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MODELLING THE GAS FLOW IN PERMEATE CHANNEL IN MEMBRANE GAS SEPARATION PROCESS

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This paper analyses the real behaviour of the fluid in the channels of a three-end membrane module. The commonly accepted mathematical model of membrane separation of gas mixtures in such modules assumes a plug flow of fluid through the feed channel and perfect mixing in the permeate channel. This article discusses the admissibility of accepting such an assumption regarding the fluid behaviour in the permeate channel. Throughout analysis of the values of the Péclet number criterion, it has been demonstrated that in the industrial processes of membrane gas separation, the necessary conditions for the perfect mixing in the permeate channel are not met. Then, CFD simulations were performed in order to establish the real fluid behaviour in this channel. It was proved that in the permeate channel the fluid movement corresponds to the plug flow, with the concentration differences at both ends of the module being insignificant. In view of the observations made, the admissibility of concentration stability assumptions in the mathematical models for the permeate channel was discussed.

Keywords: gas separation, perfect mixing, Péclet number, CFD

1. INTRODUCTION

Along with the development of various membrane techniques, mathematical models in the literature began to describe processes implemented using such techniques. This also happened in the case of membrane gas separation. The first attempts to the mathematical modelling of membrane gas separation process were made several dozen years ago (Rautenbach and Dahm, 1986; Walawender and Stern, 1972; Weller and Steiner, 1950). The models created at that time still refer to the majority of the later and current models, both to those related to the processes carried out in three-end modules, as well as to those carried out in four-end modules.

Further works on the mathematical models of the membrane gas separation process were mainly concerned with the impact of adopting different assumptions on the results obtained. For example, Wang et al. (2002) and Scholz et al. (2012) used the real-gas equations in their models, in contrast to many models using the equations of state for ideal gas. The thermal effects accompanying the process of membrane gas separation were included in their models by Cocker et al. (1999), Marriott and Sørensen (2003) and Scholz et al. (2012). In addition, Wang et al. (2002), Marriott and Sørensen (2003) and Scholz et al. (2012) modelled the impact of concentration polarization on the considered membrane process. In turn, Szwast and Szwast (2015) in their model studies took into account the phenomenon of energy transfer to a flux penetrating the membrane by the flux where penetration occurs.

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With regard to three-end membrane modules, presented in Fig. 1, the mathematical models found in the literature differ in assumptions about the fluid behaviour in the membrane module channels. Often the same authors in one paper present and compare models that differ significantly in the assumptions taken. Therefore, in some models, plug flow was assumed in both channels of the membrane module (Davis, 2002; Mazzotti et al., 2016; Perrin and Stern, 1985; Shindo et al., 1985; Walawender and Stern, 1972; Weller and Steiner, 1950), which seems to be intuitive. However, a majority of authors have been considering models that assume perfect mixing of fluid in both channels (Mazzotti et al., 2016; Perrin and Stern, 1985; Shindo et al., 1985; Walawender and Stern, 1972; Weller and Steiner, 1950), while the others assume a plug flow in the feed channel and perfect mixing in the permeate channel (Davis, 2002; Mazzotti et al., 2016; Pfister et al., 2017; Rautenbach and Dahm, 1986). In addition, Pfister et al. (2017) state that currently the most commonly used model is the one that assumes a plug flow in the feed channel and perfect mixing in the permeate channel.

Fig. 1. Schematic view of three-end module

The issue of plug flow in the feed channel does not seem to be a debatable for the author in contrast to the existence of perfect mixing in the permeate channel. Therefore, this paper focuses on a theoretical analysis, supported by CFD calculations, concerning a possible occurrence of the perfect mixing in the permeate channel of three-end membrane modules and the admissibility of the application of perfect mixing assumption. In the author's opinion, the literature does not discuss this issue. We can only find a few remarks that fluid behaviour in the permeate channel in industrial membrane processes differs from that of the perfect mixing, without rationale given for such a statement (Katoh et al., 2011).

