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Investigation of Applicability of Polyimide Membranes for Air Separation in Oxy-MILD Zero-Emission Power Plants

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Abstract. Primary element of an oxy-combustion plants is ambient air separation unit. This paper presents the results of experimental research concerning the parameters of the separation of N_2/O_2 from ambient air, using capillary polymer membranes, potentially applicable in oxy-combustion technology, under variable operational conditions. Collected data were utilized to approximate continuous functions describing the variability of essential parameters of the air separation based on such membranes. The functions were introduced to develop a complete mathematical model of the separation unit, intended to be applied in oxy-Moderate or Intense Low Oxygen Dilution (oxy-MILD) zero-emission plants. Computational analyses were performed for three variants of the unit's configuration: serial connection of membrane modules, unit with retentate recirculation and unit with permeate recirculation. The results of the research, in the form of sets of characteristic curves, depicting parameters of the separation process as a function of the variable operational conditions, show that crucial differences to the subsequent separation parameters (permeate purity, real selectivity coefficient, recovery coefficient) and with regard to the power consumed, were obtained. The highest parameters of the module were gained for serial connection, whereas the lowest – for permeate recirculation. The lowest energy consumption was acquired for the retentate recirculation variant.

1 Introduction

Technological processes of energy generation are mainly based on the combustion of fossil fuels, such as hard coal, lignite, natural gas, or crude oil. The by-products of those processes include a series of volatile chemical compounds. Among them are CO_2 , N_2 , H_2O , SO_x , and NO_x , as well as volatile organic compounds. In addition, particulate matter, formed due to the imperfect oxidation of coal, which is commonly lifted with the above-mentioned gases, should be listed from the outset [1,2,3,4]. Due to their toxic influence on humans and the natural environment, a number of such compounds should be separated from the stream of exhaust gases before its emission to the atmosphere. Similarly, compounds affecting global warming should be separated as well [1,5,6,7]. All technologies, devoted to reduce emissions of potentially dangerous compounds from the solid fossil fuels, are commonly denoted as the clean coal technologies (CCT) [1,2].

Following the concept of the common utilization of clean coal technologies in commercial power generation units, zero-emission power plants units are designed. These units are characterized by the almost neutral environmental impact of their operation [6,8]. Considering the reduction of CO_2 emissions, the above-mentioned units utilize technology such as carbon capture and storage (CCS) installations. In order to

introduce such installations, three technological concepts are used: pre-combustion – capturing CO_2 before the combustion of the fuel, post-combustion – capturing CO_2 after the process of combustion, and oxy-combustion – combustion of the fuel under high oxygen concentration conditions [8,9].

The main aim of the oxy-combustion process is an increase in the percentage share of carbon dioxide in the total stream of exhaust gases [9]. The oxygen is produced in an air separation unit, where ambient air is separated into streams of oxygen and nitrogen with remaining residual gases. Rise in the efficiency of the unit with simultaneous decrease in emissions of selected pollutants, as NO_x and CO , is characteristic for the innovative Moderate or Intense Low Oxygen Dilution (MILD) technology [10]. In the oxy-MILD combustion technology, comprising both abovementioned technologies, the oxygen concentration in the oxidizer cannot exceed 40%, since excess oxygen content results in a drop of content of heat absorbing gases, such as nitrogen and carbon dioxide. The main effect of their shortage is a crucial increase in the temperature of the exhaust gases [10]. The separation of oxygen from ambient air using membrane methods uses semipermeable films (membranes) made from polymeric and other materials [11,12]. Their vital advantage, comparing to commonly implemented, commercially

mature technology of pressure swing adsorption (PSA), is lack of permanent adsorbents and requirement for alternating depressurization of the adsorber vessel.

The membrane separation module (membrane separator) is formed by a set of single membrane modules, connected in parallel, in series, or with any combination of these simple connections. Such constructions are required to have a compact size, which is a crucial feature in the case of widespread introduction of carbon capture installations to existing power plants and other industrial units [13,14]. The selection and type of membrane modules, dedicated to be used during the construction of a given membrane separator, depend mainly on the available expenditure and the nominal operational parameters of the unit [3,6,15]. Thus, the optimal configuration of a membrane separation unit with regard to its internal construction remains an essential issue.

The main objective introduced with the paper is experimentally-based analysis of operational parameters of selected variants of the separators' configuration. As a novel approach, semi-empirical model, constructed on the basis of the experiment, was utilized to predict complex parameters of the separator.

