Wiktor KLUZIŃSKI, Paweł GIERYCZ
Technical University of Radom, Radom

AIR SEPARATION IN PVTMS MEMBRANE MODULE

Key words

Gas separation, membrane module, air, polyvinyltrimethylsilane.

Summary

The air separation was carried out using Russian industrial (*Kriogenmash*) PVTMS membrane module. The investigations have been performed in a pilot plant scale installation especially designed for this purpose. The separation measurements have been done, at different pressure ratios, for four types of membrane module sets as follows: one membrane module; a set of two parallel membrane modules; a set of two serial membrane modules with permeate from the first one feeding the second module; and, a set of two serial membrane modules with retentate from the first one feeding the second module. Obtained separation results have been discussed from the point of view of efficiency and conditions of using PVTMS membrane modules for such purposes. The results have been also used for evaluation of quality and properties of the membrane module.

Introduction

Recently, a rapid implementation of membrane techniques to industrial processes may be observed. Membrane industrial installation for the separation of liquids is commonly used, but presently the separation of gas mixtures in the industrial membrane modules is becoming more and more important [1–5].

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

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

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

This work concerns investigations of gas separation on the Russian industrial (*Kriogenmash*) PVTMS membrane module. The separation measurements have been done for air at different pressure ratios and flow rates. The four following types of different membrane module sets have been used in the investigation:

- One membrane module,
- A set of two parallel membrane modules,
- A set of two serial membrane modules with permeate from the first one feeding the second module, and
- A set of two serial membrane modules with retentate from the first one feeding the second module.

1. Experimental

The air separation was carried out using a Russian industrial (*Kriogenmash*) PVTMS membrane module. The investigations have been performed in a pilot plant scale installation especially designed for this purpose [6].

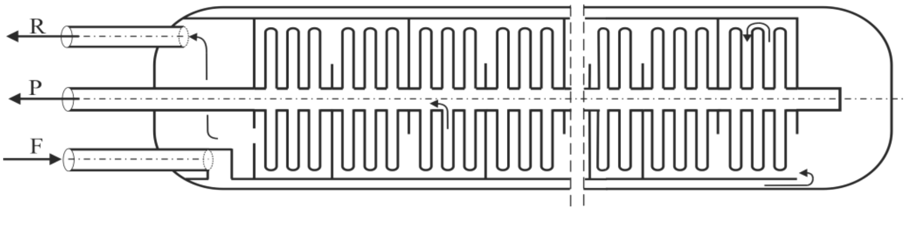

Fig. 1. PVTMS membrane module (F – feed, P – permeate, R – retentate)

The PVTMS membrane module is schematically displayed in Fig. 1. It was filled with a package consists of 180 flat semi-permeable elements located in a series-parallel way. The geometric area of the whole package was equal to 12 m^2 and the package was made of polyvinyltrimethylsilane (PVTMS). The basic data of the package is shown in Table 1.

Table 1. Process and geometric data of the PVTMS membrane module

No	Parameters	Designed values	Measured values
1	Separated air parameters: molar flow rate (mol/s) pressure (MPa) temperature (°C)	 0.465±0.031 1.5-2,5 0-35	 0.494 1.55 16
2	Molar flow rate of nitrogen fraction (mol/s)	0.130±0.006	0.125
3	Volume contribution of oxygen in nitrogen fraction (%) (not more than)	5	3.79
4	Pressure in the module (Mpa)	1.5-2.5	1.55
5	Module dimensions: length (m) diameter (m)	 1.5 0.29	 1.455 0.282
6	Mass of the module (kg)	96.5	96.5

The scheme of pilot plant scale installation with single PVTMS membrane module is shown in Fig. 2.

