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GAS SEPARATION IN MMK-PMP-ST AND LAMBDA MEMBRANE MODULE

Key-words

Gas separation, membrane module, air, hydrogen, nitrogen, poly-4-methylopentene-1.

Summary

The air separation was carried out using two MMK-PMP-ST and one LAMBDA industrial (Institute of Chemical Fibers, Łódź, Poland) membrane modules. The investigations have been performed in a pilot plant scale installation especially designed for this purpose. The separation measurements have been done at pressure ratio equal to 0.1 and 0.2. An extra investigation, concerning the separation of the hydrogen, has been done using the LAMBDA module, for the hydrogen-nitrogen mixture. Obtained separation results have been discussed from the point of view of efficiency and conditions of using membrane modules for such purposes. The results have been also used for evaluation of quality and properties of the membrane modules.

Introduction

Recently, a rapid implementation of membrane techniques to industrial processes may be observed. Membrane industrial installation for the separation of liquids are commonly used, but also the separation of gas mixtures in the industrial membrane modules are now becoming more and more important and are showing the highest dynamic among other separation techniques implemented in modern industry [1–5].

Classical gas separation methods, such as absorption, adsorption, cryogenic methods, etc., are highly efficient and developed and technologically fully elaborated and need very complicated and expensive installations to be implemented. In the opposite the membrane, installations are simple and very energy saving.

Membrane separation can be applied together or instead of other separation processes and decrease technological costs. The membrane separation techniques are mainly used in such processes of air separation, hydrogen recovery in the petroleum industry, methanol and ammonia production, and purification of natural and biogas from carbon dioxide, desulphurization and drying of natural gas, flue gas desulphurization, drying of gas streams, removal of organic solvent vapours, etc.

Most of the applications, because of their purity, are connected with environment protection. They enable obtaining reagents less concentrated in end streams for its further recycling or degradation.

This work concerns investigations of gas separation on MMK-PMP-ST and LAMBDA industrial (Institute of Chemical Fibers, Łódź, Poland) membrane modules. The separation measurements have been done for air, at different pressure ratios and flow rates and for two types of membrane modules differing in separation area.

1. Experimental

The air separation was carried out using MMK-PMP-ST1 and LAMBDA industrial (Institute of Chemical Fibers, Łódź, Poland) membrane modules. The investigations have been performed in a pilot plant scale installation especially designed for this purpose [6].

The MMK-PMP-ST membrane modules, differing in the separation area, are schematically displayed in Fig. 1 and the LAMBDA module in Fig 2. They are filled with a packages of poly-4-methylopentene-1 capillary synthetic fibers: external diameter 39 μm, internal diameter 19 μm, packing density 17000 m^2/m^3, operational temperature 273-313 K, operational pressure up to 2.5 MPa.

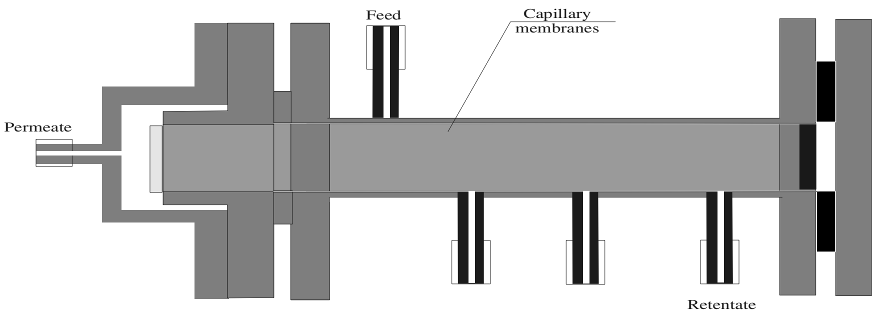

Fig. 1. MMK-PMP-ST membrane module: length 1.15 m, diameter 0.105 m, separation area 151 m^2 (ST1) and 168 m^2 (ST2)

