Development of heterogenous capillary membranes with programmable properties made of PEBA copolymer for CO_2 removal and testing their properties

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ABSTRACT

The process of membrane gas separation is a technique of increasing interest in industrial applications. In many cases, the membrane gas separation process can replace or support commonly used technologies for gas mixtures separation, such as adsorption, absorption or cryogenic distillation. One of the areas in which the research on the development and implementation of new types of membranes is particularly intensive is the technology of CO_2 removal from mixtures containing also CH_4 or N_2. The need to extract CO_2 from these mixtures results from economic, legal, ecological and technological reasons. A solution that can improve the process properties of membranes is the development of heterogeneous membranes. Heterogeneous membranes are structures consisting of a polymeric continuous phase and an organic or inorganic dispersed phase. The presence of additives can improve both the permeability of the membrane and its selectivity, as well as the mechanical properties. However, in addition to developing a new material and examining its properties, it is also necessary to propose a method for manufacturing membranes from these materials on an industrial scale and to determine their process properties based on tests on gas mixtures. For this purpose, heterogeneous capillary membranes obtained by dip coating method were developed. PEBAX® 2533 copolymer and additives such as SiO_2, zeolitic imidazolate frameworks (ZIF-8) or PSS-octaphenyl substituted (POSS-Ph) were used to produce them. The permeability and selectivity of the developed membranes were determined on the basis of tests using pure gases (CH_4, CO_2 and N_2), as well as gas mixtures (CO_2/CH_4 and CO_2/N_2). The process conditions used in the research, that is, feed pressure and temperature, were determined on the basis of the authors' previous research [1] and mathematical-statistical analysis. On the basis of the conducted tests, the usefulness of the produced composite capillary membranes for conducting the process of separating gas mixtures in which CO_2 is one of the components has been proven.

Keywords: Membrane gas separation; CO_2 removal; Heterogeneous membranes; PEBA copolymer

1. Introduction

The process of membrane separation of gas mixtures can be carried out on an industrial scale. This process can in some cases replace conventional separation methods such as cryogenic distillation, adsorption and absorption. It can also be one of the stages in the multistage process, thanks to which it is possible to increase the efficiency of the whole process and reduce its energy consumption. The membrane gas separation process has a number of advantages, which include relatively low investment costs, no need to regenerate the solvent or adsorption bed, no waste in the form of spent beds, and no energy-intensive phase transformations [2,3]. However, despite the increasing use of the membrane gas separation process, there is still a need to conduct research on the development of new materials and

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on the assessment of the possibility of using the developed materials in process conditions. One of the industrial areas where intensive research is being conducted on the use of the membrane gas separation process is the area of technologies for removing CO_2 from biogas [4], natural gas [5] or waste gases [6]. The need to separate CO_2 from mixtures results from economic, legal, ecological and technological reasons.

Non-porous polymer membranes are most often used for membrane separation of CO_2-containing mixtures. In order to improve the process properties of membranes, new materials are developed [7–10] or existing materials are modified. One of the methods of materials modification is to add inorganic or inorganic-organic particles to the polymer solution already at the stage of membrane production. Membranes consisting of a continuous polymer phase and a dispersed non-polymer phase are called mixed matrix membrane or heterogeneous membranes. The use of fillers in polymeric membranes can lead to an improvement in membrane permeability or selectivity, importantly, without compromising the latter property [11,12]. Based on the literature data, the most commonly used fillers include metal–organic frameworks compounds [13,14], POSS (polyhedral oligomeric silsesquioxane) [15,16] and various forms of carbon [17,18]. However, in addition to developing a new material and examining its transport, structural and mechanical properties, the possibility of using this material for the production of membranes that can be used in industrial conditions should also be assessed. Thus, one of the steps in the development of new membranes should be to determine a method for producing membranes with a capillary geometry that enables effective increase of membrane surface area in a membrane module. One of the types of membranes with such a geometry is a composite capillary membrane consisting of a supporting layer and a selective layer applied to it. The use of a supporting layer can further improve the strength of the selective layer. For these two reasons, composite capillary membranes can be used in industrial conditions [19–21].

