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EFFECT OF MEMBRANE SEPARATION PROCESS CONDITIONS ON THE RECOVERY OF SYNGAS COMPONENTS

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Abstract. The presented study focuses on inspecting the dependency between process conditions, especially permeate and retentate pressure and component recovery of H_2, CO, and CO_2 during a membrane separation of model syngas. Experiments with both pure components and a model mixture were performed using a laboratory membrane unit Ralex GSU-LAB-200 with a polyimide hollow fibre module with 3000 hollow fibres. Permeability values were established at 1380 Barrer for H_2, 23 Barrer for CO, and 343 Barrer for CO_2. The measured selectivities differ from the ideal ones: the ideal H_2/CO_2 selectivity is 3.21, while the experimental values range from over 4 to as low as 1.2 (this implies that an interaction between the components occurs). Then, the model syngas, comprised of 16 % H_2, 34 % CO, and 50 % CO_2, was tested. The recovery of each component decreases with an increasing permeate pressure. At a pressure difference of 2 bar, the recovery rate for H_2, for a permeate pressure of 1.2 bar, is around 68 %, for 2.5 bar, the values drop to 51 %, and for 4 bar, the values reach 40 % only. A similar trend was observed for CO_2, with recovery values of 59 %, 47 % and 37 % for permeate pressures of 1.2 bar, 2.5 bar and 4 bar, respectively.

Keywords: Membrane separation, syngas improvement, components recovery, hollow fibre module.

1. Introduction

One of the main challenges for scientific teams in the past years has been finding a solution to mitigate climate change and decrease the production of CO_2 and greenhouse gases. In addition to other approaches, waste utilization is one of the most promising ways. Specifically, for biomass, gasification offers a suitable solution for the biomass-to-fuels and biomass-to-chemicals conversion. Many studies have shown that the product of gasification can be used as a feed for various downstream technologies, including Fischer-Tropsch synthesis, methanol production, and other processes that have been used for coal-gasification-produced syngas [1]. Taking into account the environment, many scientific teams have published innovative approaches, including syngas fermentation using specific bacteria [2]. As biosyngas (biomass gasification-produced syngas) contains H_2, CO, CO_2, and minor amounts of CH_4 and other components, it is necessary to adjust its composition and eventually remove the impurities before using it as feedstock for the mentioned technologies. Membrane operations are one of the possible solutions for such adjustments. To implement membrane operations in the technology process, it is necessary to describe the processes.

Currently, the focus of scientific teams researching membrane operations is on the separation of two components. Several studies have been published describing a two-component separation. Choi et al. [3] studied H_2/CO separation – the effect of the operating pressure was described for H_2:CO ratios of 3:1, 5:1 and 7:1 and showed that permeance increased with a higher H_2 concentration. The effects of increasing flow rate and operating pressure on separation factors and permeance. A study presented by Huang et al. [4] focuses on H_2 and CO_2 recovery and describes the dependency between the recovery of components and the area of the module. The article presents that it is necessary to increase the area near exponentially to achieve a lower CO_2 concentration in the retentate.

Besides the two-component separation, the scientific field of interest is the numerical simulation and the solution of multicomponent separation. A study published by Lee et al. [5] proposes a numerical model of multicomponent membrane separation for CO_2 containing mixtures in counter-current hollow fibre modules based on the Newton-Raphson method. The numerical solution was compared with the experimental data using a gaseous mixture consisting of 14 % CO_2, 6 % O_2, and 80 % N_2. Another approach to numerical modelling of membrane separation was presented by Qadir et al. [6] and involved fluid dynamics within CFD simulations. The study reflects different process parameters in the simulation; however, mainly binary mixtures were studied. Another similar paper on numerical modelling was presented by Alkhamis et al. [7], who proposed the dependence of Reynolds (Re) and Sherwood (Sh) numbers on the separation parameters during the CO_2 and CH_4 separation. Based on simulations, applications of the spacers in the inter-fibre space was recommended to increase the CO_2 separation efficiency. However, neither of the mentioned approaches offers an effective enough description of the processes. Also, there is not much data on the membrane separation of H_2-CO-CO_2 and ev. CH_4 mixtures (syngas), and not many studies have been published. Therefore, our studies are focused on the syngas membrane separation and a further description of the processes.