2 Materials and Methods

2.1 Methodology of the experimental research

The scheme of the experimental setup, utilized during the experimental part of the research, is presented in Fig. 1. The methodology of experimental research consisted in supplying the module (fig. 1, point 1) with a compressed gaseous mixture at initial temperature of 15°C, stored in external tanks (fig. 1, point 2) of 10m³ total volume under a pressure of 200 bar. In order to reduce and stabilize the pressure in the experimental unit, multiple two-stage pressure reducers were applied (fig. 1, point 3). The setup was equipped with the feed heater (fig. 1, point 9) to increase and stabilize temperature of the inflowing mixture at stable level of 23°C. The synthetic mixture, utilized during the investigations, simulated dry air and consisted exclusively of nitrogen (79%) and oxygen (21%). At the outflow duct of the tank, a set of instruments (fig. 1, point 4), including a gauge manometer and a thermocouple, were located. At the same duct, a throttling valve (fig. 1, point 5), an additional flow stabilizer, was located. The gaseous mixture was supplied to the membrane module, which consisted of a NM-B02A capillary membrane produced by UBE Industries Ltd, Japan. The choice was based on its widespread commercial availability and relatively low price compared to similar membranes produced by other manufacturers, crucial for the investment costs in the case of large-scale separation units [11,14,16].

The gaseous products of the separation process were transferred to the measurement and control units, containing pressure sensors (fig. 1, point 6), thermocouples, and rotameters (fig. 1, point 7). The control function of the unit was fulfilled by additional throttling valves (fig. 1, point 8), responsible for the

regulation of the flow of the gases transported to certified gas composition analyzers.

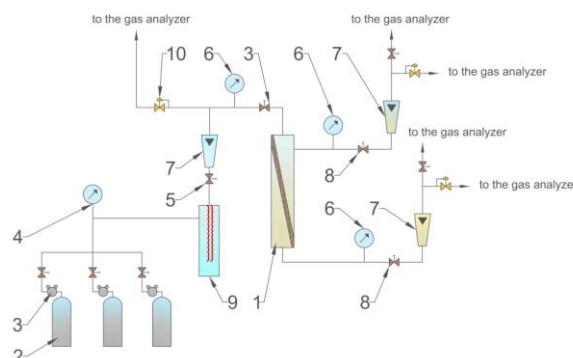


Fig. 1. Scheme of the experimental test stand: 1 - membrane module, 2 - external tanks of gaseous mixture, 3 - pressure reducers, 4 - unit of measuring instruments, 5 - throttling valve, 6 - gauge manometer, 7 - rotameter, 8 - control/throttling valves, 9 - the feed heater and humidity control unit, 10 - safety valve.

During the experimental phase of the research, the values of selected separation process parameters were identified, including: concentration of O₂ (Y_{O₂}) or N₂ (Y_{N₂}) in the separated flow, recovery coefficient of O₂ or N₂ (R), and the real separation factor (α). According to the literature [10,11,17,18], the parameters mentioned were described as:

- a) purity of the permeate, the concentration of oxygen in the permeate stream, Y_{O₂}
- b) recovery coefficient R, the ratio of elementary oxygen flows in the permeate and feed streams, defined by equation (1):

$$R = \frac{n_p Y_{O_2}}{n_F X_{O_2 F}} \quad (1)$$

- c) real separation factor α, defined as the ratio of the concentrations of the ingredients of the mixture in the permeate stream relative to the ratio of the concentrations of the ingredients in the retentate stream, defined for oxygen with respect to nitrogen, as given by equation (2):

$$\alpha = \frac{\left(\frac{Y_{O_2}}{Y_{N_2}}\right)}{\left(\frac{X_{O_2 R}}{X_{N_2 R}}\right)} \quad (2)$$

These values were obtained on the basis of direct measurements of the temperatures and capacities of the feed, permeate, and retentate streams, performed by measurement and control units located in subsequent ducts, as well as the oxygen and nitrogen concentrations identified by the gas analyzers.

2.2 Description of the model

On the basis of the experimental research, crucial empirical functions, describing the dependence of vital parameters of the separation process quality on the environmental conditions, were identified. Regression functions, obtained for a single membrane module,

stated average regression functions characterized by the highest value of the Pearson product-moment correlation coefficient and were acquired using the respective empirical data analysis. The acquired regression equations were further used as fundamental functions of the mathematical model of the separation unit. As discussed in [19], to obtain results of satisfactory accuracy, a computational model of a separation unit was extended to include description of the Joule-Thomson effect, appearing in the case of real units.

