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The application of membrane separator arranged in series-parallel mode to removal of carbon dioxide from flue gases generated in heat and power industry

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ABSTRACT

In the article, results of the study on the impact of selected process parameters, i.e., transmembrane pressure and feed mixture volumetric flow rate, on carbon dioxide separation using three UMS-A2 capillary polymer membranes made by the UBE Industries, are discussed. The membrane system was arranged in series-parallel mode. The study is a continuation of researches on membrane separator systems, which were carried out in Institute of Machines and Energy Devices within Task No. 1, "The study of the technology for high-performance "zero-emission" coal-integrated blocks with the capture CO_2 from combustion gases" of Strategic Programme: Advanced Technologies for Energy Generation. In preceding studies, three membranes M1, M2, M3 arranged in series M1-M2-M3 and parallel modes M1‖M2‖M3 [1–10] fed with simulated flue gases mixture of composition 15% CO_2, 15% O_2, 70% N_2 were used. Systems were operated at different volumetric feed flow rates and constant feed pressure. In the discussed study, the permeate obtained during the preceding research, of composition 57% CO_2, 23% O_2, 20% N_2, was used as a feed for membrane separation. Because these are only three membrane, next membrane configuration connections is the arrangement of mixed series-parallel.

Keywords: CO_2 capture; Membrane separation; Membrane

1. Introduction

Carbon dioxide is known as an environmentally harmful gas. Its emission generated by carbon combustion is ca. 34% of the overall worldwide CO_2 emission to the atmosphere [1]. Hence, in 2007, European Union set "2020 Climate and Energy Package", which mainly aims and assumes the reduction of greenhouse gases emission, including CO_2, to the atmosphere. This target may be obtained by a decrease of energy losses, an increase of both, energy generation efficiency and share of renewable and nuclear energy in overall energy balance as well as CO_2 sequestration (i.e., *CCS – Carbon Capture and Storage*) [1].

Introduction of membrane techniques to industrial scale processes was possible only after the development of suitable membrane module constructions, which enabled to obtain high separation membrane area in a relatively low volume of the module [11]. Moreover, the significant improvement in membranes dedicated to separation of carbon dioxide from flue gases, considering their permeability and selectivity, temperature and chemical resistance, life-time elongation, modular arrangement and low costs of production and exploitation may be observed [11–19]. Additionally, the preservation of gaseous phase of a feed stream during membrane separation is one of the main advantages of the technique, as it significantly improves process energy demand.

A membrane separator is a device, which comprises a set of membrane modules arranged in a series or a parallel modes or their combination. The selection of a proper membrane module and membrane separator construction depends mainly on their costs and desired process parameters [11–19]. Hence, the optimal combination of modules is very important. Generally, membrane separators characterize with relatively small dimensions, what is an additional advantage considering

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CO_2 capture introduction to existing heat and power plants. Additionally, such separators reveal operational simplicity and lack of mechanical parts, what results in a decrease of exploitation costs [1,4]. The main disadvantage of membrane separation is the need of proper preliminary cleaning of a raw gas stream (flue gases) due to dust, sulphur compounds and other contaminants content. Their presence in a treated stream affects separation efficiency and may damage a membrane material [3,4]. It also increases energy demand of the process.

2. Methods of evaluation of membrane separator

The laboratory stand for membrane CO_2 separation is illustrated in Fig. 1. For the experiment purposes, a mixture of gases comprised three (CO_2 15%, O_2 15%, N_2 70%) or two (CO_2 50%, N_2 50%), (N_2 80%, CO_2 20%) components was prepared and stored in 50 L cylindrical tanks at 200 bar pressure.

The measuring system equipped with two gas analyzers, i.e., double-channel analyzer of CO_2 by Atest Gaz and the analyzer for O_2, CO_2 and CO content by Servomex, model 4900, was used. In order to assure the highest purity of gas mixture sample fed into the analyzer, the stand was equipped with the system for induction and preparations of a sample. Double-channel analyzers of CO_2 and O_2 by Atest Gaz was built into the system at the gas path and it was used to prepare the sample of gas to the measurement. It consisted of:

- the set of electromagnetic valves,
- the dehydrator along with the small pump of the condensate,
- charcoal filters (responsible for the removal coarse-grained solid contaminants, hydrogen sulphide, ammonia and other aggressive substances),
- exact filters (for removal of eventually remaining coarse-grained particulates),
- gas distributor (the dryer and the air fan hold the humidity of the sample up to the value close to atmospheric – 30%–60% RH),
- small pumps of gas and the shock-absorber of the small pump (at the lack of the pressure or at the vacuum pressure it secures the specific gas flow up 0.5 l min^{-1}),
- the flow-meter and the sensor for flow stop detection, and
- additional external shock-absorber of the pressure.