The study's primary goal is to inspect the dependency between process conditions (specifically permeate and retentate pressure combination) and the separation process results represented by component recovery and or permeate and retentate concentrations. Experimental data for the H_2-CO-CO_2 mixture are published along with several observations and dependency descriptions for permeate composition dependency on stage cut and component recovery dependency on pressure conditions.

2. Materials and methods

All experiments were performed using the experimental setup, the defined model syngas mixture and the following equations for computation described further below.

2.1. Experimental equipment

Measurements were made using a laboratory membrane unit Ralex GSU-LAB-200 manufactured by MemBrain that allows a module exchange. The unit operates with pressures ranging from 1 to 10 bar in the retentate (and feed) branch, 1 to 5 bar in the permeate bar and is equipped with a temperature-regulating circuit that can maintain module temperature between room temperature and 60 °C. The measured values are pressure p_i, temperature T_i, and mass flow m_i in each branch (feed – F, retentate – R, permeate – P), and the temperature of the module coating T_S. The composition of each flow is measured using a gas analyser that switches between flows following a user-defined scheme. Figure 1 below shows a simple scheme of the measurement.

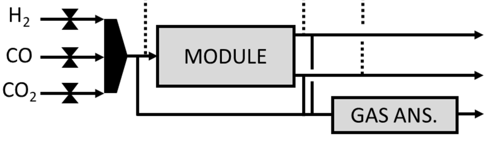

Figure 1. Scheme of measurement with indicated measured values. "Gas Ans." stands for the Gas analyser.

The module used in the study is a polyimide-polyetherimide hollow fibre module (manufactured by MemBrain, the exact mixture being kept a secret) consisting of 3000 hollow fibres with a diameter $D_e = 0.3\,\mathrm{mm}$, the thickness of the wall $W = 6\,\mu\mathrm{m}$ and an active length of $L = 290\,\mathrm{mm}$, defining the total area of the module $S = 0.514\,\mathrm{m}^2$. The feed enters into the fibres; the retentate is collected from the end of the fibres, and the permeate from the inter-fibre space. The whole bundle of fibres is covered in a tube and equipped with flanges on both ends.

The laboratory unit is connected to the supply of pure gases, including H_2, CO, CO_2, and N_2 (used for washing before and after each measurement to maximize the measurement reliability).

2.2. Model gas and measurement conditions

For the experiments with pure gases, gas sources for hydrogen H_2 of 5.0 gas purity, carbon monoxide CO of 4.7 gas purity, and carbon dioxide CO_2 of 4.0 gas purity, were used. The model mixture representing the biomass-gasification-produced syngas was defined to contain 16 %mol H_2, 34 %mol CO and 50 %mol CO_2. The concentration of each component in the feed flow is defined by the feed molar flows for each gas directly using the membrane unit interface.

Based on the extensive literature study, the composition was chosen: The values represent the oxygen (or air) gasification from wood biomass. Biomass gasification using air as the agent and wood as feedstock produces syngas with composition varying in 10–20 %mol for H_2, 30–45 %mol for CO and 35–55 %mol for CO_2.

The model mixture was tested at approximately constant temperature $T_M = 22\,^\circ\mathrm{C}$ (with a deviation smaller than 1 °C). The feed gas flow rate was maintained at $100\,\mathrm{NL\,h^{-1}}$ ($4.464\,\mathrm{mol\,h^{-1}}$). The pressure conditions were defined by the permeate pressure varying at levels $p_P = 1\,\mathrm{bar}$, $p_P = 2.5\,\mathrm{bar}$ and $p_P = 4\,\mathrm{bar}$. The total pressure difference ranged from 0.45 to 8 bar. (The lowest pressure difference was defined by the unit's limits and the module and was different for each pressure level.) The pressure conditions (permeate and retentate pressure) are defined within the unit interface and are maintained constant using an integrated regulation system.

2.3. Methods of data evaluation

The ideal gas behaviour was considered for all measurements (incl. pure component measurements). The ideal behaviour's deviation was estimated in the previous study and reached values smaller than 2 %, with an average below 1 % for all three components (H_2, CO and CO_2) and their mixtures.

Values acquired from experiments consist of pressure for each branch (permeate p_P, retentate p_R, feed p_F), mass flows of each branch, and composition of the flows (represented by the concentration of the components in %mol) and temperatures of the flows.

