

Syngas Components Recovery during Membrane Gas Separation

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Membrane operations are a promising way of improving and adjusting the composition of the biomass gasification product – syngas – before it can be further transformed into fuels and energy. The presented study focuses on the recovery of individual components (H₂, CO, CO₂) during membrane separation under varying conditions – pressure difference and the feed composition. Model syngas mixtures with four different compositions containing between 12-24 %mol H₂, 34-39 %mol CO and 43-49 %mol CO₂ were tested under different pressure differences ranging from 1 to 8 bar (retentate pressure ranging from 2 to 10 bar, permeate pressure from 1 to 4 bar), at temperature 22 °C. Results of the study indicate exponential dependency existence between total pressure drop and the components recovery. The data were approximated with fixed parameter for minimal pressure difference for each component ($p_0 = 0.5$ bar for H₂ and $p_0 = 0.7$ bar for CO₂) and with variable exponent coefficients. The coefficients in exponent are strongly dependant on permeate pressure (ranging from 0.33 to 0.88 bar⁻¹ for different permeate pressures for CO₂ recovery) and vary with feed composition as well (from 0.75 to 0.83 bar⁻¹ across different mixtures for CO₂ at fixed permeate pressure).

1. Introduction

In recent past, the need for alternative ways of waste elimination and or its transformation into useful chemicals have grown and has attracted attention of many scientific teams across the world. One of the promising ways for such transformation is biomass gasification. The product of the gasification, syngas, is composed of H₂, CO, CO₂ and CH₄, which leads to many fields of its utilization - it can be burned to produce heat and energy or further transformed into chemicals and fuels. Some of the possible final products of such technology for syngas conversion are methanol and various Fischer-Tropsch products including waxes, tars, oils, gasoline and other, as mentioned by Krylova (2014).

Syngas must be treated before using it as feedstock for the final transformation technologies. Along with different conventional technologies such as various absorption processes (Rectisol™, Selectol™ and other), adsorption processes and different scrubbing options, membrane operations can be used (Woolcock and Brown, 2013). Membrane separation of gases can both help with removing the impurities from the gas and with adjusting the ratios of the main components (H₂, CO, CO₂ and CH₄).

For proper implementation of the membrane operation to the technological process for biomass conversion into chemicals through gasification, it is necessary to describe the process. So far, the focus of the scientific field was focused on two main approaches. One approach focuses on describing binary mixtures treatment consisting of syngas components. Choi et al. (2015) presented a study on H₂/CO separation describing stagecut-permeance limits and the fact that permeance drops with increasing flowrate. Huang et al. (2020) studied the dependency between components recovery on the area of the module, presenting the effect of the desired concentration on the size of the module for H₂/CO₂ separation. Casado-Coterillo (2019) studied the dependency of CO₂/N₂ and CO₂/CH₄ selectivity depending on presence of water vapors in the feed and shown that further study in the field of multicomponent non-ideal mixtures is necessary for proper implementation of the membrane processes. The second mentioned approach focuses on numerically describing and solving the multicomponent separation. Lee et al. (2017) proposed a numerical solution for multicomponent mixtures containing CO₂ separation in counter-current hollow fiber modules, which was based on differentiation of the

process. Alkhamis et al. (2015) used numerical application of fluid dynamics on membrane separation for CO₂ and CH₄ mixtures and proposed Re number and Sh number dependency on different parameters and mass change of the components on both criteria. Medi and Nomvar (2020) tested different numerical models for gas separation via membranes, suggesting variable order numerical differentiation formula. Currently, an efficient approach for estimating the results of multicomponent gas mixture separation is missing.

The membrane separation process is dependent on many parameters – permeate and retentate pressure, feed gas composition, membrane module parameters, temperature, load of the module and other. To describe the relation between the outcome of the membrane separation process and the process conditions, it is necessary to inspect the dependency on each parameter separately. The aim of the study is to present a description of the dependency between components recovery and pressure difference, permeate pressure and the composition of the feed gas.