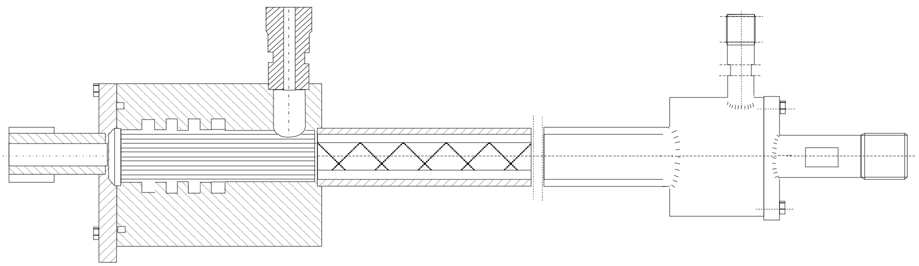

Fig. 2. LAMBDA membrane module: length 1.05 m, diameter 0.025 m, and separation area 8.9 m^2

The scheme of the pilot plant installation with MMK-PMP-ST or LAMBDA membrane module is shown in Fig. 3.

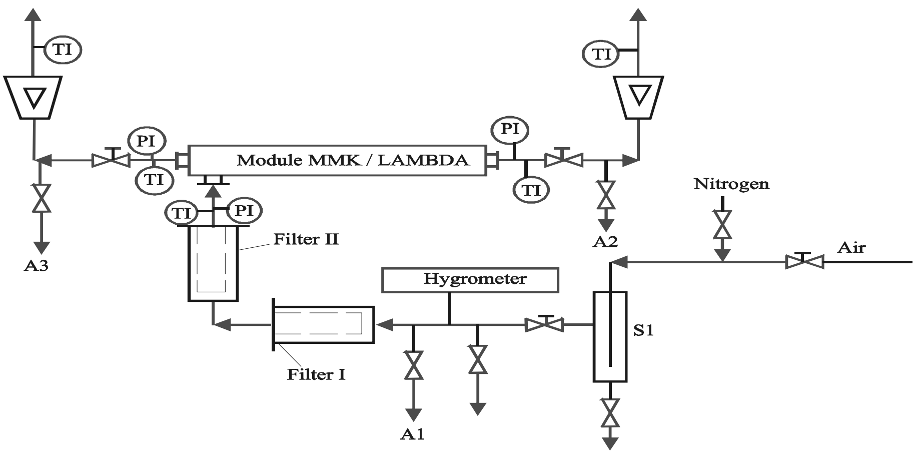

Fig. 3. Scheme of the installation with MMK-PMP-ST or LAMBDA membrane modules

The membrane module is fed by the compressed dry air going through two-steps filtration: on filter I (sintered metallic powder) and filter II (tarflene powder). Intensity of the flow is regulated by the system of valves and measured by the industrial rotameters RIN 160, RIN 250 i RIN 400. The concentration of O_2 in the feed, permeate and retentate stream, respectively, was measured by a "Chrom 5" chromatograph [6].

Air separation was investigated in stable conditions, which were obtained for the measured differences of pressure after 1-2 hours.

During the experiment, the following data were measured:

a) Concentration of all components in the feed,
b) Concentration of all components in the permeate,
c) Concentration of all components in the retentate,

d) Volume flow of the permeate,
e) Volume flow of the retentate,
f) In-flow and out-flow temperature of membrane module,
g) Out-flow temperature of rotameters,
h) In-flow and out-flow pressure of membrane module.

2. Results

The obtained results and the measured parameters of the process are given in Table 1 (for the MMK-PMP-ST1 module), Table 2 (for the MMK-PMP-ST2 module) and Table 3 (for the LAMBDA module). The tables also show the calculated values of $\theta = P_\omega/F_\alpha$ – the stage cut (P_ω, F_α – molar intensity of permeate outflow and feed flow, respectively) and $\delta = p_l/p_h$ – ratio of pressure of permeate (p_l) and retentate (p_h) flows. These (θ – reduced flow and δ – reduced pressure) parameters are very useful in mathematical modelling of gas separation permeators [1].