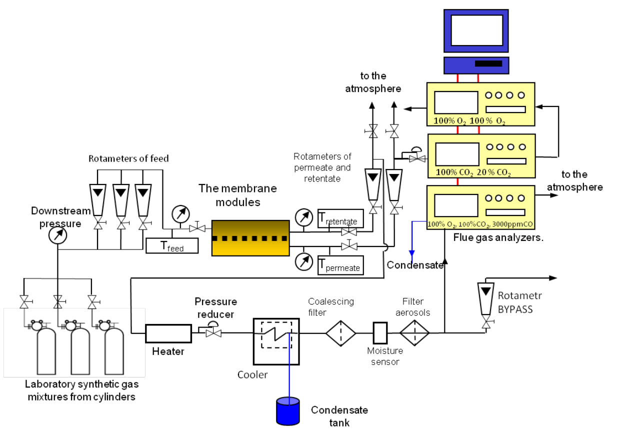

Fig. 1. The scheme of the laboratory site for carbon dioxide membrane separation research.

During the preceding research, we used dry reference gas mixtures: 50% CO_2, 50% N_2 and 20% CO_2, 80% N_2 placed in cylinders, to identify the operating parameters of the individual membranes and after separators. Then, dry reference gas mixtures of the composition: 4% O_2, 15% CO_2, 81% N_2, and 15% O_2, 15% CO_2, 70% N_2 were used in tests. That mixtures simulated synthetic flue gases generated during fuel combustion in power plants but they were dry and with no contaminants. Such procedure was due to protect membranes from damage. Gas mixture containing: 15% O_2, 15% CO_2, 70% N_2, during preceding research, was simulated up limits of concentrations oxygen and carbon dioxide in gases produced at power plants. For this reason, in the article it was named synthetic flue gases. Membranes used in this study are sensitive to contamination. A measuring system does not allow to use real flue gas, therefore synthetic reference dry gas was used to simulate a real flue gases. After completion of the tests separators: parallel and serial, it was decided to run the research in cascade of separators. Hence, a mixture of gases of composition corresponding to the permeate obtained during previous studies was prepared. Previously, separators were fed with gas mixture containing 15% O_2, 15% CO_2, 70% N_2. For this gas composition, it was decided to make a diagnosis of a separator arranged in series-parallel mode, which might be operated in cascade.

The previous test results are discussed in detail in [1–10, 20–22]. On the basis of studies and simulations surface area of a single membrane was estimated and it was found to be approximately 0.011 m^2.

During the evaluative part of investigations, separation coefficients, i.e., purity of permeate – the share of CO_2 in the permeate stream Y_{CO_2}, CO_2 recovery rate (R) and selectivity coefficient (α), were determined. Values of those coefficients were obtained using direct measurements of process streams temperature and composition (concentration of particular gases in membrane inflow and outflow stream. The evaluation criteria was based on values of coefficients, which were obtained by direct measurements or by appropriate calculations [1,3,4,8,9]:

- purity of permeate Y_{CO_2} – direct measurements
- recovery rate R defining the amount of carbon dioxide present in the feed stream, which permeated through the membrane:

$$R = \frac{n_P Y_{CO_2}}{n_N X_{CO_2}} \tag{1}$$

- selectivity coefficient α, which is defined as a ratio of volume fraction of particular components of permeate (Y_{CO_2}/Y_{N_2}) to volume fraction of corresponding components in feed (X_{CO_2}/X_{N_2}):

$$\alpha = \frac{Y_{CO_2}}{Y_{N_2}} \Bigg/ \frac{X_{CO_2}}{X_{N_2}} \tag{2}$$

The performed studies were focused on separation efficiency of three membranes arranged in series-parallel mode. In Fig. 2 the scheme of applied module arrangement is presented. The feed stream was introduced to module M1, and the retentate remaining after M1 separation was used as the feed for modules M2 and M3. Retentates from M2 and M3 modules were collected in common. On the other hand, permeates obtained at all three membranes were collected as one stream, which was further analyzed, similarly as collective stream of M2 and M3 retentates.