The aim of the work is to develop and test the process properties of capillary heterogeneous membranes with designed properties for the implementation of the process of gas mixture components separation, in particular CO_2 separation. To design the capillary membranes, the results of the authors' own research on the effect of the fillers concentration as well as of the feed pressure and of process temperature on the transport properties of heterogeneous membranes with a flat geometry were used [1].

2. Experimental

2.1. Materials and methods

A commercially available polyetheramide copolymer with the trade name PEBAX® 2533 (Arkema, France) was used to produce the membranes. This block co-polymer contains 80% by mass of PE groups in the form of poly(tetramethylene oxide) and 20% by mass of PA groups in the form of nylon-12. 2-Butanol pure p.a. was used as the polymer solvent (Sigma-Aldrich, Poland).

SiO_2 particles (SiO_2 nano-powder 10–20 nm, Sigma-Aldrich, Poland), ZIF-8 organometallic particles (zeolitic imidazolate frameworks) (Basolite Z1200, BASF, Sigma-Aldrich, Poland) and polyhedral oligomeric silsesquioxanes with a phenyl substituent POSS-Ph (PSS-octaphenyl substituted, Sigma-Aldrich, Poland) were used as inorganic fillers.

Commercially available polypropylene microfiltration membranes (Capillary Membrane MF-PP Series, Type S6/2, 3M, United States) were used as the supporting layer for the production of composite capillary membranes. Nominal pore diameter of such membranes is 0.2 μm, internal diameter 1.8 mm and membrane thickness 450 μm.

In the study of the process properties of the membranes, CO_2, CH_4 and N_2 gases of purity class 3.0 and gas mixtures of CO_2/CH_4 (40%/60% - the authors' own analysis) and CO_2/N_2 (45%/55% - the authors' own analysis) were used. The gases and mixtures were supplied by Air Products, Poland.

2.1.1. Test of capillary membranes process properties

In the tests of composite capillary membranes, the values of permeability coefficients for pure gases, ideal selectivity coefficients, as well as the real values of selectivity coefficients for measurements carried out for gas mixtures were determined.

In order to determine the process properties of the produced membranes, the values of permeation coefficients and ideal selectivity coefficients were determined. In these tests, the retentate was not discharged from the membrane module and these tests were carried out using clean gases. In the case of the tests with pure gases, it is not necessary to use the retentate because the feed and the retentate composition are exactly the same during the process. Discharging the retentate from the membrane module leads to the unnecessary waste of the gas.

The value of the permeability coefficient was determined by Eq. (1):

$$P_i = \frac{p_P \cdot Q_{Pi} \cdot l_m}{R \cdot T_p \cdot F_m \cdot (p_N - p_P)} \tag{1}$$

where p_P is the permeate pressure (Pa), p_N is the feed pressure (Pa), Q_{Pi} is the permeate volumetric flow (m³/s), l_m is the thickness of the tested membrane (m), F_m is its area (m²), T_p is the process temperature (K), and R the universal gas constant (J/K·mol).

The unit of membrane permeability coefficient used is the barrer. It is a non-SI unit and can be converted by Eq. (2):

$$1\ barrer = 3,35 \times 10^{-16}\ \frac{mol \cdot m}{Pa \cdot s \cdot m^2} \tag{2}$$

The value of the ideal selectivity coefficient was determined from Eq. (3), which, due to maintaining the same measurement conditions for both gases, can be reduced to the quotient of the measured permeate volume flows. Such an equation finally takes the form:

$$\alpha_{A/B} = \frac{P_A}{P_B} = \frac{Q_{PA}}{Q_{PB}} \tag{3}$$

where Q_{Pi} is the permeate volumetric flow (m³/s).