The value used to describe the ability to let the gases go through the membrane is the permeability P_i of each gas. The permeability is defined as the molar flow rate of gas permeating through a unit of area of the module per second caused by a unit of partial pressure difference of the module and can be described by the following equation (1):

$$P_i = \frac{n_i}{S \cdot \Delta p_i} W, \tag{1}$$

where P_i is the permeability of the component in [$\mathrm{mol\,m^{-1}\,s^{-1}\,bar^{-1}}$], n_i is the molar flow in [$\mathrm{mol\,s^{-1}}$], W is the thickness of the module wall in [m], S is the total surface of the fibres of the module in [$\mathrm{m^2}$], and Δp_i is the partial pressure difference in [bar] (for pure components, the partial pressure difference is equal to the total pressure difference). The pressure difference is defined as the difference between the retentate and permeate pressure (resp. the i-th component's partial pressure). The commonly used unit for permeability is 1 Barrer, which is defined as follows:

$$1\,\mathrm{Barrer} = 3.35 \times 10^{-11}\,\mathrm{mol\,m^{-1}\,s^{-1}\,bar^{-1}}. \quad (2)$$

To calculate the molar flow of component i, the total molar flow in a stream must be calculated from the mass flow and the concentrations. Taking the ideal gas behaviour into consideration, the following equation can be used:

$$n_x = \frac{m_x}{\sum c_i \cdot M_i}, \quad (3)$$

where n_x is the total molar flow in branch x in [$\mathrm{mol\,s^{-1}}$], m_x is the mass flow measured in branch x in [$\mathrm{g\,s^{-1}}$], c_i is the molar fraction of component i [–], and M_i is the molar weight of component i in [$\mathrm{g\,mol^{-1}}$].

To obtain the amount of i-th component in a given flow, the following equation can be used:

$$n_{i,x} = c_i \cdot n_x, \quad (4)$$

where c_i is the measured (molar) fraction of the i component and n_x is the total molar flow (where x can be P for permeate and R for retentate) in [$\mathrm{mol\,s^{-1}}$].

For a better comparison with the literature, stage cut θ is defined to describe the module's properties and the process. Stage cut is defined as a ratio between molar flow in permeate and feed flows. In some papers, mass-based stage cut can also be defined, but since most scientific papers use the molar version, so does this paper. The definition of stage cut is as follows:

$$\theta = \frac{n_P}{n_F} = \frac{n_P}{n_P + n_R}, \quad (5)$$

where n_x is the molar flow in a given flow (index P for permeate, F for feed, R for retentate) in [$\mathrm{mol\,s^{-1}}$].

To inspect the interaction between components, the ideal and actual selectivities are compared. The selectivity is expressed as:

$$\alpha_{i,j} = \frac{P_i}{P_j}, \quad (6)$$

where $\alpha_{i,j}$ is the selectivity of the component i over j (further in the text labelled $\alpha(i,j)$, to improve readability) and P_i and P_j are the permeabilities of the components i, j. The ideal selectivity is computed from pure component permeability and actual selectivity from the measurement with mixtures.

The primary quantity used in the study is component recovery R_i. Recovery was selected because it can be compared between different module types and process conditions and provides useful information for a possible implementation. Component recovery is defined as:

$$R_i = \frac{n_{i,P}}{n_{i,P} + n_{i,R}}, \quad (7)$$

where $n_{i,P}$ is the molar flow of component i in the permeate in [$\mathrm{mol\,s^{-1}}$] and $n_{i,R}$ is the molar flow of component i in the retentate in [$\mathrm{mol\,s^{-1}}$].

3. Results and discussion

First, the permeabilities of pure components were obtained to describe the properties of the module for the separation of H_2, CO and CO_2.

3.1. Pure component permeability

As mentioned above, the permeabilities Pi of pure components were measured. The values were averaged across all process conditions involved in the study (molar flow equal to $4.464\,\mathrm{mol\,h^{-1}}$, pressure differences ranging from 1 to 10 bar, permeate pressure from 1 to 4 bar, and temperature around 20–22 °C). Table 1 shows the measured permeability values for H_2, CO and CO_2.

Components	H_2	CO	CO_2
Permeability (Barrer)	1380 ± 62	23 ± 1	343 ± 11

Table 1. Permeabilities of pure components H_2, CO and CO_2 for given polyimide module.

To compare the values with similar modules in the literature, the permeance $(P/W)_i$ must be evaluated. Permeance is obtained by dividing the permeability by the thickness of the wall. The values of two different studies with hollow polyimide fibre modules published by Sharifian et al. [8] and Huang et al. [9], along with the permeance values of our study, are shown in Table 2.