2. Methods

The experiments were performed using following configuration of experimental equipment, model gas and process conditions and evaluated using equation stated further.

2.1 Model gas

The composition of the model gas was chosen based on literature review concerning syngas composition as presented in earlier papers of the authors (Seghman et al., 2019). As the composition of the syngas depends on all gasification parameters (temperature, gasification agents and biomass-to-agent ratio, catalyst presence, reactor type and other), it was necessary to fix some parameters to estimate the concentration of the components within the model mixture. For the purposes of the study, mixtures consisting of three main components were considered (H₂, CO, CO₂). The ratio of the components was estimated to match the ratio of the components in syngas produced by oxy-gasification of woody biomass. Following Table 1 shows the compositions and the labels for the mixtures used for the study. The label of each mixture directly refers to its composition – the first number represents the H₂ concentration, the second represents CO concentration and the third refers to CO₂.

Table 1: Labels and concentrations of the components in the mixtures in the study

Mixture label	CF (H ₂) (%mol)	CF (CO) (%mol)	CF (CO ₂) (%mol)
12-39-49	12	39	49
18-39-43	18	39	43
18-34-48	18	34	48
23-33-44	23	33	44

2.2 Experimental setup

The experiments were performed using laboratory unit for membrane separation of gases Ralex GSU-LAB-200 (manufactured by MemBrain) with inter-changeable modules. The unit operates at pressure range 1-10 bar in retentate branch, 1-5 bar in permeate branch and can maintain the temperature of the module between the room temperature and 60 °C. Gas composition is analyzed in an implemented gas analyzer (manufactured by EMERSON). A simple scheme of the measurement set-up is shown in the Figure 1 below.

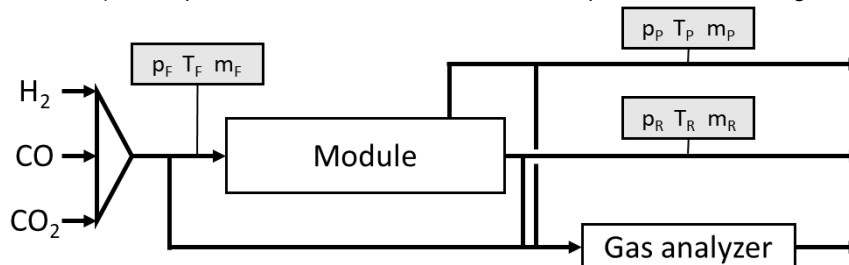


Figure 1: Experimental setup – grey rectangles show measured quantities.

The module used for the measurement is a polyimide module consisting of 3,000 hollow fibers with inside feed into the tubular space, dividing it into the hollow fibers. Permeate is collected from inter-fiber space. The inner

diameter of the fibers is 0.188 mm wall thickness is 6 μm , active length is 290 mm. Total area of the module is 0.514 m^2 . Used Module was manufactured by MemBrain.

The mixtures were tested under different pressure conditions – 18 combinations of permeate and retentate pressures were tested for each mixture. The permeate pressure was kept on three levels – 1, 2 and 4 bar. Pressure differences were maintained between 1 and 8 bar. The temperature dependency was not studied, temperature was kept constant at $T_M = 22\text{ }^\circ\text{C}$. The flowrate was maintained constant as well at $F = 4.5\text{ mol}\cdot\text{h}^{-1}$ ($\sim 100\text{ NI h}^{-1}$).