In turn, the tests performed on gas mixtures made it possible to determine the real values of selectivity coefficients according to Eq. (4):

$$\beta_{A/B} = \frac{\dfrac{x_{PA}}{x_{PR}}}{\dfrac{x_{NA}}{x_{NB}}} = \frac{\dfrac{x_{PA}}{x_{NA}}}{\dfrac{x_{PB}}{x_{NB}}} \tag{4}$$

where x_{NA} and x_{PA} are the volume fraction of component A in feed and permeate, respectively (–), and x_{NB} and x_{PB} are the volume fraction of component B in feed and permeate, respectively (–).

In addition, tests using gas mixtures were performed for different values of stage-cut parameters. This parameter determines the ratio of the permeate volumetric flow to the feed volumetric flow. This ratio significantly affects the composition of individual streams and their size, and thus the efficiency and effectiveness of the gas separation process. The stage-cut parameter is calculated by Eq. (5):

$$\Theta = \frac{Q_{Pi}}{Q_{Pi} + Q_{Ri}} = \frac{Q_{Pi}}{Q_{Ni}} \tag{5}$$

The tests were carried out on our own laboratory installation, Fig. 1. The main element of the installation is the replaceable membrane module (5). Three gas streams are associated with this module, that is, the feed, the permeate and the retentate. The installation therefore contains three branches, one for each of the streams. Each branch is equipped with temperature (1), dew point (2) and pressure (3) transducers. In addition, a regulating valve (4) was placed in each branch. The feed was supplied to the system through a reducer from a pressure cylinder. This applies to both pure gases and gas mixtures. For the measurement of the permeate and the retentate volumetric flows, electronic flow transducers, BIOS DEFENDER 220 L and BIOS DEFENDER 220 H, were used, differing in measurement ranges. Agilent Technologies 7890A gas chromatograph (Santa Clara, CA, United States) with a thermal conductivity detector was used to study the composition of individual streams.

Capillary modules of the authors' own production were used in the research. For the production of each module, 30 capillaries with an active length of 0.47 m and an outer diameter of 2.7 mm (1.8 mm + 2·0.45 mm) were used, which made it possible to achieve a mass exchange surface of 0.12 m^2. The module housing was made of PVC elements. The developed modules make it possible to conduct research by supplying the space between the capillaries with the feed and collecting the permeate from the inside of the capillary, that is, the shell side feed method. Both the construction of the module and the method of conducting the process are commonly used on an over-laboratory scale.

It should also be noted that the tests with capillary membranes were carried out for 24 h and during this time there were no significant changes in the membrane permeability and selectivity. It can therefore be concluded that during the tests, no change in the properties of the membrane was observed over time as a result of external factors such as temperature, gas pressure in the process, presence of moisture, etc.

2.2. Method of membranes preparation

The selective layer of the composite membrane was produced using the dry phase inversion method. In this method, the solvent from the membrane-forming solution is evaporated under controlled conditions. The decreasing amount of solvent in the solution leads to the transition of the polymer solution to the solid phase and, consequently, to the formation of a solid membrane [22].

The first stage of membrane production was the preparation of a membrane-forming solution. This solution consisted of the PEBAX® 2533 polymer and the 2-butanol as a solvent. Solutions with a concentration of 7% by weight of polymer were prepared. The choice of such a concentration value resulted from the team's previous experience. After dissolving the polymer, weighed amounts of fillers particles were gradually added to the solution and stirred intensively for 24 h. The final product of these stages was a membrane-forming solution with a temperature of 40°C.