Components	$\mathbf{P/W_i}$ **measured**	$\mathbf{P/W_i}$ **[4]**	$\mathbf{P/W_i}$ **[8]**
H_2	61.40 ± 2.80	241.0	97.10
CO	1.00 ± 0.03	8.7	1.28
CO_2	15.20 ± 0.50	67.0	31.10

Table 2. Permeance values obtained in this study compared to values published in other articles by Huang et al. [4] for polyimide membrane, temperature between 25–75 °C, and Sharifian et al. [8] for similar conditions. Values in [$\mathrm{nmol\,s^{-1}\,m^{-2}\,Pa^{-1}}$].

Two main observations can be made in the two tables above: First, Table 1 shows that polyimide membranes can be suitable for separating H_2 from the mixture and for adjusting the ratio (increasing CO concentration in the retentate). Second, Table 2 shows that the results presented in this article are consistent with the data available in the literature. The exact composition of the membranes can cause the difference: the module used for the study contains polyetherimide in addition to pure polyimide fibres, and the structure of the polymers can also vary between modules.

3.2. GAS MIXTURE

To demonstrate the interaction of components during the membrane separation, we compared the ideal selectivity with the measured selectivity in each case. Then, the composition of the retentate flow and the component recovery were studied.

3.2.1. SELECTIVITY COMPARISON

To prove the mutual interaction of components during a multicomponent membrane separation, ideal and actual selectivities were compared. Figure 2 and 3 show H_2/CO_2 and CO_2/CO selectivities. As seen in the figures below, with increasing stage cut, the measured selectivities decrease both for H_2/CO_2 and CO_2/CO.

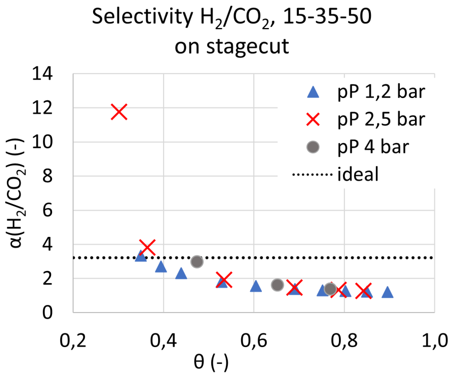

FIGURE 2. Ideal and measured selectivity for H_2/CO_2.

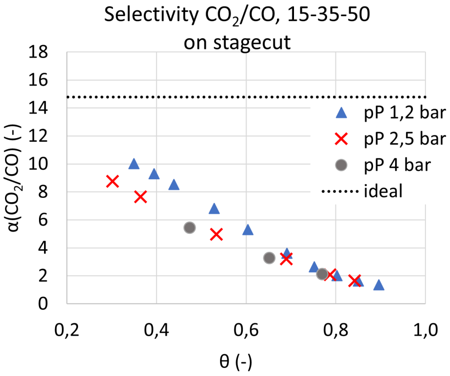

FIGURE 3. Ideal and measured selectivity for CO_2/CO

This phenomenon was also reported by Z. He and K. Wang [9], who tested the ideal and "true" selectivity for a mixture of He and CO_2. This case can be well compared with our case. The mentioned paper states that the true selectivity drops from 3.14 to 1.64 for the 1:1 mixture, from 3.35 to 0.94 for the 2:1 (CO_2:He) mixture and from 3.58 to 0.49 for the 3:1 (CO_2:He) mixture. This decrease is similar to the decreases observed in our study. Similarity can also be found in the size and type of the involved molecules – the ratios of ideal and measured (or "true") selectivities for H_2:CO_2 in our study (ratio 16:50 ∼ 1:3) correspond very well to the data presented for He:CO_2 in a ratio of 1:3.

3.2.2. PERMEATE COMPOSITION

As can be seen in Figure 4 and 5, with increasing stage cut, the concentrations of the high permeable components (H_2, CO_2) decrease. However, for CO_2, a slight maximum can be seen around stage cut $\theta = 0.40$ for $p_P = 1.2$ bar, of approximately 66 %mol, around stage cut $\theta = 0.45$ for $p_P = 2.5$ bar of approximately 62.5 %mol, and around stage cut $\theta = 0.5$ for $p_P = 4$ bar, of approximately 60.5 %mol. This observation implies that the CO_2 concentration in the permeate flow decreases with increasing permeate pressure.