The calculations were realized by executing series of computational steps each iteration. The steps mentioned included:

- a) identification of thermophysical properties of the gaseous starting mixture used for the separation (including its density, viscosity, and thermal conductivity) on the basis of the real-gas model,
- b) determination of nominal maintenance parameters of the membrane module, basing on the properties of the separated gas and empirical regression equations,
- c) estimation of the active area of the membrane, basing on the pressure drop condition,
- d) estimation of the influence of the Joule-Thomson expansion effect on the behavior of the gas flowing through the separation module,
- e) recalculation of parameters basing on results of the Joule-Thomson expansion effect estimation,
- f) estimation of power demand of the unit under set operational conditions.

The scheme of algorithm of the computations performed by mathematical model of the unit is presented in Fig. 2.

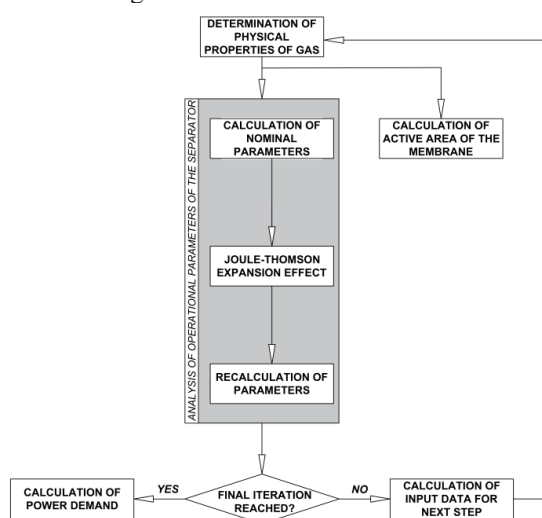


Fig. 2. Algorithm of calculations within the computational research

3 Results

3.1 Results of the experimental research

In fig. 3a to fig. 3b, the characteristic curves of recovery coefficient and permeate purity, performed for a constant retentate stream flow (Q_R) equal to 500l/h, at varying feed pressure are indicated. Results of the permeate purity (YO_2) and the oxygen recovery

coefficient (R) of the permeate as a function of the retentate stream flow (Q_R), at a constant pressure equal to 5 or 6 bar, are presented in fig. 4a and fig. 4b, respectively. In fig. 4c to fig. 4d results from the NM-B02A membrane module, concerning the dependence of variable permeate flow and retentate pressure on the real separation factor (α), are indicated.

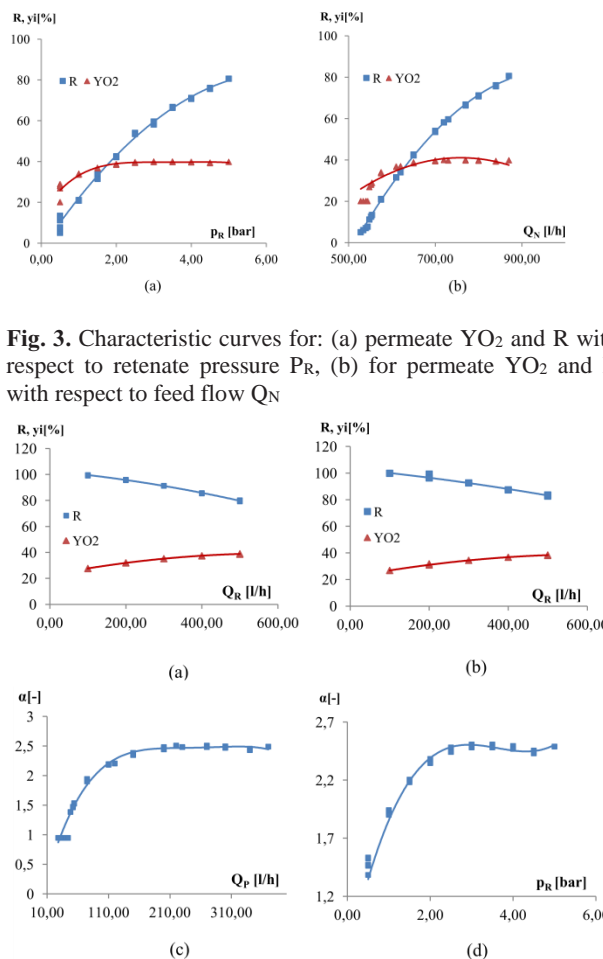


Fig. 3. Characteristic curves for: (a) permeate YO_2 and R with respect to retentate pressure p_R , (b) for permeate YO_2 and R with respect to feed flow Q_N

