Pressure effect at permeability and deformation of the hollow fiber membrane gas separation module

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Abstract. In this paper, the deformation effect in the gas separation process of the hollow fiber membrane module is considered. A technique of gas permeability measurement in a commercial gas separation hollow fiber membrane module is provided. It is determined that permeability and selectivity are nonlinearly dependent on the pressure of the feed stream, this is justified by competing factors. The results of this work will allow introducing the membrane modules into hybrid gas separation units, in particular, into the drying unit of compressed gas.

1. Introduction
Membrane technologies are widely used in industry. The hollow fiber gas separation membrane modules can be used in various installations [1, 2] for helium extraction from natural gas, oxygen enrichment, drying of hydrocarbon gases, etc. Gas separation units can be membrane (consist of one or more membrane modules) or hybrid (for example, these units have adsorption or absorption stage in combination with a refrigerator or a membrane stage).

A bundle of tightly packed hollow fibers is installed in a cylindrical body - a membrane module. Depending on the design of the membrane module, the feed flow is supplied into the hollow fiber or to the inter-fiber space. Typically, the hollow fiber of the gas separation module consists of a porous support and a selective layer applied to the outer surface.

2. Problem statement
Companies that manufacture membranes and membrane modules, primarily deal with the complex solution of industrial problems, less often the implementation of membrane modules. The technical characteristics of the membrane modules don’t contain information about the material, permeability and membrane area. Consumers of ready-made membrane modules are companies that are engaged in the creation of installations for industry and transport. The absence of parameters for a commercially available hollow fiber membrane module complicates the process of the development and the creation of gas separation units.

To determine these parameters, a technique of gas permeability measurement has been developed on the basis of experimental investigations.

We should take into account the possible deformation of the hollow fiber in the nonstationary gas flow regime. The outer and inner diameter of the hollow fiber can be increased by supplying flow at a high pressure inside of the hollow fiber or can be narrowing if the feed flow is supplied to the inter-fiber space.

In the case of supplying the feed flow into the hollow fiber, it is appropriate to talk about deformation (expansion) of the fiber (Figure.1.).
Figure 1. Hollow fiber deformation

The hollow fiber consists of a thin diffusion (selective) layer of several nanometers thick [3] and a porous support with a gradient porosity. The pore size in the hollow fiber decreases from the inner radius to the outer radius.

The deformation of a hollow fiber is approximately described by the variation equations between inner and outer radius of a thick-wall cylinder:

\[ dr = \frac{r}{E} \left[ P_h \left( \frac{r^2 + r^2}{r^2 - r^2} + \mu \right) - 2P_l \left( \frac{r^2}{r^2 - r^2} \right) \right], \]

\[ dR = \frac{R}{E} \left[ 2P_h \left( \frac{r^2}{r^2 - r^2} \right) - P_l \left( \frac{r^2 + r^2}{r^2 - r^2} + \mu \right) \right], \]

where \( r \) – inner radius of the hollow fiber, \( R \) – outer radius, \( \mu \) – Poisson ratio, \( E \) – modulus of elasticity, \( P_h \) – high pressure of the feed flow, \( P_l \) – low pressure of the permeate flow. It is important that equations (1) and (2) are linearly dependent on high and low pressures.

To establish the parameters of commercial gas separation hollow fiber membrane modules, experimental investigations were carried out with a clean gas (nitrogen or oxygen) in the "locked" regime (the permeate flow is blocked). Gas from the high pressure cylinder was supplied to the input of the unit. The pressure of the feed flow was raised by a gas pressure regulator to 10 ATMG for oxygen and 14 ATMG for nitrogen at a pitch of 1 ATMG, permeate flow was measured for each feed flow pressure value. Experimental investigations were carried out on a hollow fiber membrane module in which the feed flow is supplied into the hollow fiber. As the permeability values and the membrane area values are unknown for commercially available membrane modules, reduced permeability is determined from formula:

\[ \pi_i^* = \pi_i \times S = \frac{p}{(P_h - P_l)}, \]

where \( \pi_i \) – the permeability of \( i \) component, \( S \) – membrane area, \( P \) – permeate flow.