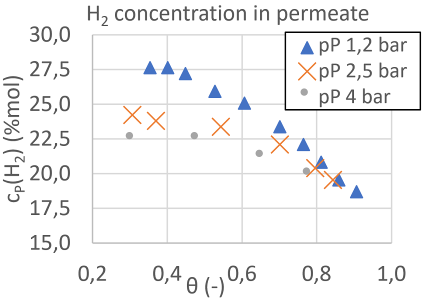

FIGURE 4. H_2 concentration in the permeate flow at stage cut.

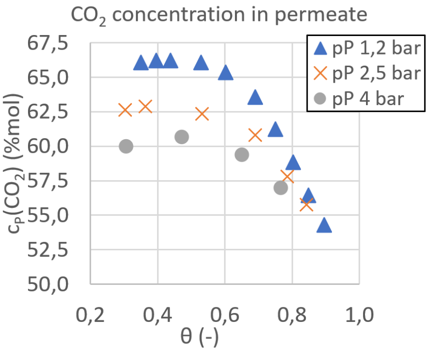

FIGURE 5. CO_2 concentration in the permeate flow at stage cut.

A similar trend of decreasing H_2 and CO_2 concentrations when separating a ternary gas mixture containing 45 %mol H_2, 40 %mol CO_2, 15 %mol CH_4 using two different modules (dual membrane module and polyimide module) was reported by W. Xiao et al. [9]. Their experiments were performed with stage cut ranging from 0.1 to over 0.4, and the concentration (mole fraction in the original paper) decreased from 68 %mol to 60 %mol for CO_2 and from 41 %mol to 32 %mol for H_2 when using the polyimide hollow-fibre module.

3.2.3. Components recovery

One of the dependencies that appear when inspecting multicomponent gas membrane separation is that the recovery of the component achieved at a certain pressure is dependent on the permeability of the component. The component with the highest permeability (H_2) reaches the highest recovery among the components at any pressure difference. However, the recovery does not increase proportionally with the permeability of the pure component – the permeability of H_2 is four times higher than the permeability of CO_2. Figure 6 shows data for all three components (H_2, CO, and CO_2) for permeate pressure $p_P = 2.5$ bar. The described dependencies can be observed.

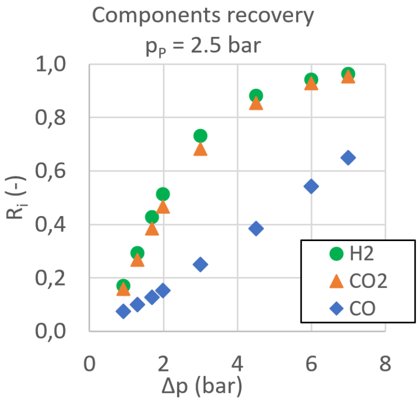

Figure 6. Component recovery for H_2, CO and CO_2 for permeate pressure $p_P = 2.5$ bar.

Another observed effect is the effect of the permeate pressure. The two more permeable components, H_2 and CO_2, reach lower values of component recovery with an increasing permeate pressure. The recovery for CO increases with pressure difference; however, it does not depend on the permeate pressure within the range of the statistical uncertainty. This implies that the differences between recoveries for different permeate pressures increase with increasing permeability of the pure component. Figure 7–9 show the recoveries for the three components.

W. Xiao et al. [9] have reported similar trends for component recovery concerning the CO_2 in the ternary mixture of H_2:CO_2:CO (in ratio 45:40:15, respectively) as the published data follow the trend. However, the data for H_2 seem to differ as the recovery seems to reach its limit below 0.4. This difference can be caused by the nature of the module. To describe the dependency of recovery on the total pressure drop and other process parameters, it is necessary to test model mixtures of different compositions (same components, different concentrations).

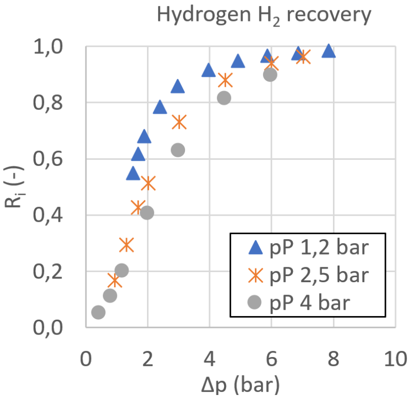

Figure 7. Hydrogen recovery on total pressure drop.