For the purpose of this work, it should be noted that the assumption of the existence of perfect mixing of fluid in one or both channels of the membrane module has already appeared in older models (Perrin and Stern, 1985; Rautenbach and Dahm, 1986; Shindo et al., 1985; Walawender and Stern, 1972; Weller and Steiner, 1950) and is also accepted in the latest models (Davis, 2002; Mazzotti et al., 2016; Pfister et al., 2017).

2. CONDITIONS FOR PERFECT MIXING

The conditions for perfect mixing are considered to be the situation in which there is no gradient of all the physical quantities describing the state of the fluid, in particular concentration, temperature and pressure in the whole considered volume of fluid. In an isothermal process, the conditions of perfect mixing in the permeate channel require stable pressure and concentration of components along the overall length of the module and at all points of each cross-section. However, it should be noted that the lack of pressure gradient along the length of the membrane module would lead to the situation where the gas in this channel would remain immobile and would not leave the membrane module. Due to the fact that the permeate leaves the membrane module, the existence of a zero pressure gradient is impossible. The pressure difference at both ends of the membrane module does not have to be large to make the permeate move towards the outlet. For this reason, the issue of a pressure gradient will not be considered further. Instead, the considerations will focus on the distribution of concentrations of gas mixture components in the permeate channel.

It should be noted that homogeneity of concentrations of gas mixture components in the permeate channel could occur in two cases. The first case is the penetration through the membrane from the feed channel into the permeate channel of the gas flux with the same composition along the overall length of the membrane module. The second case is the infinitely quick mixing of the whole fluid volume in the permeate channel.

Considering the former, it should be pointed out that in a process that aims at separating the feed mixture components, the composition of the feed (transformed into the retentate) always varies along the module length, which given a desirable stability of gas composition in the permeate prevents the maintenance of the stability of the composition of gas passing through the membrane along the overall length of the module. It must be remembered that the composition of the gas penetrating the membrane in the elementary module section is a function of the feed composition and permeate composition (Katoh et al., 2011; Makaruk and Harasek, 2009; Szwast and Szwast, 2015). Thus, the variability of the feed composition along the length of the membrane module prevents the occurrence of the first case. Obtaining a negligible change in the concentration of feed components in the membrane process along the length of the module is only possible if the feed flux is much bigger than the permeate flux. However, running the process in such a way is economically groundless.

Considering the second case of establishing the conditions of perfect mixing in the permeate channel, it should be stated that the practice of process running, and even more the construction of membrane modules used for gas separation, do not allow stirring in the permeate channel, which would ensure mixing of gas in this channel. The only way in which gas can be mixed in the permeate channel is gas mixing at the molecular level, that is due to the diffusion (dispersion) phenomenon. The criterion number for this phenomenon is the Péclet number, defined by Eq. (1) and being a measure of the ratio of the speed of mass convection movement to diffusion rate (Ingham et al., 2008):

$$Pe = \frac{uL}{D} \tag{1}$$

Mixtures in flow systems where the Péclet number approaches zero are considered to be perfectly mixed. Meanwhile in the flow systems where the Péclet number approaches infinity, the flow of fluid is considered to be plug flow (Ingham et al., 2008). The literature indicates the value of $Pe = 1$, as a maximum limit value at which the predominance of diffusional over convective movement can be assumed in the systems and this value is considered as the limit of possible perfect mixing of the fluid contained in the system (Geschke et al., 2004).

Given the value of gas diffusion coefficients, which are in the range of 10^{-5} m^2/s, and the length of modules in the range of single meters, the achievement of perfect mixing would be possible only if the velocity of gas convection in the permeate channel does not exceed the speed of 10^{-6} m/s. Such speed would practically mean the permeate immobility in the module. In real membrane processes, the permeate velocities leaving the module are much higher, which means that the Péclet number reaches values exceeding $Pe = 1$. This means that there are no conditions in the permeate channel that allow gas in this channel to be considered as perfectly mixed.