Since the intensities of out flows were measured and the feed flow was calculated as their sum, the permanent control of overall and oxygen balance has to be performed:

$$F_\alpha x_\alpha = F_\omega x_\omega + P_\omega y_\omega \qquad (1)$$

where:

F_α, F_ω, P_ω – molar feed, retentate and permeate flow, respectively [mol/s],
x_α, x_ω, y_ω – molar fraction of oxygen in the feed, in retentate and in permeate.

The relative percentage deviation of the oxygen in "in–out" flow E (%) can be expressed by the equation:

$$E = 100\cdot[1 - (F_\omega x_\omega + P_\omega y_\omega)/F_\alpha x_\alpha]. \qquad (2)$$

The values of such calculated deviations are shown in the last column in Tables 1-3.

Table 1. Results of air separation in the MMK-PMP-ST1 membrane module at constant temperature T = 293 K

No. Exp.	F_α (mmol/s)	x_α	F_ω (mmol/s)	x_ω	P_ω (mmol/s)	y_ω	p_h (MPa)	p_l (MPa)	θ	δ	E (%)
1	41.3	0.21	27.90	0.175	13.40	0.285	0.74	0.11	0.324	0.1	-0.3
2	27.1	0.21	13.80	0.151	13.30	0.271	0.74	0.11	0.491	0.1	0.1
3	21.1	0.21	6.47	0.115	14.60	0.252	0.81	0.11	0.692	0.1	0.1
4	33.2	0.21	11.30	0.117	22.10	0.258	1.18	0.12	0.666	0.1	-0.1
5	23.8	0.21	15.30	0.175	8.65	0.271	0.53	0.11	0.363	0.2	-0.1

Table 2. Results of air separation in the MMK-PMP-ST2 membrane module at constant temperature $T = 293$ K

No. Exp.	F_α (mmol/s)	x_α	F_ω (mmol/s)	x_ω	P_ω (mmol/s)	y_ω	p_h (MPa)	p_l (MPa)	θ	δ	E (%)
1	70.8	0.21	58.30	0.192	12.5	0.295	0.64	0.11	0.177	0.2	-0.1
2	90.6	0.21	76.20	0.194	14.3	0.297	0.71	0.11	0.158	0.2	0.0
3	100.0	0.21	84.80	0.209	15.2	0.308	0.74	0.11	0.152	0.1	-6.7
4	134.0	0.21	120.00	0.199	13.7	0.302	0.68	0.11	0.102	0.2	0.4
5	160.0	0.21	143.00	0.199	16.8	0.305	0.81	0.11	0.105	0.1	0.1
6	180.0	0.21	163.00	0.200	16.8	0.306	0.81	0.11	0.093	0.1	0.2
7	67.2	0.21	45.40	0.171	21.8	0.293	1.03	0.12	0.324	0.1	-0.3
8	58.3	0.21	43.30	0.181	15.0	0.293	0.75	0.11	0.257	0.1	0.1
9	45.9	0.21	31.10	0.173	14.8	0.287	0.74	0.11	0.322	0.1	0.1
10	33.5	0.21	18.70	0.156	14.8	0.278	0.74	0.11	0.442	0.1	0.1
11	24.8	0.21	10.70	0.133	14.1	0.268	0.72	0.11	0.569	0.2	0.1
12	19.9	0.21	3.48	0.075	16.4	0.239	0.82	0.11	0.824	0.1	0.0
13	45.9	0.21	20.50	0.135	25.4	0.271	1.23	0.12	0.553	0.1	-0.1

Table 3. Results of air separation in the LAMBDA membrane module at constant temperature T = 293 K