During research, concentrations of CO_2 and O_2 were measured directly using combustion gas analyzers. Additionally, flows and temperature of gases incoming to and outcoming from the separator were directly measured. During all tests, the temperature of gases was maintained constant and equal to 22°C. For the one test measurement time was about 6 h.

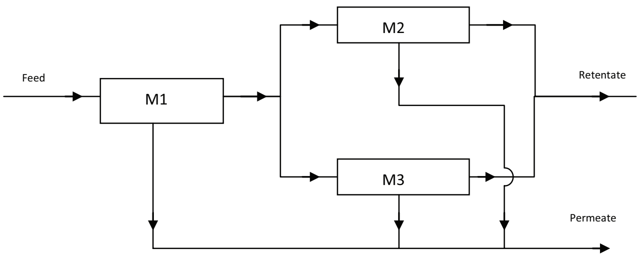

Fig. 2. The scheme of combined series-parallel membrane separator mode.

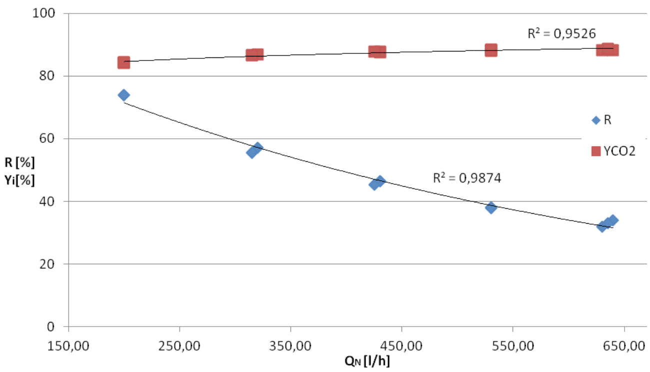

Fig. 3. Separation coefficients Y_{CO_2} and R as a function of volumetric flow rate Q_N of feed of composition 57% CO_2, 23% O_2, 20% N_2.

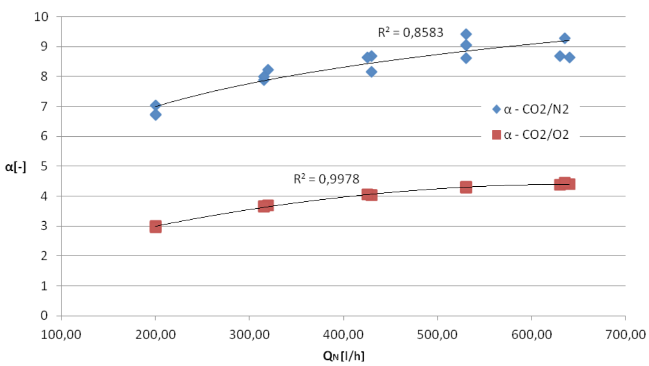

Fig. 4. Selectivity coefficients α_{CO_2/N_2} and α_{CO_2/O_2} as a function of volumetric flow rate Q_N of feed of composition 57% CO_2, 23% O_2, 20% N_2.

In the discussed study, permeate obtained during the preceding research (synthetic flue gases) is used as a feed in the present study. The constructed membrane separator was supplied with synthetic gaseous mixture of composition 57% CO_2, 23% O_2, 20% N_2. During the study, feed flow rate was changed within the range of 200 to 640 l h^{-1}, while the feed pressure was variated from 5 to 6 bars.

Selectivity coefficients α for nitrogen and oxygen were calculated using Eq. (2) [3]. The rate of carbon dioxide recovery was calculated using Eq. (1). Results obtained during performed experiments are presented in Figs. 3–13.

3. Discussion of results

In Figs. 3–8 characteristics of separation coefficients R, Y_{CO_2} and α in dependence of volumetric flow rates of feed, retentate and permeate, respectively, are presented. In Figs. 9 and 10 separation coefficients R, Y_{CO_2} and α as a function of feed pressure are shown. In Fig. 11 concentration of permeate, Y_{CO_2}, as a function of feed pressure is given.

Values of selectivity coefficient decreased with the decrease of feed volumetric flow rate and were in the range of α_{CO_2/N_2} = 6.7–9.4 and α_{CO_2/N_2} = 3–4.4.