To check how far the value of the Péclet number deviates from unity in the real process conditions, the catalogue data of the manufacturer of membrane modules for gas separation were taken. The data for the Generon module, model 210 (generon.com) was used for the calculations. This module is designed to obtain nitrogen from the air. Thus, for a 95% pure product, the permeate flow is approximately 0.5 Nm^3/h with a housing diameter of 48 mm. Assuming that the channel available for the permeate inside the housing is half of the enclosed space (the remaining part is occupied by the capillary tubes) (Thundyil and Koros, 1997), the linear velocity of the gas leaving the permeate channel equals approx. 0.15 m/s. This value and the assumption that the gas velocity increases from zero at the closed end of the permeate channel to a maximum value of 0.15 m/s at the open end of the permeate channel allow to estimate the average permeate velocity in the membrane module at 0.075 m/s. In view of the interdiffusion coefficient for nitrogen and

oxygen at the temperature of 25 °C being 1.71×10^{-5} m^2/s (Giddings and Seager, 1962) and the catalogue length of the module being 686 mm, the calculated value of the Péclet number is $Pe = 3009$. Analogical calculations carried out for the Model 7200HPHF module (permeate flow rate approx. 140 Nm^3/h), lead to a Péclet number of $Pe = 79851$.

Given the calculation results presented above, it can be stated that under real process conditions the Péclet number is much greater than unity, i.e. from the maximum limit of the necessary precondition for perfect mixing.

3. NUMERICAL MODELLING OF FLUID BEHAVIOUR

Information on fluid behaviour in the membrane module channels can be provided by the results of numerical simulations performed using CFD (Computational Fluid Dynamic) packages. For this paper simulations of the process were carried out using the simplest possible module, i.e. containing one capillary tube. Such a simplified geometry of the membrane module is justified in modelling. It should be noted that increasing the number of parallel capillaries built in the same module does not change the distribution of molar fraction of the gas mixture components since in each individual capillary the process occurs exactly in the same way. The model module was a pipe with an inner diameter of 3×10^{-3} m and a length of 1 m, Fig. 2. Coaxially, one capillary with an outer diameter of 1×10^{-3} m was placed with the module housing. In subsequent simulations, different values of the membrane thickness were assumed, respectively 0.5×10^{-6} m, 1×10^{-6} m and 2×10^{-6} m. The feed fed the interior of the capillary tube, and the permeate appeared in the channel delimited by the external surface of the capillary tube and the inner surface of the module housing. Simulations were carried out for co-current and counter-current flows of feed and permeate.

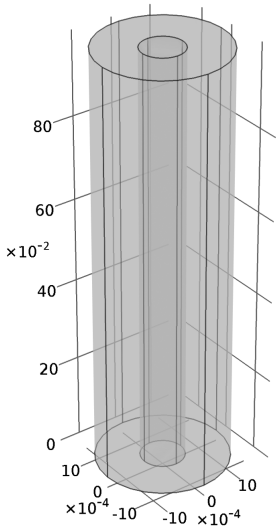

Fig. 2. Geometry used in numerical calculations

In the meshing procedure the physics-controlled mesh has been used. The grid density was considered as acceptable when further increase of the number of elements did not change the computed value of component molar fraction. Finally, the feed channel consists of 25976 elements (8662 boundary elements), while the permeate channel consists of 75121 elements (11677 boundary elements). The feed was a mixture of CO_2 and N_2, as a simplified off-gas model, in a molar ratio of 1 : 1. Simulations were carried out using data for two different membranes, with significant differences of gas permeability values and of ideal separation factor. The first of them was a membrane made of Pebax 2533 copolymer characterised

