscillation of the oxygen concentration and the number of cycles to enter the regime during the experimental studies are presented in Table 1. An addition to the system of flowing surge vessels allows to decrease the oscillations of product oxygen concentration up to 0.1%, but the output to the stationary mode of such a system amounted to about 13 cycles. The experimental dependences of the oscillation amplitude of the oxygen concentration as a function of the number of operating cycles of adsorbers of the PSA stage are shown in Fig. 5. The data on the oscillation amplitudes of the oxygen concentration and the number of cycles for entering the operation mode during the experimental research are presented in Table 1.
Table 1. The characteristics of the hybrid system operation modes.

|     | $A_{max}$, $O_2$% | $A$, $O_2$% | $N_{eq}$ | $N_{op}$ |
|-----|-------------------|-------------|----------|----------|
| PSA | 34                | 6           | 10-20    | 1        |
| HMS | 32                | 2           | 25-30    | 1        |
| HMSR| 19                | 0.1         | 40       | 3        |

In the table 1 value $A_{max}$ corresponds to the maximum fluctuation of concentration in each of the processes, value $A$ corresponds to average deviation of concentration in the stationary mode, $N_{eq}$ – the number of operating cycles of the adsorbers of the PSA stage before reaching the stationary mode, and $N_{op}$ is the number of operating cycles of the adsorbers of the PSA stage before entering the operation mode, when oxygen concentration in the product flow reaches the value, higher than 50%.

To compare the obtained experimental data with the obtained data of previous works, similar in design and in purpose of the systems, the data on the operation of the PSA of the system with two adsorbers and regeneration at atmospheric pressure [3] - curve 1, the PSA of the system using a countercurrent expulsion and compensation stage [5] - curve 2 and the investigated three-absorber system - curve 3, as well as a single membrane module [6] - curve 4 is presented on the Figure 6.

![Figure 6. Oxygen concentration in the waste flow: the PSA of the system with two adsorbers and regeneration at atmospheric pressure (1); the PSA of the system with the use of countercurrent expulsion and compensation stage (2); proposed hybrid membrane-sorption (3); single membrane module (4).](image)

It can be seen from the figure that the maximum concentration of product oxygen – 90% in the PSA process can be obtained by using both countercurrent expulsion and vacuum regeneration, but due to the fact that a large part of the product flow is actually discharged during expulsion, such a system loses in the efficiency to the system offered in this work. The membrane module, which allows to obtain an oxygen concentration of not more than 50%, is in advance of the PSA scheme with regeneration of the sorbent at atmospheric pressure without countercurrent expulsion, which allows obtaining only 30-35% of oxygen, while the proposed method gives 70% oxygen under the same conditions.
conditions, which in 2 times greater than the PSA method without expulsion and is more effective than the method of the PSA with the expulsion, by saving an expulsion flow in the system.

Taking into account the positive effect of the introduction of the countercurrent expulsion stage and the compensation stage shown in Figure 6, it can be assumed that the application of similar stages into the proposed hybrid membrane-sorption system will increase the concentration of the product flow of the system up to 90-93%, and also increase system performance in whole. On the figure 3 a scheme of organization of the flows with the stage of countercurrent expulsion and the compensation stage is proposed. The scheme of flows, experimentally tested in this work, is taken as the basis of the scheme. The scheme assumes a part of the product flow from the adsorber A, which was previously sent to the adsorber B, to be redirected to the countercurrent expulsion of the adsorber C, and the flow discharged from the adsorber C at this time is redirected to the adsorber B to shorten the filling stage. With such a flow organization, the general balance equation for flows (1) will be preserved and will look like:

\[ F' = P' + W'' , \]  

(2)

where \( W'' \) will be determined by the following relations:

\[ W'' = W' - W' , \]  

(3)

\[ W' = G' , \]  

(4)

where \( W' \) - total waste flow of the PSA stage of the hybrid system, \( W' \) – the part of the waste flow, directed to fill the adsorber B during the compensation stage, and \( G' \) – the part of product flow of the adsorber A, directed to the countercurrent expulsion of the adsorber C.

According to this scheme, the organization of the flows in proposed hybrid membrane-sorption system would allow to obtain the concentration of the produced oxygen equals to the level of 90-93%, with increased energy efficiency in comparison with the system [5].

4. Conclusions

Investigation of the three-adsorber scheme used in the hybrid membrane-sorption system was carried out. System consists of sorption and membrane units, connected into the recirculating contour. The three-adsorber scheme allows to obtain enriched with oxygen system’s product flow up to 70% without using additional devices and methods of sorbent regeneration on the PSA stage, that is impossible to reach similar oxygen concentration in the product flow without using proposed organization of the flows in the system. Moreover, there is a need to conduct less than 40 work cycles of adsorbers to achieve similar concentration, which allows to reach the stationary mode of the system much faster. The ways of system’s improvement for obtaining oxygen concentration higher than 90% are proposed in this work.

Such systems will find a use in industrial air separation to the components, in development of mobile and compact energy-efficient gas separation systems based on hybrid membrane-sorption technologies, oxygen generators which are suitable for feeding of artificial lung ventilation devices, oxygen concentrators for rehabilitation during post-surgery period and also for the prevention of various diseases including cardiovascular diseases. Furthermore, such hybrid systems have a potential of application in industrial gas drying as well as natural gas drying.

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