Fig. 4. Experimental characteristic curves: (a) for the permeate YO_2 and R as a function of retentate flow Q_R for a pressure of 5 bar, (b) for the permeate YO_2 and R as a function of retentate flow Q_R for a pressure of 6 bar, (c) for α with respect to permeate flow Q_P , (d) for the real separation factor α with respect to retentate pressure p_R .

3.2 Results of the computational analysis

The first of the investigated configuration variants involved the serial connection of successive modules by the permeate duct (stream flow of the permeate from one module became the feed for the next one). The configuration is schematically presented in fig. 5. In fig. 6a and fig. 6b, the results of the model-based analysis concerning the serial connection of modules are presented. The graph shown in fig. 6a depicts an estimation of the separation factor on number of modules, depending on feed flow Q_N . The results of further investigation, shown in Fig. 6b, indicate the influence of the number of modules connected in series on the permeate purity YO_2 . measurements of the temperatures and capacities of the feed, permeate, and

retentate streams, performed by measurement and control units, as well as the oxygen and nitrogen concentrations identified by the gas analyzers.

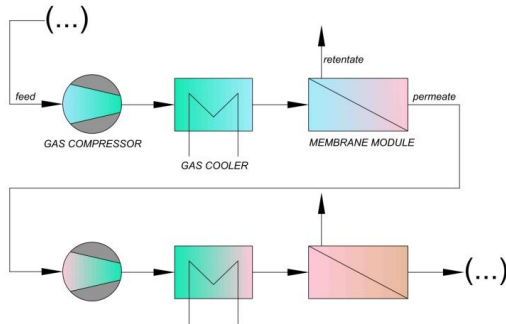
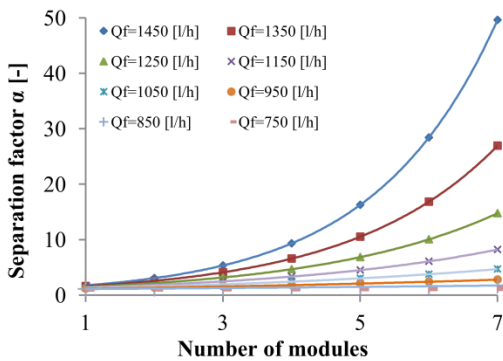
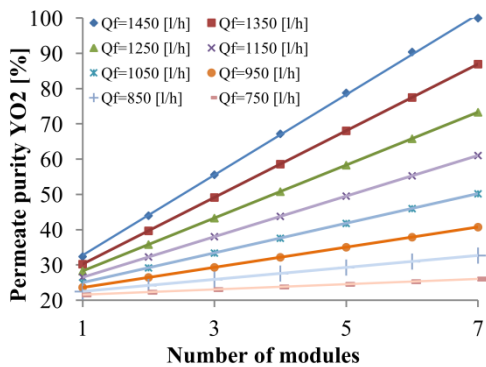


Fig. 5. Scheme of the membrane separator with serial connection of modules (variant I)



(a)



(b)

Fig. 6. Characteristic curves of the variant with serial connection of modules: (a) dependence of separation factor on number of modules in series for varying feeds, (b) dependence of purity of the permeate on number of modules in series for varying feeds

The results of further analysis, concerning the second of the investigated separator configurations, based on a single-module separation unit with multiple retentate recirculation (fig. 7), are shown in fig. 8a to fig. 8b.