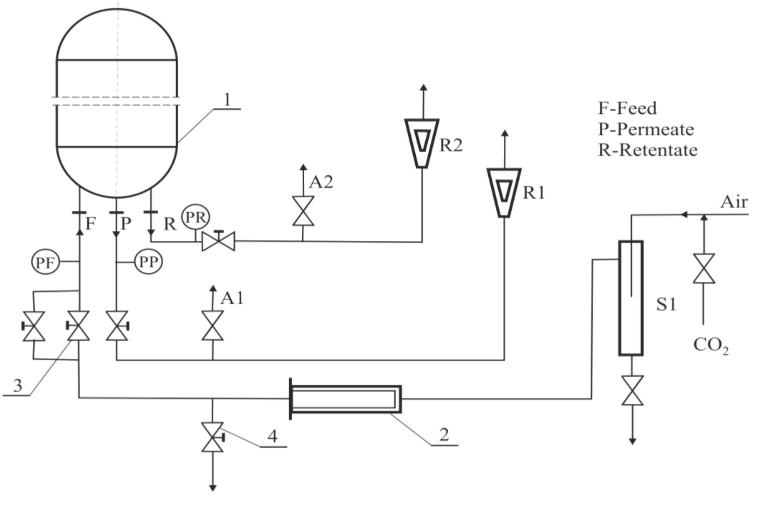

Fig. 2. Scheme of the installation with PVTMS membrane module (1 – membrane module, 2 – filter, 3, 4 – valves, S1 – separator, R1, R2 – rotameters)

The module (1) is fed by the compressed dry air going through the separator (S1) and filter (2). Intensity of the flow is regulated by the system of two valves

(3) with a partly open “blown” valve (4). Air fraction reach in oxygen (permeate) went out through outlet (P) and air fraction reach in nitrogen (retentate) went out through outlet (R). The intensities of these two flows were measured using two rotameters (R1) and (R2). The concentration of O_2 in permeate flux 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.

2. Results

The first series of experiments was carried out using this installation by compressing air before the membrane and obtaining the product – permeate (air reach in oxygen) on the other side of the membrane.

Table 2. Results of air separation in the PVTMS membrane module

No. exp.	T (K)	F_α (mol/s)	x_α	F_ω (mol/s)	x_ω	P_ω (mol/s)	y_ω	$p_{h.}$ (MPa)	p_l (MPa)	θ	δ	E (%)
1	297	0.372	0.21	0.1120	0.066	0.2600	0.279	1.10	0.18	0.699	0.2	-2.3
2	296	0.393	0.21	0.1020	0.068	0.2910	0.284	1.22	0.19	0.740	0.2	-8.5
3	298	0.202	0.21	0.0521	0.052	0.1490	0.268	0.73	0.13	0.738	0.2	-0.5
4	290	0.136	0.21	0.0446	0.072	0.0918	0.280	0.51	0.11	0.675	0.2	-1.2
5	288	0.455	0.21	0.0856	0.054	0.3700	0.260	1.77	0.27	0.813	0.2	-5.5
6	296	0.507	0.21	0.0806	0.050	0.4270	0.248	2.05	0.35	0.842	0.2	-3.3
7	294	0.268	0.21	0.0980	0.139	0.1700	0.266	1.10	0.50	0.634	0.5	-4.6
8	292	0.299	0.21	0.0870	0.135	0.2120	0.254	1.10	0.48	0.709	0.4	-4.4
9	291	0.265	0.21	0.1000	0.136	0.1650	0.267	1.10	0.50	0.623	0.5	-3.6
10	277	0.254	0.21	0.1350	0.115	0.1190	0.294	0.67	0.14	0.469	0.2	5.3
11	276	0.458	0.21	0.2360	0.129	0.2100	0.295	1.13	0.22	0.459	0.2	3.9
12	274	0.513	0.21	0.1660	0.085	0.3470	0.254	2.07	0.40	0.676	0.2	5.1
13	273	0.563	0.21	0.2500	0.135	0.3120	0.262	1.92	0.68	0.554	0.4	2.3
14	274	0.454	0.21	0.1550	0.130	0.3000	0.242	2.22	1.11	0.661	0.5	2.7
15	279	0.449	0.21	0.1100	0.097	0.3400	0.239	2.25	0.97	0.757	0.4	2.5
16	278	0.563	0.21	0.2450	0.125	0.3170	0.266	1.90	0.66	0.563	0.3	2.8
17	277	0.605	0.21	0.2970	0.127	0.3070	0.277	1.79	0.56	0.507	0.3	3.4
18	279	0.441	0.21	0.1500	0.125	0.2910	0.240	2.22	1.16	0.660	0.5	4.3
19	278	0.381	0.21	0.1410	0.135	0.2400	0.253	2.05	1.14	0.630	0.6	0.6
20	291	0.275	0.21	0.1630	0.154	0.1120	0.292	0.53	0.13	0.407	0.2	-0.1
21	291	0.355	0.21	0.1850	0.138	0.1700	0.283	0.76	0.15	0.479	0.2	1.2
22	290	0.364	0.21	0.2110	0.150	0.1540	0.292	0.68	0.15	0.423	0.2	-0.2
23	289	0.431	0.21	0.2940	0.167	0.1380	0.305	0.63	0.14	0.320	0.2	-0.8
24	291	0.428	0.21	0.2600	0.154	0.1670	0.295	0.75	0.16	0.390	0.2	-0.6
25	291	0.421	0.21	0.2770	0.173	0.1440	0.289	0.72	0.24	0.342	0.3	-1.3
26	290	0.278	0.21	0.1730	0.178	0.1050	0.267	0.72	0.36	0.378	0.5	-0.8