by permeability $P_{CO_2} = 133.8$ barrer and $P_{N_2} = 7.9$ barrer and the ideal separation factor $\alpha_{CO_2/N_2} = 16.9$ (Szwast, 2017b). It should be noted that 1 barrer $= 3.35 \times 10^{-16}$ mol·m·Pa^{-1}·s^{-1}·m^{-2}. The second membrane was a membrane made of Polypyrrole 6FDA/PMDA (25/75)-TAB characterised by permeabilities $P_{CO_2} = 3.13$ barrer and $P_{N_2} = 1.46$ barrer and the ideal separation factor $\alpha_{CO2/N2} = 2.1$ (Zimmerman and Koros, 1999). In all simulations, it was assumed that the feed was introduced at 1×10^6 Pa, the retentate was throttled to 0.95×10^6 Pa, and the permeate channel was open to the atmosphere, that is, the outlet pressure of the permeate was 0.1×10^6 Pa.

To perform numerical simulations, the Comsol Multiphysics® package was used. Tubular membrane was modelled in 2D axisymmetric geometry. Transport of Concentrated Species and Laminar Flow physics interfaces as well as Fick's permeation equation were applied to the calculations (Szwast, 2017a).

Figure 3 presents the results of simulations obtained using data on the membrane made of Pebax 2533 polymer, i.e. characterised by higher gas permeability values and higher value of the ideal separation factor. Figure 3 shows the results of simulations obtained using data on a membrane made of Polypyrrole 6FDA/PMDA (25/75)-TAB polymer, i.e. characterised by lower gas permeability values and a lower value of the ideal separation factor. The figures show the right half of the axial section of the module. The left compartment is the feed space, and the right compartment is the permeate channel.

Since readings from Figs. 3 and 4 are quite cumbersome, the CO_2 molar fraction values that represent faster permeating component at both ends of both module channels are shown in Tables 1 and 2, and were read from the diagrams shown in Figs. 2 and 3, respectively. In addition, the average values of the Péclet number and permeate linear velocity for each case considered are given in these tables, assuming a value of the interdiffusion coefficient for CO_2 and N_2, i.e. constituents of the mixture representing the feed, at 24 °C being 1.92×10^{-5} m^2/s (Giddings and Seager, 1962). The last column of these tables shows the relative percentage change in the molar fraction of CO_2 along the overall length of the permeate channel.

Table 1. CO_2 molar fraction obtained in numerical simulation for high permeability membrane

Thickness [μm]	Flow	Permeate linear velocity [m/s]	Péclet number	Feed inflow	Retentate outflow	Permeate dead-end	Permeate outflow	Δx_p [%]
0.5	co-current	0.2337	12172	0.5000	0.3800	0.9442	0.9253	2.04
	counter-current	0.2151	11203	0.5000	0.3100	0.8836	0.9094	2.84
1	co-current	0.1192	6207	0.5000	0.4073	0.9442	0.9337	1.12
	counter-current	0.1185	6171	0.5000	0.3953	0.9169	0.9277	1.16
2	co-current	0.0625	3255	0.5000	0.4517	0.9442	0.9376	0.70
	counter-current	0.0624	3248	0.5000	0.4478	0.9320	0.9344	0.26

The analysis of Fig. 2 leads to a conclusion that the gas flow through the feed channel is close to the plug flow, and the molar fraction of CO_2, as a faster permeating component, decreases with the length of the feed channel. In turn, regarding the permeate channel, it can be stated that also in this channel the flow is similar to the plug flow, as evidenced by the spatial distribution of the CO_2 molar fraction. For this paper, it is important that such a distribution of the CO_2 molar fraction in the permeate channel does not indicate that perfect mixing takes place in this channel. This is additionally confirmed by the values of the Péclet number listed in Table 1. In addition, it should be noted that perfect mixing conditions in the cross-section of the permeate channel are also not substantiated. The profile of the molar fraction in the selected cross-section in the permeate channel is slightly curvilinear. The higher the value of the Péclet number in a given case, the greater the curvilinear nature of this profile.