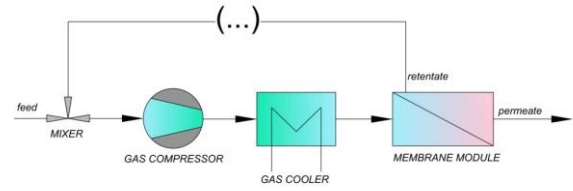
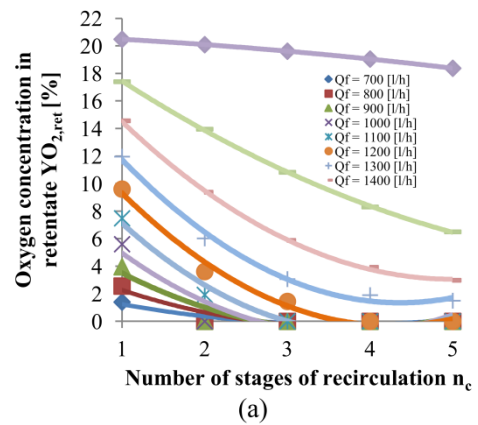
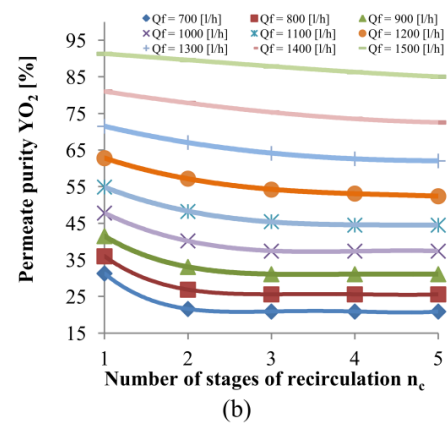


Fig. 7. Scheme of the separator with multiple recirculation of the retentate (variant II)

Figure 8a depicts the dependence of oxygen concentration X_{O2R} in the retentate as a function of the number of retentate recirculation stages n_c and primary feed flow values Q_N . The dependence of permeate purity on the number of stages of retentate recirculation for varying feed flows Q_N is indicated in Fig. 8b.



(a)



(b)

Fig. 8. Characteristic curves of the variant with multiple retentate recirculation: (a) oxygen concentration in the stream flow as function of retentate recirculation stages for variable feed flows, (b) permeate purity as function of retentate recirculation stages for variable feed flows

The last of the analyzed variants of the membrane separation unit configurations was the single-module unit with multiple permeate recirculation n_{CP} , presented schematically in fig. 9. Results of the computation of minimal and maximal power demand of the configurations: serial connection of the modules (variant I), retentate recirculation (variant II) and the permeate recirculation (variant III) are presented in Table 1.

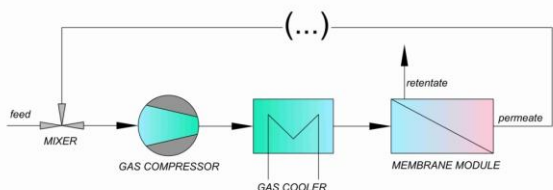


Fig. 9. Scheme of the separator with multiple recirculation of the permeate (variant III)

The graph, presented in fig. 10 indicate the dependence of the permeate purity Y_{O_2} on the number of recirculations for this case of the separator configuration.

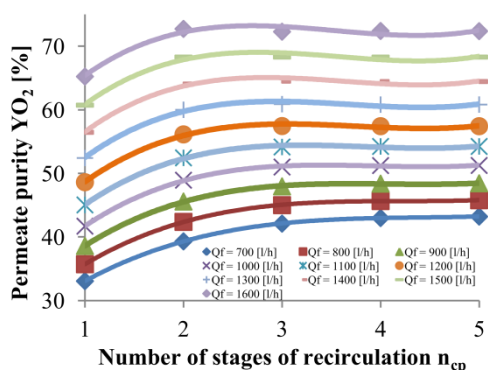


Fig. 10. Dependence of permeate purity on number of recirculation stages for variable feed flows

Table 1. Estimation of minimal and maximal power demand of investigated variants

	Min. power demand, W	Max. power demand, W
Serial connection of the modules	12	90
Retentate recirculation	7	58
Permeate recirculation	20	201

4 Discussion

At a constant retentate stream flow (Q_R) equaling 500l/h, with an increasing pressure of the retentate, the rise of the recovery coefficient (R) and the permeate purity (Y_{O_2}) was observed, as seen in fig. 3a. Figure 4c, indicating the characteristic curve for the separation factor (α) with respect to the permeate stream flow (Q_P), shows that at constant retentate stream flow value (Q_R) equal to 500l/h with increasing permeate flow (Q_P), a rapid increase in separation factor (α) appeared.