The obtained results and the measured parameters of the process are given in Table 2. In the last two columns are shown the calculated values of $\theta = P_\omega/F_\alpha$ – the stage cut (P_ω, F_α – molar flow rate of permeate and feed, respectively) and $\delta = p_l/p_h$ – ratio of pressures of permeate (p_l) and retentate (p_h). θ – reduced flow and δ – reduced pressure are practical parameters useful in mathematical modelling of gas separation permeators [1].

Fig. 3 and Fig. 4 show dependencies of feed flow concentration on the feed flow ratio in the membrane module at different pressures ratios – δ.

The investigations have been performed for a range of pressure differences of both sides of the membrane equal to 0.36–1.70 MPa and the stage cuts θ = 0.32–0.84. Depending on the driving force of the process – Δp, the stage cut θ and the temperature, the oxygen concentration in the permeate changes from 23.9% to 30.5% vol.

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:

$$F_\alpha x_\alpha = F_\omega x_\omega + P_\omega y_\omega \tag{1}$$

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 air, in retentate and in permeate.

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

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

The values of such calculated deviations are shown in the last column on Tab. 2.

Fig. 3 shows dependencies of oxygen in permeate and nitrogen in retentate concentration on stage cut in the membrane module at different pressure ratios – δ. The concentration of oxygen in permeate increases with decreasing of stage cut and pressure ratio.

The obtained results also allow for the calculation of the cost of reached in oxygen air produced in the module by the determination of the intensity of permeate flow as a function of pressure difference $\Delta p = p_h - p_l$ [4]. The resulting dependence $P_\omega = f(\Delta p)$ allows for the calculation of the production of 1 m^3 oxygenated (24–30% vol.) air knowing the price of 1 m^2 of the membrane and the price of gas pressing.