No. Exp.	F_α (mmol/s)	x_α	F_ω (mmol/s)	x_ω	P_ω (mmol/s)	y_ω	p_h (MPa)	p_l (MPa)	θ	δ	E (%)
1	1.314	0.21	0.67	0.156	0.645	0.290	1.05	0.10	0.491	0.095	5.7
2	3.088	0.21	2.39	0.188	0.694	0.322	1.04	0.10	0.225	0.096	-3.9
3	4.433	0.21	3.78	0.199	0.651	0.330	0.92	0.10	0.147	0.109	-3.9
4	0.992	0.21	0.37	0.143	0.620	0.276	0.92	0.10	0.625	0.109	-7.7
5	27.776	0.21	27.03	0.207	0.744	0.353	1.04	0.11	0.027	0.106	-0.4
6	26.139	0.21	24.68	0.204	1.463	0.356	1.58	0.11	0.056	0.070	-1.2

Figures 4, 5 and 6 show dependencies of out-flow concentrations on the feed-flow ratios in the investigated MMK-PMP-ST and LAMBDA membrane modules for the same pressures ratios – $\delta = 0.1$. Fig. 7 shows this dependence in the MMK-PMP-ST2 module for $\delta = 0.2$.

Figures 4, 5 and 6 show dependencies of oxygen in permeate and nitrogen in retentate concentration on stage cut-in the investigated membrane module at the same pressure ratio – $\delta = 0.1$. The concentration of oxygen in permeate increases in all cases with decreasing of stage cut and pressure ratio. The highest increase in the oxygen concentration in permeate, up to 40.5% vol., can be noticed for the MMK-PMP-ST2 membrane module. The MMK-PMP-ST1 and the LAMBDA modules gave results on the same level of accuracy of about 30–35%. The bigger separation area of the MMK-PMP-ST2 module can explain this increase.

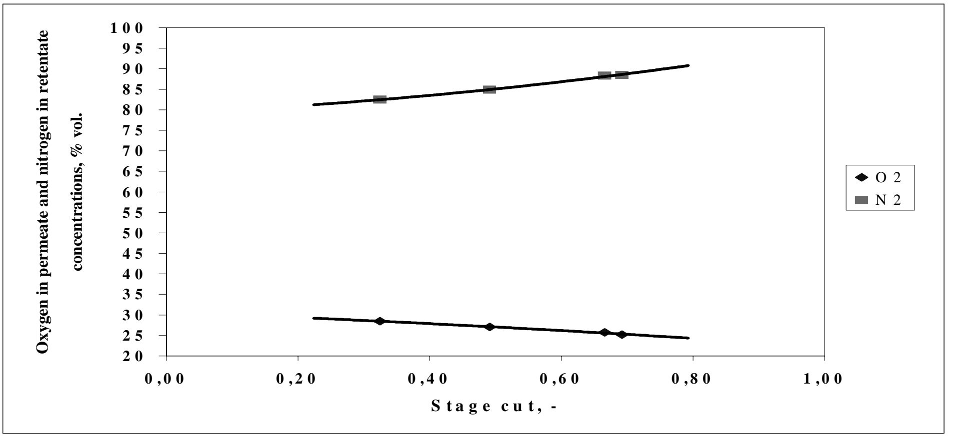

Fig. 4. Oxygen in permeate and nitrogen in retentate concentrations versus stage cut-in the MMK-PMP-ST1 membrane module at pressure ratio $\delta = 0.1$