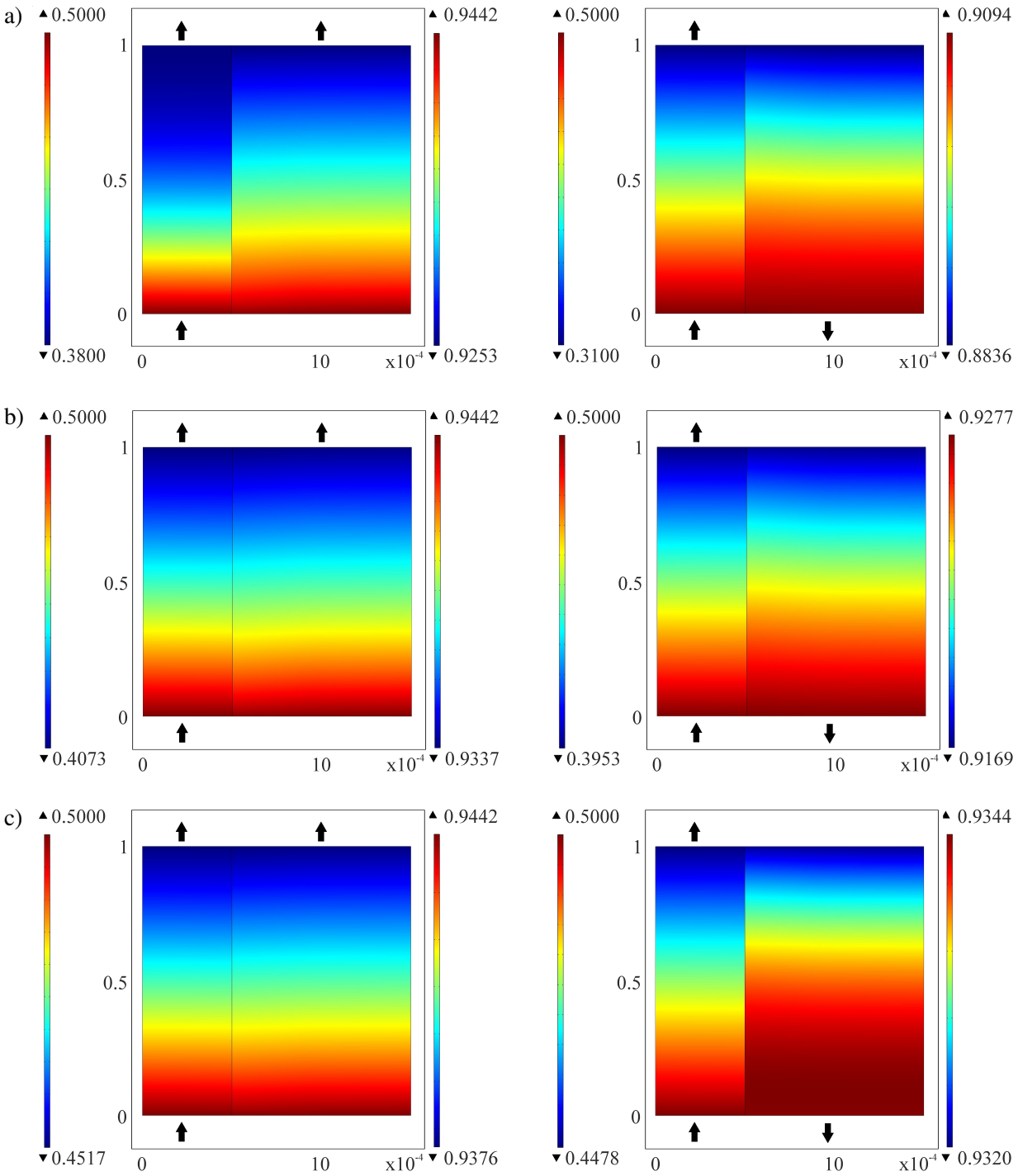

Fig. 3. CO_2 molar fraction in CO_2/N_2 mixture separation process by high permeability membrane; co-current flow in the left picture, countercurrent flow in the right picture; membrane thickness: a) 0.5 μm, b) 1 μm, c) 2 μm

From this paper's objective's perspective, it is particularly important that despite the flow being close to the plug flow, the relative change in the molar fraction of CO_2 along the overall length of the permeate channel is small and amounts only to a fraction of a percent to about 3% (Table 1).