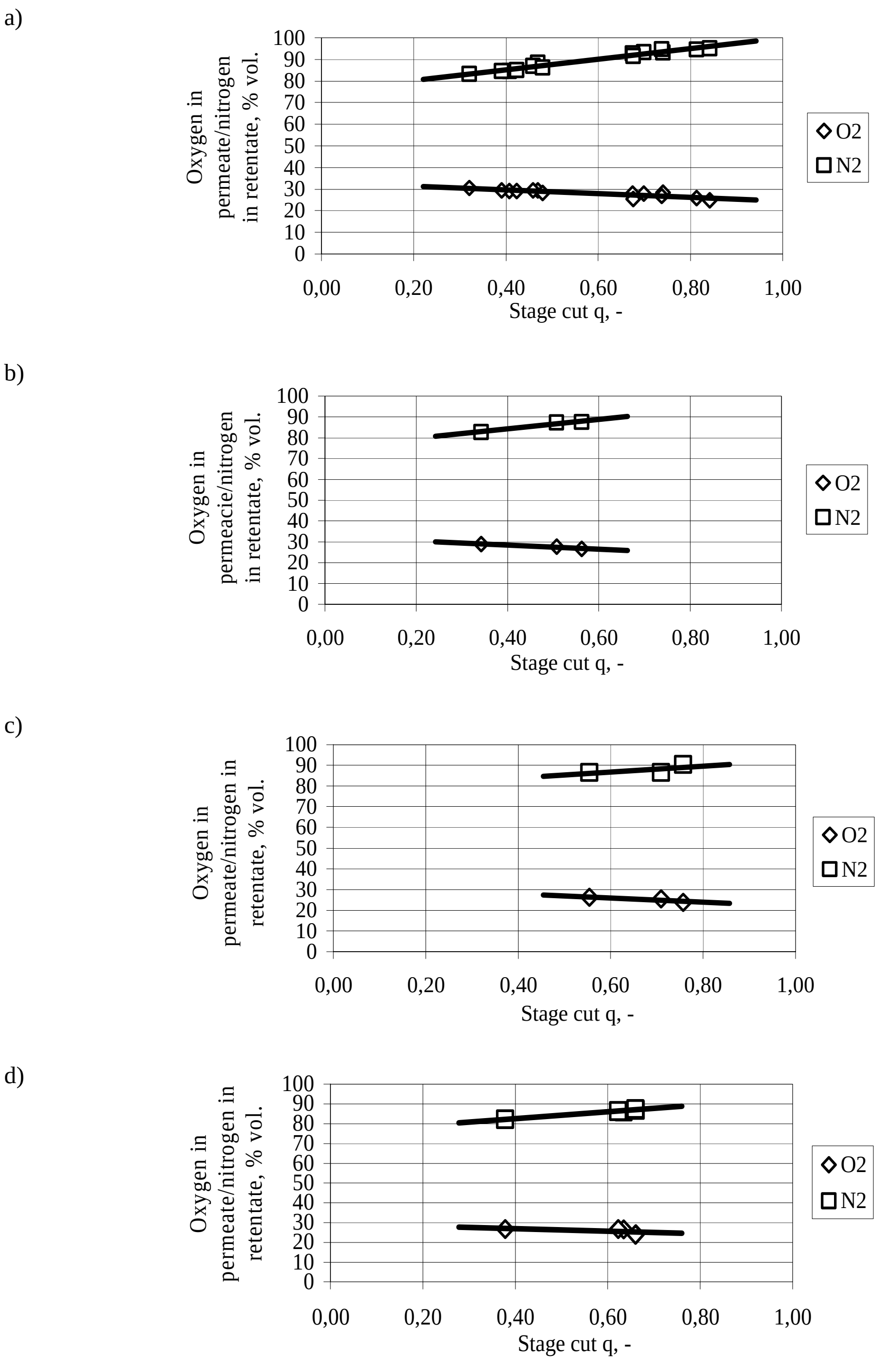

Fig. 3. Oxygen in permeates and nitrogen in retentate concentrations versus stage cut in the PVTMS membrane module at pressures ratio equal to: a) 0.2, b) 0.3, c) 0.4, d) 0.5