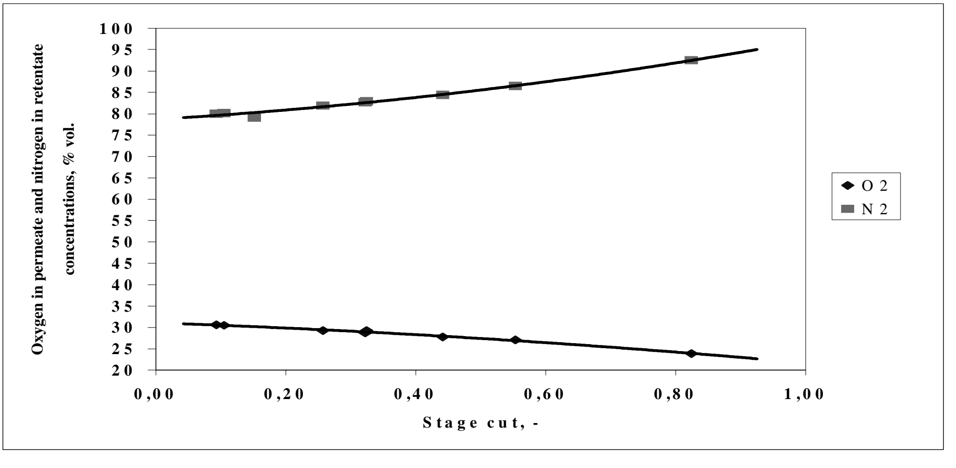

Fig. 5. Oxygen in permeate and nitrogen in retentate concentrations versus stage cut-in the MMK-PMP-ST2 membrane module at pressures ratio $\delta = 0.1$

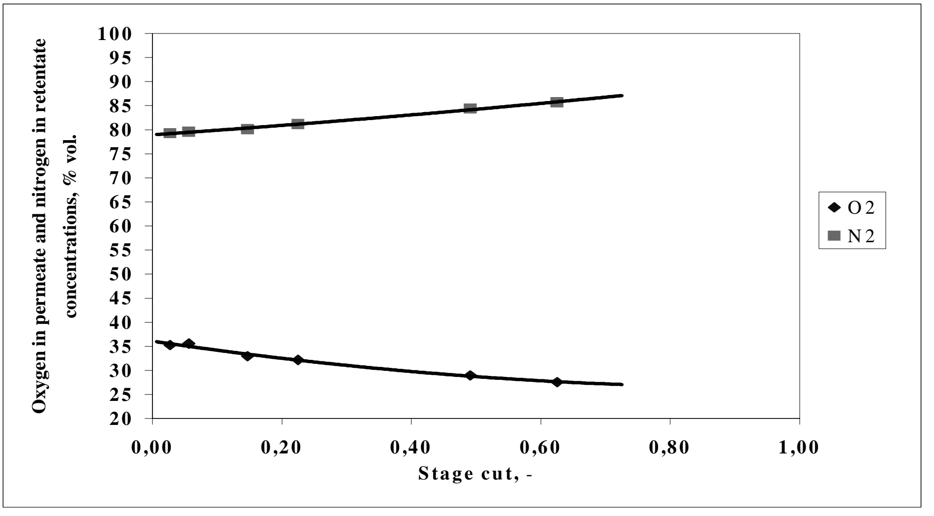

Fig. 6. Oxygen in permeate and nitrogen in retentate concentrations versus stage cut-in the LAMBDA membrane module at pressures ratio $\delta = 0.1$