2.3 Used definitions

For the evaluation of the experiments, ideal gas behavior was considered. Deviations from the ideal behavior were estimated using compressibility factors with maximal deviation reaching 2 % and average deviation less than 1 %. To describe the ability of each component to permeate through the module, its permeance P/L_i was evaluated. The permeance describes the relation between molar amount of the gas flux permeating through unit of area of the membrane per unit of time under effects of unit of pressure difference and is defined in Eq(1) used by O'Brien-Abraham et al. (2007) and others:

$$P/L_i = \frac{n_i}{S \cdot \Delta p} \quad (1)$$

where P_i is the permeability of the component i ($\text{mol m}^{-1}\text{ s}^{-1}\text{ Pa}^{-1}$), n_i is the measured molar flow (mol s^{-1}), L is the length of the module (m), S is the total area of the module fibers (m^2), and Δp is the pressure difference defined as:

$$\Delta p = p_R - p_P \quad (2)$$

where p_R is the retentate pressure (Pa) and p_P is the permeate pressure (Pa). Commonly used unit of permeability is 1 Barrer = $3.35 \times 10^{-16}\text{ mol m}^{-1}\text{ s}^{-1}\text{ Pa}^{-1}$.

The observed quantity is the component recovery R_i . The recovery of component i can be computed as follows:

$$R_i = \frac{n_{i,P}}{n_{i,P} + n_{i,R}} \quad (3)$$

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

To calculate the amount of each component in permeate and retentate flow, measured concentration of the component i in the branch and measured total molar flow in the branch n_x can be used as follows:

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

where c_i is the measured concentration of the i -component (-) and n_x is the total molar flow (where x can be P for permeate and R for retentate) (mol s^{-1}).

To calculate the total molar flow in a given stream from the mass flow and the concentrations, following equation can be used:

$$n_x = \frac{m_x}{\sum c_i \cdot M_i} \quad (5)$$

where n_x is the total molar flow in branch x (mol s^{-1}), m_x is the measured mass flow in branch x (g s^{-1}), c_i is the concentration of component i (%mol) and M_i is the molar weight of the component i (g s^{-1}).

3. Results and discussion

Firstly, to evaluate the ability of the gases to permeate through the given module, their permeability at the process conditions used for further experiments and evaluation was measured. Using Eq(1) above, following values of permeance were obtained for the included gases and compared with literature sources. See Table 2 for measured permeance P/r values and values obtained from literature sources. Values presented by Sharifian et al. (2019) use similar hollow fibers to those used in this study. Data presented by Huang et al. (2020) were measured using material with high hydrogen permeance. As seen in the Table 2, the ratio of the permeances correlates with the values obtained from sources using similar materials.

Table 2: Pure components permeances compared to similar studies in literature presented by Sharifian et al. (2019) and by Huang et al. (2020). (Units from literature sources converted to match.)

Component	P/L _i (nmol s ⁻¹ m ⁻² Pa ⁻¹) measured	P/L _i (nmol s ⁻¹ m ⁻² Pa ⁻¹) Sharifian et al. (2019)	P/L _i (nmol s ⁻¹ m ⁻² Pa ⁻¹) Huang et al. (2020)
H ₂	61.40 ± 2.80	97.10	241.0
CO	1.00 ± 0.03	1.28	8.7
CO ₂	15.20 ± 0.50	31.10	67.0

Summary analysis covering all four mixtures was then carried out. As presented by Mazzotti et al. (2016), total flux of the component is dependent on the total pressure difference exponentially, with pressure difference in the exponent. This definition also respects the fact that the limit for infinite pressure difference is the feed rate. Similar dependency is expected for components recovery – if the flux of the component presented by Mazzotti et al. (2016) transformed into recovery, an exponential equation similar to the Eq(6) can be obtained. This dependency can also be observed in other fields. Equation (6) follows:

$$R_i = 1 - \exp[-A * (\Delta p - p_0)] \quad (6)$$

where R_i is the recovery of component i , Δp is the total pressure difference (bar) and A (-) and p_0 (bar) are the approximating coefficients. Based on that assumption of similarity between component flux (derived by Mazzotti et al., 2016) and the trends observed in the figures below (Figure 2a and Figure 2b), the data were approximated with Eq(6). The pressure difference shift p_0 is added to the equation to represent the nature of components competing during small pressure differences and to respect the trends observed in the data.