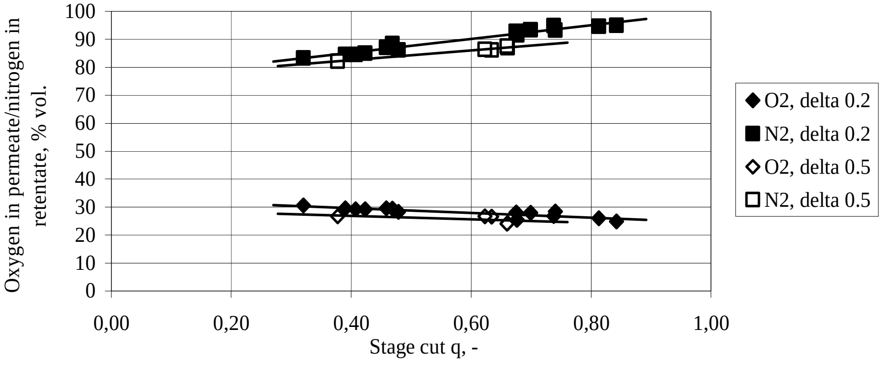

Fig. 4. Oxygen in permeate and nitrogen in retentate concentrations versus stage cut in the PVTMS membrane module – influence of the pressures ratio

Nowadays, because of the high costs of the gas compressing, more and more such membrane processes are leading to the use of the vacuum pump. Such investigations were also carried out in this work using the PVTMS membrane module.

In this case, the gas was transferred through the membrane module by the suction of the product using the vacuum pump. On the inlet to module extra (compared to the atmospheric) pressure had to be kept to overcome the flow and apparatus resistance on the retentate side. In this installation, a fan was used for this purpose.

The investigations of air separation with a vacuum pump were performed for pressure differences of Δp = 0.081 to 0.127 MPa and stage cuts from θ = 0.41 to θ = 0.79. The obtained results are shown in Table 3 and Fig. 5.

Table 3. Results of air separation in the PVTMS membrane module with a vacuum pump at constant temperature T = 293 K

No. exp.	F_α (mol/s)	x_α	F_ω (mol/s)	x_ω	P_ω (mol/s)	y_ω	p_h (MPa)	p_l (MPa)	θ	δ
1	0.0905	0.21	0.0384	0.173	0.0521	0.238	0.113	0.022	0.575	0.2
2	0.0893	0.21	0.0446	0.162	0.0446	0.252	0.113	0.026	0.500	0.2
3	0.0905	0.21	0.0459	0.165	0.0446	0.250	0.113	0.025	0.493	0.2
4	0.1178	0.21	0.0694	0.180	0.0484	0.256	0.117	0.025	0.411	0.2
5	0.0744	0.21	0.0223	0.156	0.0521	0.235	0.154	0.034	0.700	0.2
6	0.0781	0.21	0.0322	0.160	0.0459	0.243	0.117	0.024	0.587	0.2

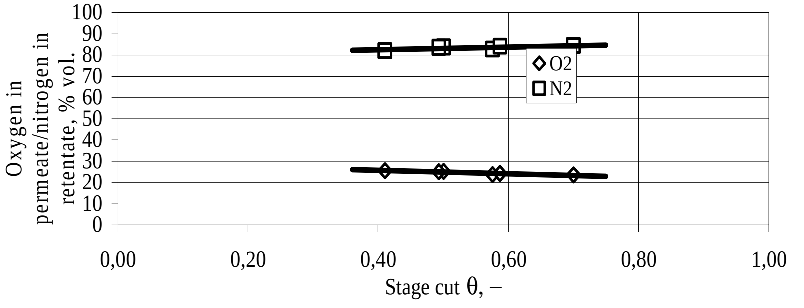

Fig. 5. Oxygen in permeate and nitrogen in retentate concentrations versus stage cut in the PVTMS membrane module for vacuum separation at pressures ratio equal to 0.2

An extra investigation has been performed to increase the efficiency of the process (increasing of the membrane area and feed flow). For this purpose, three different sets of the membrane modules have been prepared:

a) Two parallel connected PVTMS membrane modules with a vacuum pump,
b) Two PVTMS membrane modules connected in series where permeate from the first module serves as a feed flow for the second module, and
c) Two PVTMS membrane modules connected in series where retentate from the first module serves as a feed flow for the second module.