The above conclusions from the analysis of the data presented in Fig. 2 and Table 1 relate to co-current feed and permeate flows as well as to counter-current flows.

Analogous observations can be made for a membrane with lower permeability for which the corresponding results are shown in Fig. 3 and in Table 2, wherein the relative changes in the molar fraction of CO_2 along

the entire length of the module are much smaller and do not exceed fractions of a percent, due to smaller changes in the molar fraction of CO_2 along the length of the feed channel.

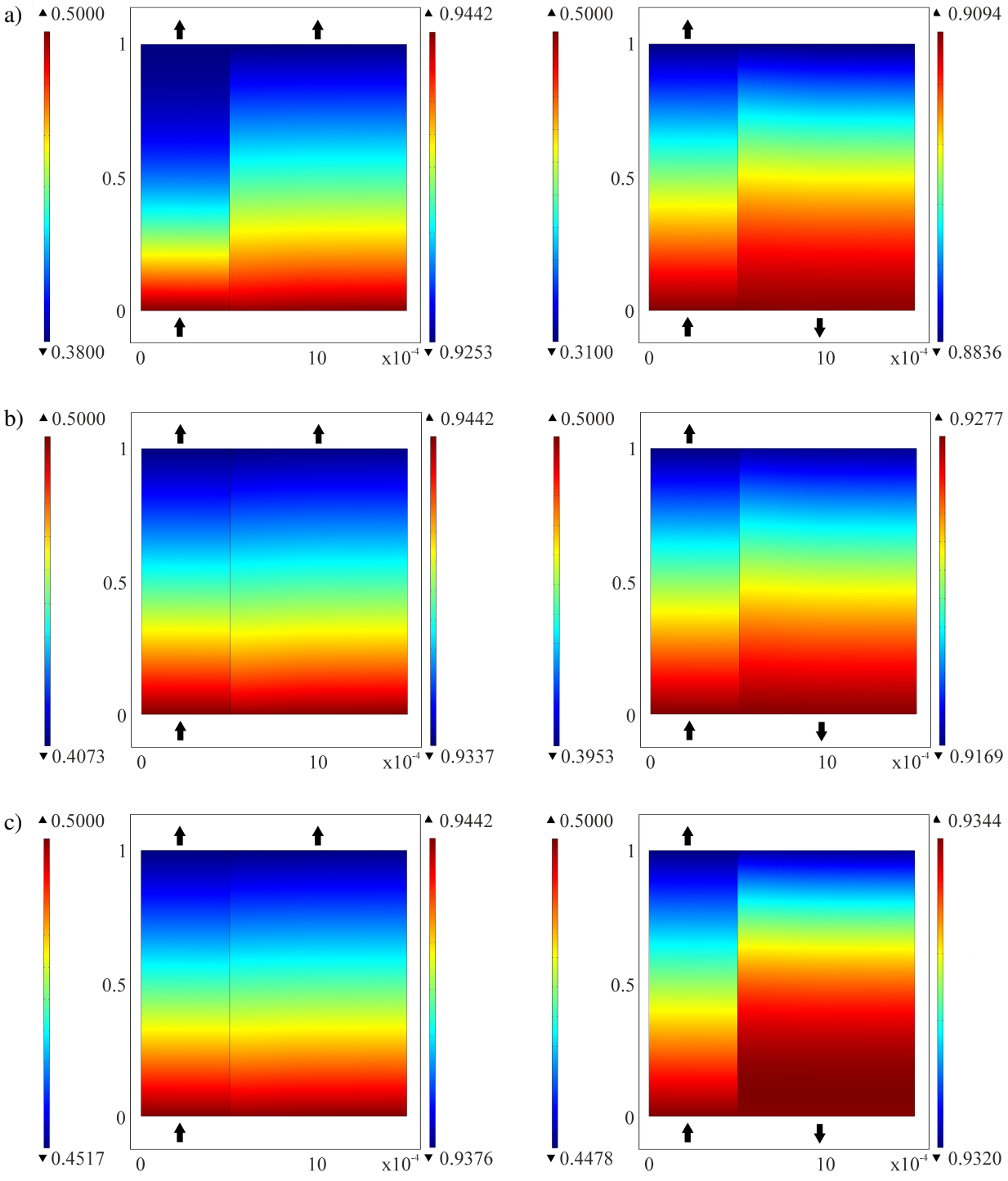

Fig. 4. CO_2 molar fraction in CO_2/N_2 mixture separation process by low permeability membrane; co-current flow in the left picture, countercurrent flow in the right picture; membrane thickness: a) 0.5 μm, b) 1 μm, c) 2 μm

It should be noted that in the most extreme situation (a membrane of high permeability and the smallest thickness and counter-current flow) despite almost 40% change in the molar fraction of CO_2 along the feed channel, differences in the molar fractions of this component at both ends of the permeate channel differ by less than 3%.

Table 2. CO_2 molar fraction obtained in numerical simulation for low permeability membrane

Thickness [μm]	Flow	Permeate linear velocity [m/s]	Péclet number	Feed inflow	Retentate outflow	Permeate dead-end	Permeate outflow	Δx_p [%]
0.5	co-current	0.0086	441	0.5000	0.4975	0.6815	0.6806	0.13
	counter-current	0.0085	441	0.5000	0.4973	0.6797	0.6806	0.13
1	co-current	0.0043	220	0.5000	0.4978	0.6817	0.6813	0.06
	counter-current	0.0042	220	0.5000	0.4987	0.6808	0.6813	0.07
2	co-current	0.0022	110	0.5000	0.4993	0.6818	0.6816	0.03
	counter-current	0.0021	110	0.5000	0.4993	0.6814	0.6816	0.03