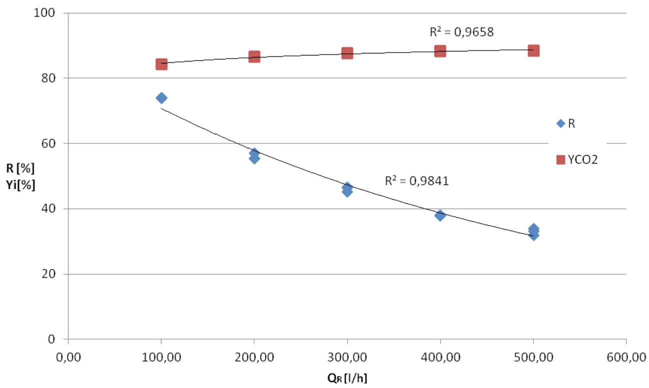

Fig. 5. Separation coefficients Y_{CO_2} and R as a function of volumetric flow rate of retentate Q_R obtained after separation of feed of composition 57% CO_2, 23% O_2, 20% N_2.

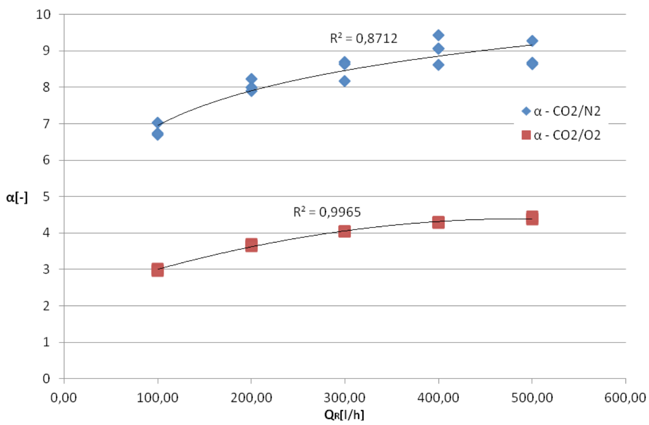

Fig. 6. Selectivity coefficients α_{CO_2/N_2} and α_{CO_2/O_2} as a function of volumetric flow rate of retentate Q_R obtained after separation of feed of composition 57% CO_2, 23% O_2, 20% N_2.

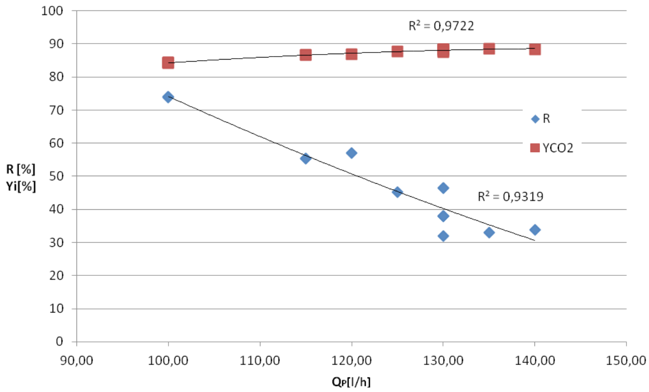

Fig. 7. Separation coefficients Y_{CO_2} and R as a function of volumetric flow rate of permeate Q_P obtained after membrane separation of feed of composition 57% CO_2, 23% O_2, 20% N_2.

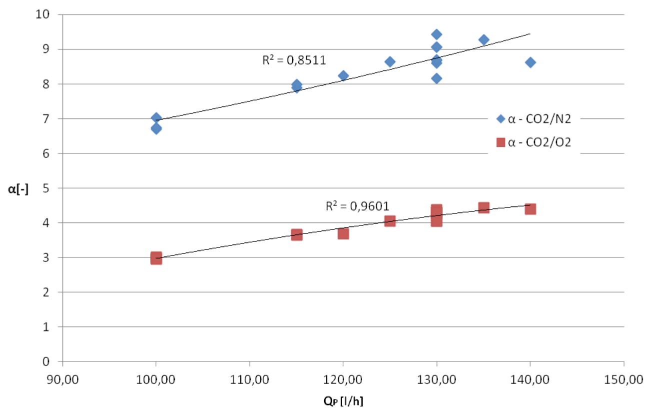

Fig. 8. Selectivity coefficients α_{CO_2/N_2} and α_{CO_2/O_2} as a function of volumetric flow rate of permeate Q_P obtained after membrane separation of feed of composition 57% CO_2, 23% O_2, 20% N_2.