3. Results and discussion

Experimental investigations of the nonstationary flow of oxygen and nitrogen through a selective membrane in a "locked regime" were performed in this work with a variation of the feed flow pressure. From the experimental research, the dependence of the reduced permeability (3) on the pressure of the feed flow was obtained. Fig. 2a, 2b. The data obtained from experimental investigations is approximated by the of least square method of the second order.

On the Figures 2a and 2b, curve 1 corresponds to the process of a gradual increase in the pressure of the feed flow, curve 2 shows a gradual decrease in the pressure of the feed flow. When the pressure is decreased, the values of the reduced permeability are lower than values at the process, in which the pressure is increased, so hysteresis is observed. At a feed flow pressure of 8 ATMG, the maximum of reduced oxygen permeability is observed (Figure 2a). This maximum is not observed for the nitrogen in the measured pressure range.
Figure 2. The dependence of the reduced permeability on the feed flow pressure a) – oxygen, b) – nitrogen.

On the Figure 3, the nonlinear dependence of the oxygen / nitrogen average selectivity value (the average between the selectivity when the feed stream pressure increases and decreases) of the investigated membrane module from the feed flow pressure was shown. An experimental investigation has shown that permeability and selectivity are not constant values.

Figure 3. The dependence of O₂/N₂ selectivity on the high pressure feed flow.

Obtained results aren’t described by equations (1) and (2). The reason for the nonlinear dependence of the reduced permeability and selectivity on the of the feed flow pressure can be associated with several competing factors. The pressure growth increases the permeability of the gas. As the pressure increases, the inner and outer radius of the hollow fiber increases also, and, as a consequence, the selective layer area increases, and the thickness decreases (Figure.1), this leads to the increase of permeability. The deformation of the porous support also influences on the reduced permeability, since its thickness (support packing), the area and the porosity vary over the entire thickness of the support, which leads to a decrease in the permeability of the porous support.

The presence of a maximum value of the oxygen reduced permeability at 8 ATMG (and its absence for nitrogen) is justified by the fact that the oxygen permeability is higher than the nitrogen permeability. At a critical value of the pressure of the feed flow, the effect of the porous support compacting dominates over the growth factors of permeability when the pressure of the feed flow increases.

It is also determined from experimental investigation that a change in the reduced permeability is observed with time. (Figure.4a, 4b).

The experiment was carried out as follows: the pressure of the feed flow was gradually increased to a certain pressure (3 ATMG), then within 7 minutes the pressure of the feed stream remained constant, the permeate flow was measured. The experiment was repeated at different pressures. The experimental investigation was carried out in a similar manner at the pressure decrease for nitrogen and oxygen.
The reduced permeability decreases in 3 minutes, at a constant pressure of the feed flow, and after 3 minutes the value of reduced permeability becomes constant; it was determined from experimental investigation. The flowing process of pure gas through the selective membrane becomes stationary. With a smooth pressure decrease of the feed flow (curves 2 in Figure 4.) the permeability has been transforming into a stationary value per 3-4 minutes.

The experiment was repeated after a few hours, and the values of the reduced permeability were the same. It has been established that for the values of the feed flow pressure up to 14 ATMG, the deformation of the fibers under investigation is elastic, although the relaxation time of the geometric dimensions is about 10 minutes (under the experimental conditions).

Conclusions
In the present work, the nonstationary process of nitrogen and oxygen flow in a commercially available hollow fiber membrane module has been investigated.

From the obtained experimental data, it follows that the reduced permeability increases nonlinearly with increasing pressure, and the selectivity decreases nonlinearly. Taking into account the fact that the hollow cylinder deformation model depends on the pressure linearly, this effect can be explained by a combination of competing factors: the area increase of the selective layer and the support, and the thickness decrease of the selective layer and porous support, the decrease of pores size, and a change in the porosity of the support.

It was also determined, that for the investigated membrane module, the time to enter the stationary mode is equal to 3-4 minutes. The deformation is elastic, and the relaxation time is approximately equal to 10 minutes.

The results obtained in this work have the practical importance in the investigation process, development and creation of the membrane/hybrid systems for compressed gas drying, in particular, for the drying of the compressed air.

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