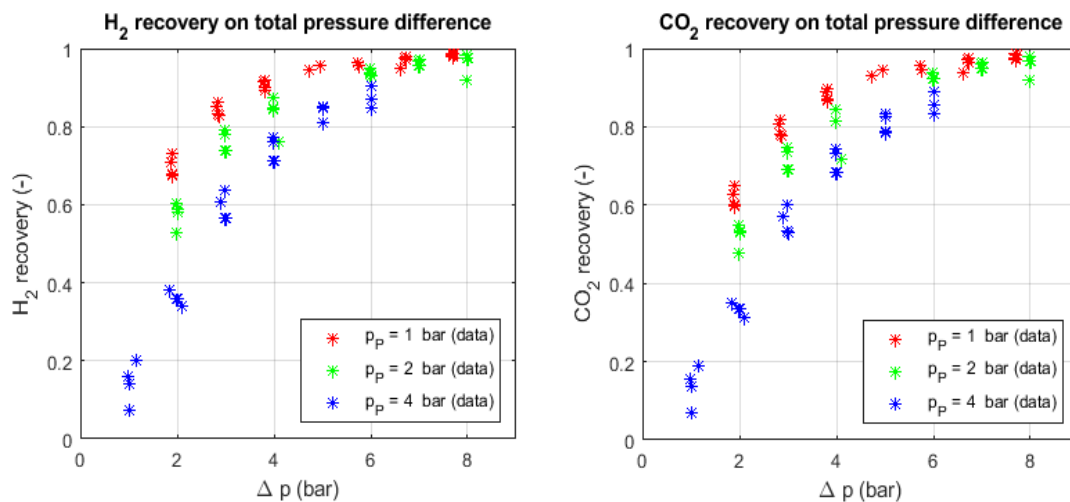


Figure 2 – Components recovery for all four mixtures, for hydrogen H₂ (a) and for carbon dioxide CO₂ (b) measured at temperature $T_M = 22$ °C at feed flowrate $F = 100$ NI h⁻¹.

The values for parameter p_0 were obtained as average of p_0 parameters among all four mixtures with higher weight for pressure levels with $p_P = 4$ bar as the data are closer to the intercept. For CO₂ recovery, the parameter was set to $p_{0,CO_2} = 0.7$ bar, and for H₂ recovery, the parameter was set to $p_{0,H_2} = 0.5$ bar. Figures 3a and 3b show the data approximated with the exponential equation. Figure 3a shows approximation of the H₂ data from mixture 19-38-43 approximated with fixed parameter $p_0 = 0.5$ bar, Figure 3b shows the approximation with fixed $p_0 = 0.7$ bar for CO₂ recovery and for mixture 19-38-43. Better optimization of the parameter p_0 will be performed in the future studies after the data set is widened. As shown in Figures 3a and 3b below, the exponential approximations with fixed parameter show good representation of the data.

The following tables (Table 3 for CO₂ and Table 4 for H₂) show the coefficients A_j for each mixture and each permeate pressure p_P . The uncertainties of the parameters are included in the table. As seen, the uncertainties of the coefficients A_j reach from 2 to 25 %, with average of 11 %. The values with 25 % uncertainty appear only at one configuration which indicates measurement error.