The dip-coating method was used to apply the membrane-forming solution to the porous supporting layer. This method consists in immersing the object to be coated, in this case a microporous polypropylene membrane, in a solution from which a new layer is to be produced, that is, a selective layer. For the implementation of the dip-coating process, a special stand was used, the main element of which is the KSV NIMA Dip Coaters device. This device allows the membrane to emerge from the solution at a constant withdrawal speed. In addition, the setup includes a thermostatic tank with a layer-forming solution. Maintaining a constant temperature of the solution at 40°C is necessary to ensure the stability of the viscosity and surface tension of the solution. The whole apparatus is enclosed in a chamber ensuring constant conditions for the process. After the coating process, the membranes were left in the chamber until complete evaporation of the solvent. The thickness of the produced selective layer ranged from 30 to 40 μm, depending on the type of filling. The thickness of the selective layer was determined on the basis of the cross-section of the sample. The PhenomPro Microscope (PhenomWorld, Eindhoven, Netherlands) was used for scanning electron microscopy studies.
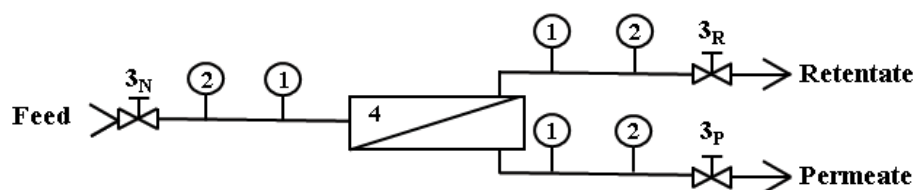

Fig. 1. Model of the installation for testing the process properties of capillary membranes; 1 - Pressure transducer, 2 - Temperature transducer, 3 - Regulating valve (N - feed, P - permeate, R - retentate), 4 - membrane module.

2.3. Statistical and mathematical analysis

To perform the mathematical and statistical analysis of the results obtained for flat membranes, which were presented in our own article [1], a complete 3^k trivalent plan was used, which is one of the design of experiments (DoE) methods. The DoE method is a group of tools that make it possible to determine the relationships between the factors influencing the process and the results of this process. It is used to find cause and effect relationships existing in a given system [23–25]. This method allows us to quickly find mutual relationships between the considered variables and the results.

The purpose of using this method in this work is to find such conditions (fillers concentration, temperature, pressure) in which a high value of membrane permeability for a selected component (specifically CO_2) and a high value of membrane selectivity for this gas component are obtained. Thus, for the production of composite hollow fiber membranes, which were produced, fillers of additives with concentrations resulting from the analysis were used. Similarly, the determined values of feed pressure and process temperature were the values of process parameters at which experiments were carried out using composite capillary membranes on a laboratory installation.

According to the 3^k complete trivalent design procedure, each input quantity, that is, fillers concentration, process temperature and feed pressure, was assigned three levels of values: minimum (–1), average (0) and maximum (+1). Table 1 shows the assignment of three levels to specific values of these variables. In turn, in order to find the values of input parameters for which the highest value of CO_2 permeability through the membrane and the highest value of CO_2/N_2 and CO_2/CH_4 selectivity are obtained, the criterion of maximizing CO_2 permeability and minimizing N_2 and CH_4 permeability should be adopted in the analysis.

In order to find the desired output value, in this case the permeability value of the tested gases, the second-order equation was used [26]:

$$y_{\varphi_i} = \beta_0 + \sum_{i=1}^{3} \beta_{\varphi_i} \varphi_i + \sum_{i=1}^{3}\sum_{j=1}^{3} \beta_{\varphi_{ij}} \varphi_i \varphi_j + \sum_{i=1}^{3} \beta_{\varphi_{ii}} \varphi_i^2 \qquad (6)$$

where β_0, β_{φ_i}, $\beta_{\varphi_{ij}}$ oraz $\beta_{\varphi_{ii}}$ are the calculated polynomial coefficients and φ_i and φ_j are input quantities. This estimation equation uses Statistica 13.1 (StatSoft Europe GmbH), which was used to analyze the data.

In this type of analysis, that is, using a 3^k complete trivalent design procedure, there cannot be a linear relationship between the input data. This condition is fulfilled. Another requirement of the analysis method is to assign an appropriate level to each of the three input parameters, that is, maximum (+1), average (0) and minimum (–1). This makes it possible to calculate the coefficients of Eq. (6). Finding the coefficients of the estimating equation allows us to solve it, which also means finding the input data values for which you will obtain the desired response value.

A complete three-value research plan requires 27 experiments to be performed for the conditions indicated in this work (3 parameters with 3 values of each parameter). This is how much has been done for one type of inorganic filling. All the results of the experiments have been presented in the work [12].