To sum up the above considerations, taking into account the results of numerical simulations presented here and the discussion on the value of the Péclet number, it can be concluded that perfect mixing conditions in the permeate channel of the three-end membrane module are not met. However, due to minor changes in the molar fraction of the selected mixture component along the entire length of the membrane module, the assumption of an even distribution of concentrations of individual components of the gas mixture in the overall volume of the permeate channel seems to be acceptable. In computational practice it boils down to the same simplifications as in the assumption of perfect mixing, although from the formal perspective of the chemical engineering it is appropriate not to use the formula of perfect mixing.

4. CONCLUSIONS

Mathematical models commonly used in the literature to describe the process of membrane separation of gas mixtures conducted in a module with three ends assume a perfect mixing of gas in the permeate channel. The analysis of the process based on the dimensionless number, i.e. the Péclet number, revealed that it is practically impossible to meet the conditions necessary for perfect mixing. In turn, the results of numerical simulations clearly indicate that the behaviour of fluid in the permeate channel differs from the perfect mixing conditions and points to the situation typical to plug flow.

The analysis of the differences in concentrations of gas mixture components obtained from numerical simulations at both ends of the permeate channel indicates their low value. Even with a relatively big change in the concentration of gas mixture components in the feed space along the overall length of the module, the concentration differences at both ends of the permeate channel are relatively small. The observed small differences in concentrations at the ends of the permeate channel allow one to accept the stable concentration along the overall permeate channel. This is, of course, qualitatively identical assumption with the premise of perfect mixing. However, it does not introduce erroneous information about the origin of the assumption.

SYMBOLS

D diffusion coefficient (m^2/s)
L characteristic length (m)
Pe Péclet number
u velocity (m/s)

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