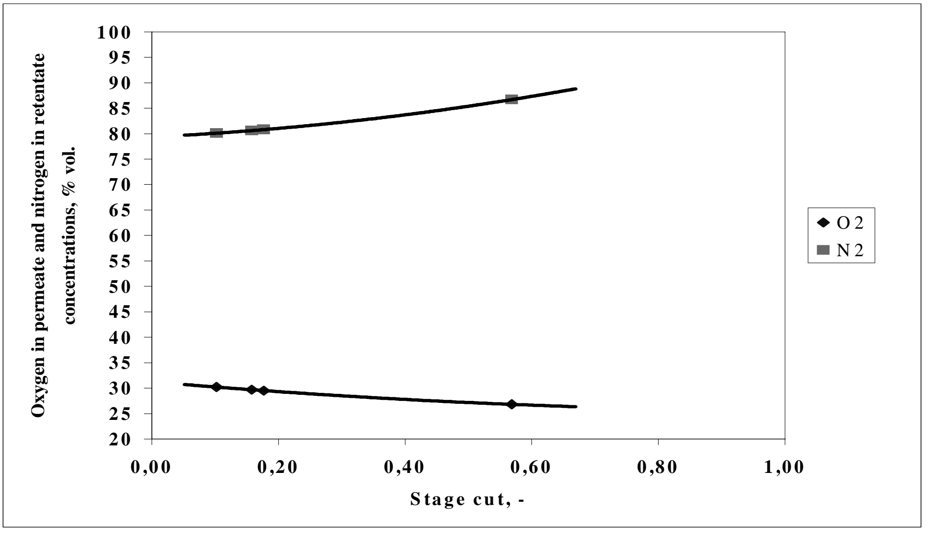

Fig. 7. Oxygen in permeate and nitrogen in retentate concentrations versus stage cut-in the MMK-PMP-ST2 membrane module at pressures ratio $\delta = 0.2$

In the case of the LAMBDA module, the increase of the oxygen concentration in permeate to 35% vol. has been obtained for very low stage cut (θ = 0.027–0.055). It means that this process is not effective enough for the industrial implementation (high costs of air compressing) and the LAMBDA module cannot be recommended for the use in industrial air separation processes.

Comparing the results for the MMK-PMP-ST2 membrane module obtained for different pressure ratio (Fig. 5 and 7), it can be seen that the concentration of oxygen in permeate increases with the decreasing of the pressures ratio, which is in agreement with our previous results [8].

The LAMBDA membrane module has been also used for separation of the hydrogen-nitrogen mixture. The whole investigation procedure was the same as in the case of air separation and obtained results are given in Table 4.

Table 4. Results of hydrogen-nitrogen mixture separation in the LAMBDA membrane module at constant temperature T = 293 K

No. Exp.	F_α (mmol/s)	x_α	F_ω (mmol/s)	x_ω	P_ω (mmol/s)	y_ω	p_h (MPa)	p_l (MPa)	θ	δ	E (%)
1	3.62	0.972	1.50	0.941	2.13	0.987	1.150	0.101	0.588	0.088	0.1
2	4.63	0.803	2.24	0.687	2.38	0.904	1.363	0.101	0.514	0.074	0.7
3	6.58	0.847	4.09	0.791	2.48	0.920	1.273	0.101	0.377	0.079	0.9

The purpose of this separation is the highest hydrogen recovery from the feed flux. Fig. 8 presents the hydrogen recovery as a function of the process conditions (the stage cut) as well as the hydrogen enrichment factor (ratio of hydrogen concentration in the permeate and the feed flow, respectively).