3. Results and discussion

According to the information presented in section 2.3 – Statistical and mathematical analysis, mathematical and statistical studies of the measurement results obtained for flat membranes and presented in the work [12] were carried out. The obtained values of the fillers concentration, feed pressure and process temperature are presented in Table 2. In turn, the values of the CO_2 permeability coefficient and ideal selectivity coefficients estimated for these parameters are presented in Table 3.

Using the determined values of fillers concentrations, capillary composite membranes were produced and then tested for pure gases under the process conditions presented in Table 2. The experimentally determined values of CO_2 permeability coefficients and ideal selectivity coefficients are presented in Table 3.

The analysis of Tables 4–6, that is, the comparison of the measured values of the permeability and selectivity coefficients for capillary membranes with the estimated values of these coefficients for flat membranes, allows us to conclude that, within the limits of measurement errors, the values obtained for composite capillary membranes are the same as for flat membranes. Therefore, it should be concluded that the proposed method of manufacturing composite capillary membranes enables the production of membranes with designed properties.

Table 1
Assignment of levels to the values of controllable input factors

Controllable input factors	Low level (–1)	Intermediate level (0)	High level (+1)
Filler concentration (%)	0	2* 0.75**	5* 2**
Process temperature (°C)	25	40	55
Feed pressure (bar)	2	4	8

*for SiO_2 and ZIF-8.
**for POSS-Ph.

Table 2
Determined values of filling concentration and process parameters

Module	Type of filler	Filler concentration (%)	Feed pressure (bar)	Process temperature (°C)
MOD_{ZIF-8}	ZIF-8	3.8	8	25
MOD_{SiO2}	SiO_2	5.0	7	27
$MOD_{POSS-Ph}$	POSS-Ph	1.6	8	27

Table 3
Comparison of the measured values of permeability and selectivity coefficients for capillary membranes with the estimated values of these coefficients for flat membranes

Module	Tested gas	Values of coefficients for capillary membranes			Estimated values of coefficients for flat membranes		
		Permeability coefficient (barrer)	Ideal selectivity coefficient (−)		Permeability coefficient (barrer)	Ideal selectivity coefficient (−)	
			$\alpha CO_2/CH_4$	$\alpha CO_2/N_2$		$\alpha CO_2/CH_4$	$\alpha CO_2/N_2$
MOD_{ZIF-8}	CO_2	207.8 ± 10.4			219.5		
	CH_4	30.2 ± 1.5	6.9 ± 0.7	29.3 ± 3.1	28.8	7.6	29.7
	N_2	7.1 ± 0.4			7.4		
MOD_{SiO2}	CO_2	187.7 ± 9.4			198.3		
	CH_4	24.4 ± 1.2	7.7 ± 0.8	27.0 ± 2.9	25.3	7.5	31.4
	N_2	7.0 ± 0.4			6.3		
$MOD_{POSS-Ph}$	CO_2	173.9 ± 8.7			184.6		
	CH_4	21.3 ± 1.1	8.2 ± 0.7	32.7 ± 3.5	22.4	8.4	31.4
	N_2	5.3 ± 0.3			5.9		

Table 4
Test results of CO_2/N_2 and CO_2/CH_4 gas mixture separation using module MOD_{ZIF-8}

θ (−)	Q_N (mL/min)	Q_P (mL/min)	Q_R (mL/min)	Permeate		Retentate		$\beta_{CO2/N2}$
				%CO_2	%N_2	%CO_2	%N_2	
FEED - CO_2/N_2 40/60								
0.1	558	51	507	81.2	18.8	36.8	63.2	6.5
0.2	314	48	266	77.2	22.9	32.5	67.5	5.1
0.5	174	37	137	73.1	26.9	24.2	75.8	4.1
0.8	39	32	7	68.4	31.6	13.3	82.5	3.3
FEED - CO_2/CH_4 45/55								
0.1	601	68	533	75.5	24.5	42.9	57.2	3.8
0.2	408	61	347	69.9	30.1	37.3	62.7	2.8
0.5	106	49	57	63.4	36.6	23.4	76.6	2.1
0.8	54	41	13	52.3	47.8	18.9	81.1	1.3