Obtained results for these three connections of the membrane modules are given in Table 4 and Fig. 6 for the two parallel connected membrane modules with a vacuum pump and Table 5 and 6 for the membrane modules connected in series where permeate and retentate, respectively, from the first module serves as a feed flow for the second module.

The results show increasing efficiency of the process in cases up to 25–40% vol. of the oxygen fraction and up to 95–99% vol. of the nitrogen fraction.

Table 4. Results of air separation in the two parallel connected PVTMS membrane modules with a vacuum pump at constant temperature T = 293 K

No. exp.	F_α (mol/s)	x_α	F_ω (mol/s)	x_ω	P_ω (mol/s)	y_ω	p_h (MPa)	p_l (MPa)	θ	δ
1	0.1252	0.21	0.0657	0.146	0.0595	0.279	0.118	0.033	0.475	0.3
2	0.1104	0.21	0.0471	0.149	0.0632	0.270	0.118	0.031	0.573	0.3
3	0.1197	0.21	0.0453	0.133	0.0744	0.256	0.137	0.053	0.622	0.4
4	0.1203	0.21	0.0273	0.133	0.0930	0.232	0.166	0.053	0.773	0.3
5	0.1184	0.21	0.0477	0.140	0.0707	0.247	0.141	0.041	0.597	0.3
6	0.1203	0.21	0.0570	0.156	0.0632	0.258	0.123	0.037	0.526	0.3
7	0.1097	0.21	0.0236	0.123	0.0862	0.231	0.182	0.055	0.785	0.3
8	0.1190	0.21	0.0558	0.153	0.0632	0.261	0.114	0.032	0.531	0.3

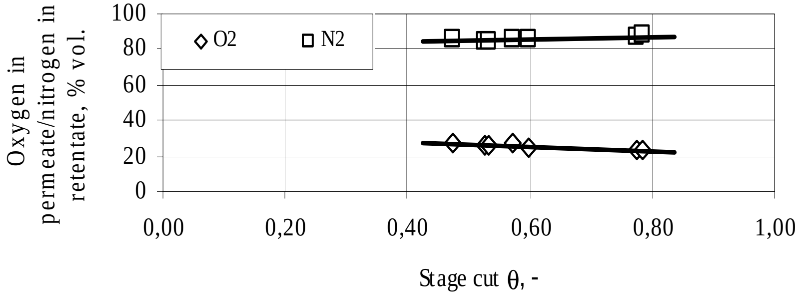

Fig. 6. Oxygen in permeate and nitrogen in retentate concentration versus stage cut in the two parallel connected PVTMS membrane modules for vacuum separation at pressures ratio equal to 0.3

Table 5. Results of air separation in the two connected in series PVTMS membrane modules (permeate strengthen)

No. exp.	T (K)	F_α (mol/s)	x_α	$F_{\omega 1}$ (mol/s)	$x_{\omega 1}$	$F_{\omega 2}$ (mol/s)	$x_{\omega 2}$	P_ω (mol/s)	y_ω	p_{h1} (MPa)	p_{h2} (MPa)	p_l (MPa)	θ	δ_2
1	279	0.448	0.21	0.109	0.097	0.1711	0.158	0.1674	0.317	2.25	0.96	0.157	0.374	0.164
2	278	0.563	0.21	0.246	0.125	0.2207	0.225	0.0967	0.360	1.90	0.65	0.138	0.172	0.212
3	277	0.605	0.21	0.298	0.127	0.2356	0.249	0.0719	0.368	1.79	0.55	0.122	0.119	0.222
4	279	0.441	0.21	0.150	0.125	0.0918	0.132	0.1997	0.290	2.22	1.15	0.210	0.452	0.183
5	278	0.382	0.21	0.141	0.135	0.0360	0.103	0.2046	0.280	2.05	1.13	0.220	0.536	0.195