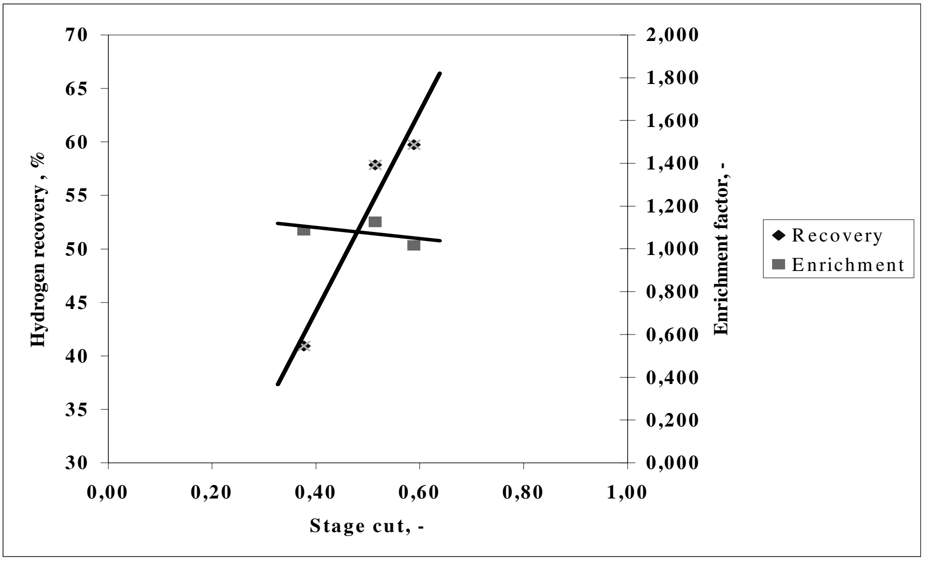

Fig. 8. Hydrogen recovery and the enrichment factor in the permeate flux versus stage cut-in the LAMBDA membrane module

Looking at Fig. 8, one can see that the hydrogen recovery increases while the enrichment factor decreases with the increasing of the stage cut. The maximum hydrogen recovery – 52% (enrichment factor equal to 1.1) is obtained for the stage cut equal to 0.45. The limited experimental data does not allow for a more general conclusion but the trend of the process is clearly shown.

3. Conclusions

The single MMK-PMP-ST membrane module used for air separation, depending on the driving force of the process – Δp, the stage cut – θ and the temperature, allows for an increase in the oxygen concentration in permeate up to 40.5% vol. (Tables 1, 2). This module efficiency meets the industrial expectation.

In the case of the LAMBDA module, the increase of the oxygen concentration in permeate to 35% vol. can be obtained, but only for a very low stage cut (θ = 0.027-0.055), which means that this process is not effective enough for industrial implementation (high costs of air compressing), and the LAMBDA module cannot be recommended for use in industrial air separation processes.

The LAMBDA module can be used successfully for the hydrogen recovery from the hydrogen-nitrogen mixture but not in an industrial scale, because of its highest efficiency is for a very low stage cut, as in the case of air separation.

When high purities of flows (permeate or retentate) are needed, the area of the membrane has to be very large, which means that the membrane modules should be connected in a series to increase the efficiency of the process. There are some other possibilities of connections of the investigated membrane modules [7], as well as different membrane modules; however, based on the obtained results, we cannot formulate any conclusions concerning such connections. It is necessary to remember that the installation with a series of modules is much more expensive, which sometimes makes its implementation impossible.

The purer product is recovered less in the one permeate stage (and opposite). The larger area of the membrane causes an increase in retentate purity, while the small area of the membrane increases purity of permeate. However it is necessary to remember that the separation effect depends not only on the area of the membrane but also on its selectivity and that the selectivity does not always increase the separation independently of the increase in the membrane area.

Increasing the feed pressure or decreasing the permeate pressure increases the purity of retentate, while for the same area of membrane, increasing the feed flow decreases the purity of retentate but does not influence the permeate flow. The concentration of a faster permeating component in permeate gradually decreases with the increasing of the stage cut θ.

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Recenzent:
Wojciech PIĄTKIEWICZ

Separacja gazów w membranowych modułach MMK-PMP-ST i LAMBDA

Słowa kluczowe

Separacja gazów, moduły membranowe, powietrze, azot, wodór.

Streszczenie

Przeprowadzono separację powietrza w przemysłowych, membranowych modułach MMK-PMP-ST i LAMBDA (wyprodukowanych przez Instytut Włókien Chemicznych w Łodzi), w półtechnicznej skali, na specjalnie zaprojektowanej do tego celu aparaturze. Pomiary wykonano dla różnych stosunków ciśnień w dwóch modułach MMK-PMP-ST różniących się powierzchnią separacji i module LAMBDA. Moduł LAMBDA zastosowano dodatkowo do separacji wodoru z mieszaniny wodór–azot. Otrzymane wyniki doświadczalne zostały przedyskutowane z punktu widzenia warunków stosowania modułów MMK-PMP-ST i LAMBDA oraz wydajności prowadzonych procesów separacji powietrza i wodoru. Ponadto posłużyły one do określenia własności i jakości badanych modułów membranowych.