The rise in the number of modules in serial connection, forming the variant I of the membrane separator (fig. 5), resulted in an exponential increase in the separation factor of the system, as indicated in fig. 6a. However, visible changes in the separation factor depended on the feed flow supplying the system: for feed flows below 1000 l/h, the value of the factor for a seven-module unit equaled roughly twice the value of the separation factor for a single-module system. significant fluctuations of the dependence were observed

for any of the investigated variants. The almost linear rise in the purity of the permeate was observed for this configuration of the separator, as presented in fig. 6b. Nevertheless, slope of the discussed trend vitally depended on the feed flow – the highest values of oxygen concentration in the permeate were observed for the largest feed flow, exceeding 1000 l/h.

As indicated in Fig. 8a, multiple retentate recirculation (fig. 7) might be used to reduce the oxygen concentration in the retentate. However, the crucial dependence of the drop in oxygen concentration both on the number of recirculation stages and the feed flow should be emphasized – for flows below 1000 l/h, triple retentate recirculation allowed to obtain retentate with almost no oxygen content. Nevertheless, an increase in the feed flow resulted in a significant rise in the number of recirculation stages required to obtain such an effect. For flows exceeding 1300 l/h, the oxygen fraction in the retentate was significant, even in the case of its recirculation for five times. Nevertheless, rise in the number of retentate recirculation stages resulted in drop of the permeate purity, especially visible for low feed flows. As indicated in Fig. 8b, for feed stream flow of 700 l/h, introduction of double retentate recirculation lead to drop permeate purity exceeding 10 percentage points.

Considering the variant III of the investigated separator (fig. 9), the characteristic curve, indicated in fig. 10, showed a rise in purity with an increase in the number of stages for lower feed flows, but significant fluctuations of purity were seen for higher flows (exceeding 1300 l/h), with the peak of the purity observed for double permeate recirculation. The stable rise in the permeate purity with rise in permeate recirculation stages was observed only for feed flows below 900 l/h.

Results of estimation of the power demand, presented in Table 1, indicate, that the separator with permeate recirculation (variant III) consumes up to 2.23 times more energy than the serial connection-based unit. The retentate-recirculation based separator might be deemed as the most energy efficient construction, considering both for the minimal and maximal power demands

5 Conclusions

Research concerning the variant I configuration of the membrane separation unit, consisting of a number of modules connected in series, indicated a linear rise in the power demand of the unit with an increase in the number of module membranes present. A similar influence was indicated on increasing the feed flow. A rise in the number of modules also resulted in an exponential increase in the separation coefficient of the system, clearly depending on the feed flow. This observation led to a vital conclusion: that the serial connection of modules in a compound separation unit might lead to significant operational benefits in the case of large volumetric flows of the feed. Considering all results of the research discussed, utilization of a serial connection of single modules is the best in case of large exhaust gas

flows, since this particular configuration leads to satisfactory separation process parameters with acceptable power demand. Nevertheless, considering low feed flows, which might occur for instance during the start-up of the unit, the operational parameters of such units are insufficient for oxy-MILD technology applications.

Considering the results of the computational analysis of the system based on multiple retentate recirculation, the vital result of a non-linear fall in the oxygen concentration in the permeate following a rise in the number of recirculation stages was proven by the results acquired. The rate and value of the reduction in oxygen concentration depended strongly on the feed flow. Thus, the above-mentioned observation suggests that the introduction of retentate recirculation leads to a decrease in the operational parameters of the separation unit with regard to the purity of the permeate. This is caused by the significantly greater pressure losses between the feed and the permeate outlet than between the feed and retentate outlet in the membrane modules being considered. Therefore, the real applicability of such a configuration in oxy-MILD zero-emission power units would be marginal.

Analysis of the results of the third variant of the membrane separation unit with the multiple permeate recirculation showed the positive influence of an increase in the number of permeate recirculation stages on the permeate purity, especially considering low feed flows. Nevertheless, for high feed flows, use of the unit with further gas recirculation resulted in unstable performance and fluctuations of the permeate purity, damping with a rise in the number of stages. This observation might be explained by locally exceeding the maximum oxygen transport capacity of the investigated membrane. However, besides its potentially attractive characteristics of operational parameters, applicability of such construction of the membrane separator is marginal due to essentially higher power demand, than other constructions compared.

Considering general application of investigated units in oxy-MILD zero-emission power plants, results of the research indicate, that investigated membrane separation technology is only partially able to compete with mature cryogenic methods, basically due to low purity of the permeate. Furthermore, in the case of membrane separators, utilization of several stages of cascade seems to be required, leading to high number of compressors and vital rise in overall power demand of the unit.

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