Table 6. Results of air separation in the two connected in series PVTMS membrane modules at constant temperature T = 393 K (retentate strengthen)

No. exp.	F_α (mol/s)	x_α	$F_{\omega 1}$ (mol/s)	$x_{\omega 1}$	$F_{\omega 2}$ (mol/s)	$x_{\omega 2}$	$P_{\omega 1}$ (mol/s)	$y_{\omega 1}$	$P_{\omega 2}$ (mol/s)	$y_{\omega 2}$
1	0.275	0.21	0.163	0.154	0.0862	0.101	0.112	0.292	0.0769	0.217
2	0.355	0.21	0.185	0.138	0.0688	0.065	0.170	0.283	0.1166	0.179
3	0.365	0.21	0.211	0.150	0.1017	0.091	0.154	0.292	0.1091	0.209
4	0.432	0.21	0.294	0.167	0.2158	0.133	0.138	0.305	0.0781	0.252
5	0.428	0.21	0.260	0.154	0.1550	0.102	0.167	0.295	0.1054	0.219
6	0.421	0.21	0.277	0.173	0.2108	0.151	0.144	0.289	0.0663	0.229
7	0.278	0.21	0.173	0.178	0.0521	0.070	0.105	0.267	0.1209	0.226

No. exp.	p_{h1} (MPa)	p_{h2} (MPa)	p_{l1} (MPa)	p_{l2} (MPa)	θ_1	θ_2	δ_1	δ_2
1	0.523	0.510	0.126	0.125	0.406	0.686	0.241	0.245
2	0.758	0.748	0.152	0.170	0.478	0.806	0.201	0.227
3	0.678	0.668	0.151	0.125	0.422	0.721	0.223	0.187
4	0.628	0.588	0.140	0.125	0.319	0.500	0.223	0.213
5	0.748	0.723	0.157	0.150	0.391	0.638	0.210	0.207
6	0.718	0.688	0.235	0.280	0.342	0.499	0.327	0.407
7	0.718	0.713	0.360	0.125	0.379	0.813	0.501	0.175

The two PVTMS membrane modules connected in series have also been used for air and CO_2 separation. Obtained results (retentate strengthen) at temperature T = 393 K are given in Table 7.

Table 7. Results of air separation and CO_2 in the two connected in series PVTMS membrane modules at constant temperature T = 393 K (retentate strengthen)

No. exp.	F_α (mol/s)	$x_{\alpha C}$	$x_{\alpha O}$	$x_{\alpha N}$	$F_{\omega 1}$ (mol/s)	$x_{\omega 1C}$	$x_{\omega 1O}$	$x_{\omega 1N}$	$F_{\omega 2}$ (mol/s)	$x_{\omega 2C}$	$x_{\omega 2O}$	$x_{\omega 2N}$
1	0.200	0.068	0.2	0.74	0.120	0.047	0.167	0.786	0.0304	0.006	0.075	0.919
2	0.241	0.065	0.2	0.74	0.165	0.043	0.166	0.791	0.1029	0.023	0.134	0.843
3	0.370	0.040	0.2	0.76	0.228	0.025	0.163	0.812	0.1035	0.005	0.096	0.899

No. exp.	$P_{\omega 1}$ (mol/s)	$y_{\omega 1C}$	$y_{\omega 1O}$	$y_{\omega 1N}$	$P_{\omega 2}$ (mol/s)	$y_{\omega 2C}$	$y_{\omega 2O}$	$y_{\omega 2N}$
1	0.081	0.960	0.243	0.661	0.0893	0.066	0.208	0.726
2	0.076	0.105	0.257	0.638	0.0620	0.079	0.233	0.688
3	0.143	0.065	0.260	0.675	0.1240	0.042	0.221	0.737