In the further part of the research on composite capillary membranes, tests were carried out using the manufactured membrane modules on binary gas mixtures containing CO_2 and N_2 as well as CO_2 and CH_4. Tables 4–6 show the results of the volume fractions of gas mixture components in the feed, the permeate, the retentate and the volumetric flow of these streams as well as the calculated value of the actual selectivity coefficient $\beta_{i/j}$. Measurements were carried out for different values of the stage-cut parameter - Eq. (5), specifically for $\theta \approx 0.1$, $\theta \approx 0.2$, $\theta \approx 0.5$ and $\theta \approx 0.8$.

Based on the data presented in Tables 4–6 it can be concluded that the course of the process is similar for all tested systems. The data obtained confirm that the faster permeating component, that is, CO_2, is depleted in the retentate stream and enriched in the permeate stream. The degree of depletion/enrichment depends on the stage-cut value. Along with the increase in the value of the stage-cut parameter, that is, with the increase in the value of the permeate stream in relation to the value of the feed stream, the content of CO_2 as a faster permeating component, in the

retentate stream decreases. At the same time, the content of this component in the permeate stream increases. Thus, the driving force of the transport of this component through the membrane decreases. There may be a situation where the driving force is zero at some point along the length of the membrane module. Such a situation is undesirable from a technological point of view, because the process conducted in this way does not meet the principle of the best use of the apparatus - a part of the membrane surface does not carry out the process.

The analysis of Tables 4–6 allows us to conclude that for all the tested systems the nature of changes in the real process selectivity coefficient depending on the value of the stage-cut parameter is similar. As the stage-cut increases, the real selectivity coefficient decreases. It should be noted that the real process selectivity factor is always smaller than the ideal membrane selectivity factor. This is mainly due to the influence of one component of the gas mixture on the transport of the other. In addition, the composition of the feed along the length of the module is variable, and

Table 5
Test results of CO_2/N_2 and CO_2/CH_4 gas mixture separation using module MOD_{SiO2}

θ (−)	Q_N (mL/min)	Q_P (mL/min)	Q_R (mL/min)	Permeate		Retentate		$\beta_{CO2/N2}$
				%CO_2	%N_2	%CO_2	%N_2	
FEED - CO_2/N_2 40/60								
0.1	349	37	312	88.4	11.6	32.7	67.3	11.5
0.2	191	34	157	85.0	15.0	27.7	72.3	8.6
0.5	79	31	48	80.1	19.9	20.9	79.2	6.1
0.8	39	30	9	77.0	23.0	17.5	82.5	5.1
FEED - CO_2/CH_4 45/55								
0.1	584	68	516	72.7	27.3	42.2	57.9	3.2
0.2	276	57	219	68.8	31.2	38.9	61.1	2.7
0.5	91	43	48	58.3	41.8	29.4	70.6	1.7
0.8	47	39	8	54.9	45.1	23.2	76.8	1.5

Table 6
Test results of CO_2/N_2 and CO_2/CH_4 gas mixture separation using module $MOD_{POSS-Ph}$

θ (−)	Q_N (mL/min)	Q_P (mL/min)	Q_R (mL/min)	Permeate		Retentate		$\beta_{CO2/N2}$
				%CO_2	%N_2	%CO_2	%N_2	
FEED - CO_2/N_2 40/60								
0.1	416	41	375	85.3	14.7	30.1	69.9	8.8
0.2	231	39	192	81.9	18.1	26.0	74.0	6.8
0.5	75	35	40	79.2	20.8	18.0	82.0	5.8
0.8	40	30	10	76.4	23.6	14.9	85.2	4.9
FEED - CO_2/CH_4 45/55								
0.1	508	62	446	80.3	19.7	41.2	58.8	5.0
0.2	318	58	260	74.7	25.3	38.0	62.0	3.6
0.5	83	42	41	63.5	36.5	25.4	74.6	2.1
0.8	49	39	10	57.8	42.2	18.3	81.7	1.7

the intensity of changes depends on the value of the stage-cut parameter. This causes the process conditions to be different for different stage-cut values; different average composition of the feed - different average composition of the permeate.