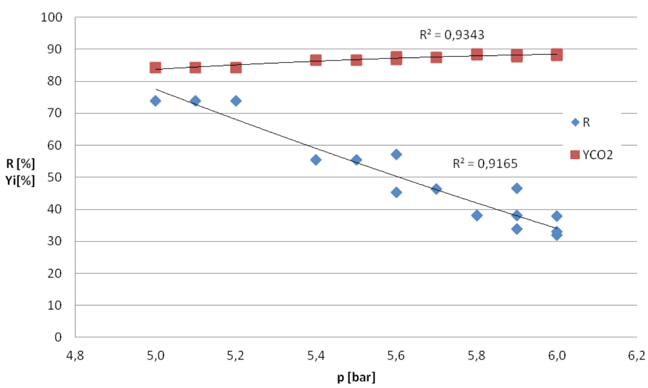

Fig. 9. Separation coefficients Y_{CO_2} and R as a function of pressure of feed of composition 57% CO_2, 23% O_2, 20% N_2.

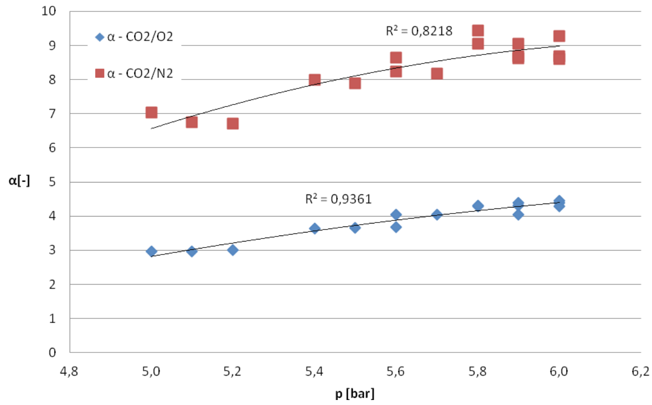

Fig. 10. Selectivity coefficients α_{CO_2/N_2} and α_{CO_2/O_2} as a function of pressure of feed of composition 57% CO_2, 23% O_2, 20% N_2.

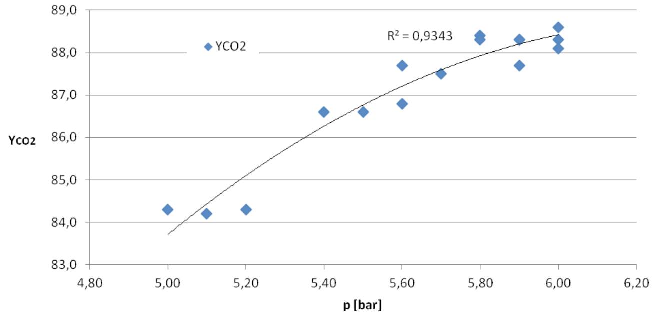

Fig. 11. Separation coefficients Y_{CO_2} as a function of pressure of feed of composition 57% CO_2, 23% O_2, 20% N_2.

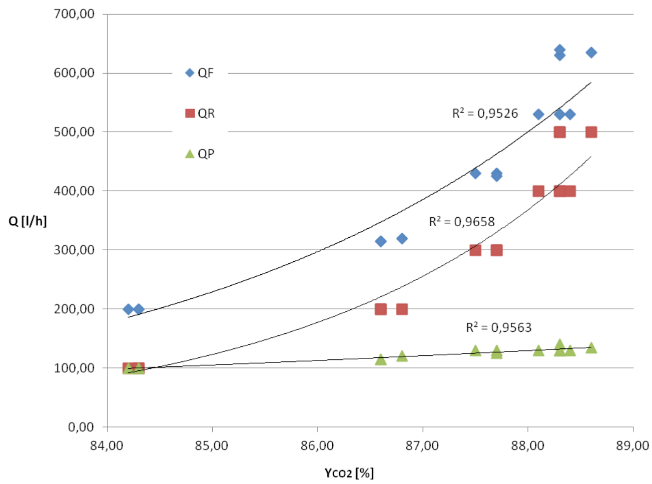

Fig. 12. The dependence of permeate concentration Y_{CO_2} on volumetric flow rates of feed, retentate and permeate for feed mixture composition CO_2 57% CO_2, 23% O_2, 20% N_2.

The highest CO_2 recovery rate R equal to 73.9% was reached at feed pressure 5 bar and feed volumetric flow rate 200 l h^{-1}. Generally, CO_2 recovery rate varied in the range of 32%–73.9% and it increased with feed pressure increase and feed volumetric flow rate decrease.