No. exp.	p_{h1} (MPa)	p_{h2} (MPa)	p_{l1} (MPa)	p_{l2} (MPa)	θ_1	θ_2	δ_1	δ_2
1	0.523	0.518	0.273	0.120	0.402	0.848	0.522	0.232
2	0.404	0.384	0.163	0.110	0.314	0.572	0.403	0.286
3	0.718	0.698	0.280	0.130	0.385	0.720	0.390	0.186

Conclusions

Using a single PVTMS membrane module 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 30.5% vol. (Tables 2, 3). This result shows the efficiency of the module is far from the industrial expectation. The efficiency of the process can be increasing up to 40% vol. of the oxygen fraction and up to 99% vol. of the nitrogen fraction in the case of a series connection of two PVTMS membrane modules (Tables 5, 6). The series of PVTMS membrane modules can be also used for the separation of an air and carbon dioxide mixture with acceptable efficiency (Table 7).

There are also some other possibilities for the connections of the investigated membrane modules [7], as well as for different membrane modules; but based on the obtained results, we can formulate some general conclusions concerning the gas separation in the membranes.

The purer product is less recovered in the one permeate stage. The larger area of the membrane usually causes an increase in retentate purity, while the small area of the membrane increases the purity of permeate. The separation effect depends on the area of the membrane and on its selectivity. However, the selectivity does not always increase the separation independently of increasing the membrane area.

Increasing of the feed pressure or decreasing of 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 concentrations of the faster permeating component in permeate decreases gradually with the increasing of the stage cut θ.

The single membrane modules should be used in gas separation mostly for the coarse separation. In the case of the expectation of high purity of the flows (permeate or retentate), the area of the membrane has to be very large, which means that the membrane modules should be connected in a series. However, this type of installation is much more expensive, which could restrict its implementation.

The proper solution is to construct an integrated installation starting with a larger flow with the one membrane module and finishing with smaller flows with smaller modules connected in a series.

References

1. Zolandz R.R., Fleming G.K.: Gas permeation. [In]: Ho W.S.W., Sirkar K.K. (eds.): Membrane handbook. Chapman&Hall, New York–London, 1992, 17–101.
2. Scott K.: Handbook of industrial membranes. Elsevier Advanced Technology, Oxford 1997.
3. Koros W.J., Mahajan R.: Pushing the limits on possibilities for large scale gas separation: which strategies, J. Membrane Sci., 2000, 175, 181.
4. Mulder M.: Basic principles of membrane technology. Kluwer Academic Publishers, Dordrecht-Boston-London 1996.
5. Scott K., Hughes R. (eds.): Industrial membrane separation technology. Chapman&Hall, London 1996.
6. Kluzinski W.: Gas mixtures separations in membrane modules. Ph.D. dissertation, University of Gdansk, Poland, 2000 (in Polish).
7. Lababidi H., Al-Enezi G.A., Ettouney H.M.: Optimization of module configuration in membrane gas separation. J. Membrane Sci., 1996, 11, 185.

Reviewer:
Wojciech PIĄTKIEWICZ

Separacja powietrza w membranowym module PVTMS

Słowa kluczowe

Separacja gazów, moduły membranowe, powietrze, poliwinylotrimetylosilan.

Streszczenie

Przeprowadzono separację powietrza w rosyjskim, przemysłowym (*Kriogenmash*), membranowym module PVTMS, w półtechnicznej skali, na specjalnie zaprojektowanej do tego celu aparaturze. Pomiary wykonano dla różnych stosunków ciśnień i czterech różnych układów modułów membranowych: pojedynczego modułu, układu dwóch równolegle połączonych modułów, układu dwóch szeregowo połączonych modułów, w którym moduł drugi był zasilany permeatem z modułu pierwszego oraz układu dwóch szeregowo połączonych modułów, w którym moduł drugi był zasilany retentatem z modułu pierwszego. Otrzymane wyniki doświadczalne zostały przedyskutowane z punktu widzenia warunków stosowania modułów PVTMS oraz wydajności prowadzonych procesów separacji powietrza. Ponadto, posłużyły one do określenia własności i jakości badanych modułów membranowych.