The literature mentions at least two more reasons for which the selective properties of the process are worse than the selective properties of the membrane. The first of these reasons is plasticization, that is, swelling of the polymer in the presence of a selected gaseous component. CO_2 has such plasticizing properties. The plasticizing effect changes the local mobility of the polymer chains and increases the free spaces between them. This, in turn, may lead to an increase in the diffusivity of other components of this mixture [27]. The second reason is the commonly known concentration polarization, that is, the phenomenon of accumulating slowly permeating molecules of a component on the membrane surface, which hinders the transport of a faster permeating component [28].

Due to the lack of strict mathematical relationships between the ideal membrane selectivity factor and the real process selectivity factor, it is not possible to predict the exact value of the real selectivity factor based on the knowledge of the membrane properties and process parameters. For this reason, it is necessary to carry out such tests on gas mixtures. It can be concluded that the highest, and therefore desirable, values of the actual selectivity coefficient of the process are obtained for low values of the stage-cut parameter. It should be noted, however, that then a large stream of the retentate with a composition not much different from the composition of the feed stream is obtained. In this case, the retentate stream carries away a large portion of the pressure energy that has been put into the process. In processes where the retentate would constitute a waste stream, this is energetically and economically unjustified. Moreover, for a low stage-cut value, the amount of permeate obtained is low in relation to the amount of feed. This is again a poor use of the energy put into the feed compression. Therefore, when designing the process, a compromise should be found between the composition of the retentate and the permeate streams and the use of energy put into the process. Of course, there are processes in which low energy
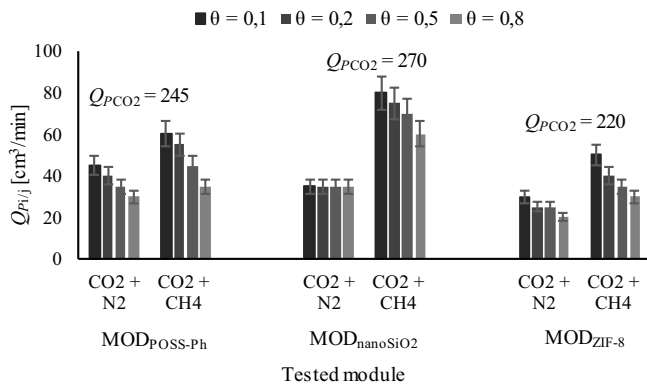
Fig. 2. Obtained permeate volumetric flow for gas mixtures.

efficiency is acceptable, so this factor is not always limiting the choice of process parameters.

The presence of a slowly permeating component in the feed also reduces the volumetric flow rate of the obtained permeate $Q_{Pi/j}$ in relation to the situation when the tested gas is pure CO_2. In addition, in the case of mixtures, the amount of the obtained stream also depends on the θ parameter, which is presented in Fig. 2. For comparison, the values of the permeate volumetric streams for CO_2, Q_{PCO2}, obtained in the tests on pure gas were also presented. The lower value of the permeate volume flow is associated with a lower driving force for CO_2 transport, which results from the lower partial pressure of CO_2 in the mixture in relation to pure gas. In addition, as in the previously discussed phenomena, along with the flow of the feed along the membrane, the concentration of CO_2 decreases, which also reduces the driving force of the process.

4. Summary

Based on the obtained results, it can be concluded that the use of a complete 3^k trivalent design for the analysis of the data obtained for flat membranes allows for determining the concentration of inorganic fillers in the membrane, the feed pressure and the process temperature to maximize the permeability of the selected component of the gas mixture and minimize the permeability of the other components of the mixture. It should also be noted that the proposed dip-coating method allows for the production of heterogeneous capillary membranes with programmable process properties.

The heterogeneous capillary membranes produced have confirmed process properties, thanks to which these membranes can perform real processes of separating components of gas mixtures, which include CO_2.

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