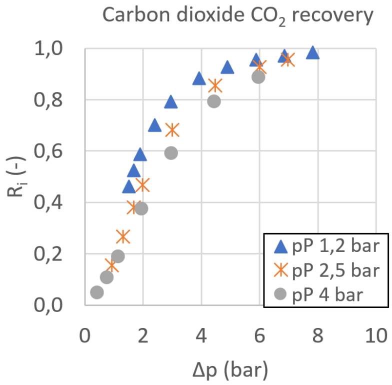

Figure 8. Carbon dioxide CO_2 recovery on total pressure drop.

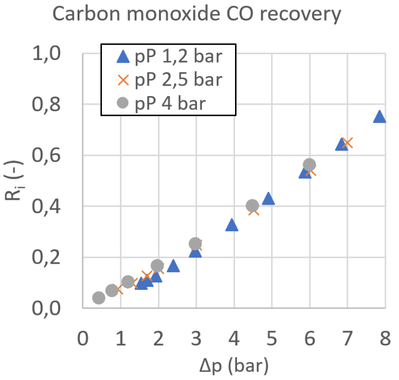

Figure 9. Carbon monoxide CO recovery on total pressure drop.

4. Conclusions

Several conclusions can be made based on the presented data. First, the tested hollow fibre module (polyetherimide-polyimide fibres manufactured by MemBrain) is suitable for H_2 and CO_2 separation, as the permeabilities of the pure components reach 1380 ± 62 Barrer for H_2 and 343 ± 11 Barrer for CO_2. The permeability of CO reached 23 ± 1 Barrer. The ideal selectivity (computed as the ratio of pure component permeabilities) for H_2/CO_2 and for CO_2/CO differ from the measured selectivities – the measured selectivities α_{H_2/CO_2} and $\alpha_{CO_2/CO}$ decrease with increasing stage cut and drop to 1/3 of the ideal selectivity for α_{H_2/CO_2} and 1/10 of the ideal selectivity for $\alpha_{CO_2/CO}$ (both at stage cut $\theta \approx 0.9$).

Regarding the concentration of H_2 and CO_2 in the permeate flow, both values decrease with increasing stage cut θ approaching 1. For the concentration of CO_2, maximum values of the concentration of $c_P(CO_2)$ can be observed at a value of 66 %mol for stage cut $\theta = 0.40$ ($p_P = 1.2$ bar), 62.5 %mol for stage cut $\theta = 0.45$ ($p_P = 2.5$ bar) and 60.5 %mol for stage cut $\theta = 0.5$ ($p_P = 4$ bar).

The component recovery dependency on the permeate pressure drop has been studied. An observed trend is that the permeability of the component affects the recovery of the component so that the components with a higher permeability (when processed in pure form) reach higher recoveries at a given pressure difference. However, the increase in recovery is not directly proportional to permeability. Also, a dependency between the component recovery and the permeate pressure has been revealed, showing that increasing the permeate pressure results in lower recoveries of the components at a given pressure drop. This can be caused by multiple reasons that have not been specified; however, the potential causes are a decrease in sorption and diffusion coefficients with increasing pressure and/or by fibre compression resulting in a decrease in its permeability.

This study shows that component recovery of H_2, CO_2, and CO can be affected by process conditions. Therefore, for a successful industrial application of the membrane separation within the field of biomass gasification, a wider sample of process conditions must be studied to develop a reliable model for describing the process. After that, membrane operations could be used for adjusting the ratio of the components by changing the pressure conditions, which would compensate for the variance in the biomass gasification product composition (caused by unstable feed composition due to biomass nature) and allow a better optimization of the technology.

List of symbols

c_i concentration in component i [%mol]

L length of the module [m]

m_F, m_P, m_R mass flow of gas in feed, permeate, and retentate, respectively [g s^{-1}]

M_i molar weight of component i [g mol^{-1}]

n_i molar flow of component i [mol s^{-1}]

p_F, p_P, p_R pressure in the feed, permeate, and retentate branch, respectively [bar]

P_i permeability of component i [Barrer]

R_i i-component recovery

S total area of the module [m2]

T_F, T_P, T_R temperature in feed, permeate, and retentate, respectively [°C]

T_M mean measurement temperature [°C]

W thickness of wall of the fibres [μm]

Δp pressure difference [bar]

θ stage cut [–]

Acknowledgements

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