In Fig. 12 concentration of permeate Y_{CO_2} in a dependence of feed, retentate and permeate volumetric flow rates is shown. Obtained values of the coefficient varied from 84.2% to 88.6%. The highest value was obtained for feed volumetric flow rate 635 l h^{-1} and feed pressure 6 bar.

In Fig. 13 the concentration of oxygen in permeate Y_{O_2} in dependence of feed, retentate and permeate volumetric flow rates is shown. The content of O_2 increased with the decrease of all streams volumetric flow rates as well as with the decrease of feed pressure. The amount of O_2 in permeate was in the range of 8%–11.5%.

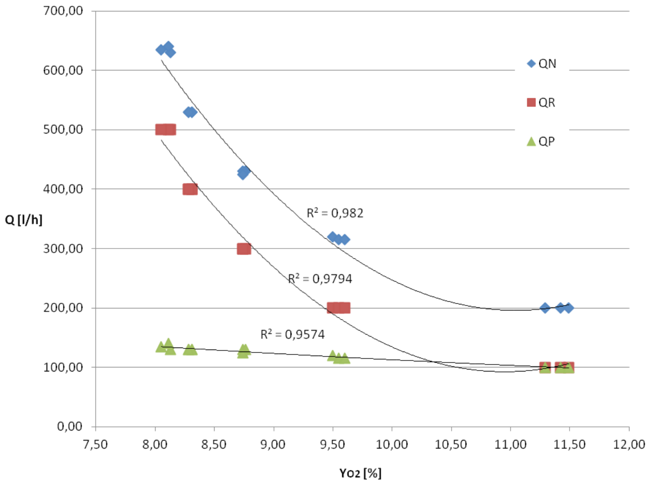

Fig. 13. The dependence of permeate concentration Y_{O_2} on volumetric flow rates of feed, permeate and retentate volumetric flow rates for feed mixture composition 57% CO_2, 23% O_2, 20% N_2.

During investigations measured volumetric flow rates of permeate were in the range of 100–140 l h^{-1} and the highest value was reached at feed flow rate equal to 640 l h^{-1}. In general, permeate volumetric flow rate decreased with both, feed volumetric flow rate and feed pressure decrease.

4. Conclusions

In the discussed study the impact of process parameters, i.e., feed volumetric flow rate (varied within 200 l h^{-1} to 640 l h^{-1}) and feed pressure (5 and 6 bars) was discussed. The applied membrane separator comprised three membranes arranged in series-parallel mode.

The performed study revealed that the concentration of CO_2 in permeate, Y_{CO_2}, was similar for all investigated process configurations. The highest values of the parameter varied in the range of 88%–88.8%, while the lowest ones changed from 83.1%–84.9%.

The highest permeate volumetric flow rate, equal to 140 l h^{-1}, was obtained for feed volumetric flow rate 640 l h^{-1} and feed pressure 6 bar.

The study enables to conclude that:

- CO_2 recovery rate is strongly dependent on feed pressure (the higher pressure the higher R);
- the decrease of feed pressure, despite feed volumetric flow rate increase, results in recovery rate decrease;
- the amount of O_2 in permeate (Y_{O_2}) depends on feed volumetric flow rate Q_F (the lower Q_F, the higher Y_{O_2});
- the decrease of both, feed volumetric flow rate and pressure, results in the increase of O_2 amount in permeate;
- permeate volumetric flow rate Q_P strongly depends on feed pressure (the higher feed pressure, the higher Q_P);
- at the decrease of feed pressure and increase of feed volumetric flow rate Q_P decreases;
- the concentration of permeate, Y_{CO_2}, strongly depends on feed volumetric flow rate;
- selectivity coefficients are mainly depended on feed volumetric flow rate.

Symbols

Y_{CO_2}	—	Concentration of the permeate for CO_2, %
Y_{O_2}	—	Concentration of the permeate for O_2, %
X_{CO_2}	—	Concentration of the feed for CO_2, %
n_P, Q_p	—	Flow of permeate, l h^{-1}
n_N, Q_N	—	Flow of feed, l h^{-1}
Q_R	—	Flow of retentate, l h^{-1}
p	—	Feed pressure, bar
R	—	Recovery rate, %
α	—	Real selectivity factor
R^2	—	Coefficient of correlation

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