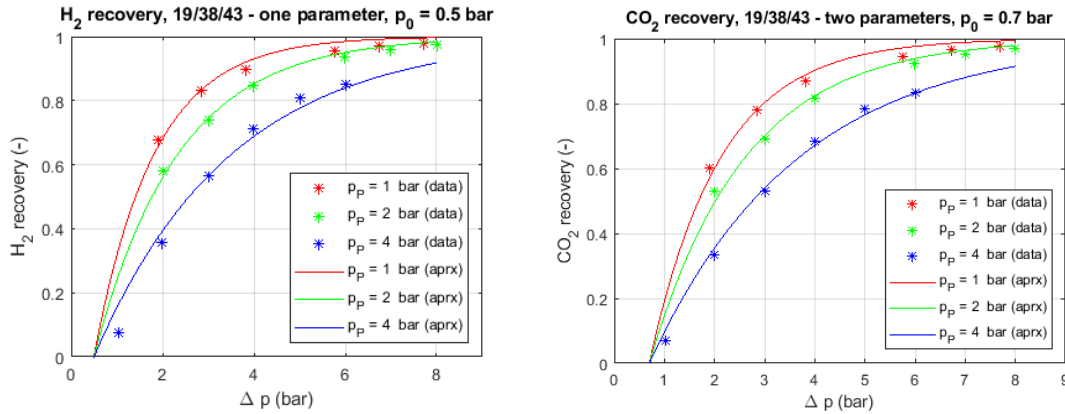


Figure 3 – H_2 recovery (a) approximation with parameter $p_0 = 0.5$ bar and CO_2 recovery (b) with parameter p_0 fixed at $p_0 = 0.7$ bar, both for mixture 19-38-43 data measured at temperature $T_M = 22$ °C and feed flowrate $F = 100$ NI h^{-1} .

Table 3: Exponent coefficients A_j for CO_2 for all mixtures and at the three different pressure levels (for permeate pressure being 1, 2 and 4 bar), with $p_0 = 0.7$ bar ($F = 100$ NI h^{-1} , $T_M = 22$ °C)

Mixture label	A_j ; $p_P = 1$ bar (bar^{-1})	A_j ; $p_P = 2$ bar (bar^{-1})	A_j ; $p_P = 4$ bar (bar^{-1})
12-39-49	0.78 ± 0.07	0.57 ± 0.07	0.40 ± 0.03
18-39-43	0.71 ± 0.07	0.53 ± 0.04	0.34 ± 0.02
18-34-48	0.81 ± 0.08	0.52 ± 0.13	0.38 ± 0.07
23-33-44	0.69 ± 0.09	0.50 ± 0.01	0.35 ± 0.03

Table 4: Exponent coefficients A_j for H_2 for all mixtures and at the three different pressure levels (for permeate pressure being 1, 2 and 4 bar), with $p_0 = 0.5$ bar ($F = 100$ NI h^{-1} , $T_M = 22$ °C)

Mixture label	A_j ; $p_P = 1$ bar (bar^{-1})	A_j ; $p_P = 2$ bar (bar^{-1})	A_j ; $p_P = 4$ bar (bar^{-1})
12-39-49	0.83 ± 0.08	0.59 ± 0.08	0.39 ± 0.03
18-39-43	0.76 ± 0.08	0.55 ± 0.03	0.33 ± 0.05
18-34-48	0.88 ± 0.10	0.55 ± 0.13	0.38 ± 0.08
23-33-44	0.75 ± 0.09	0.52 ± 0.02	0.34 ± 0.03

As can be seen in the tables above, the uncertainty in the exponent coefficients A_j is between 5 % and 15 % except for cases for 18-34-48 mixture. This mixture has a more spread data set which implicates greater deviation from the approximation.

From the presented data, it can be observed that exponent coefficients depend on permeate pressure. As seen above, with increasing pressure in permeate the exponent coefficient decreases. This shift can be caused by compression of the hollow fibers. Similar effect was described by Cerveira et al. (2018) who reported a decrease in product permeation at higher pressure differences which was caused by deformation (and plasticization) of the fibers. Another cause for the shift can be a decrease in sorption and diffusion coefficients with pressure as mentioned by Yampolskii et al. (2007).

Another possible dependency is that with changing concentration in the mixture, the exponent also changes – for H_2 the exponents decrease with increasing permeability and with CO_2 the A_j appear to increase. However, the increases and decreases in the values of A_j in both cases are within the confidence intervals and thus must be further studied on wider set of data.

4. Conclusions

From the experimental results, an exponential dependency of more permeable components' (H_2 and CO_2) recovery on the total pressure difference was observed. As seen in the presented figures, two parameter exponential equations can reliably describe the dependency. Even after fixing the p_0 coefficient referring to shift on the Δp -axis, the uncertainty in the evaluation of the parameters ranged from 5 % to 15 %. The data indicate that permeate pressure and composition of the feed affect the recovery rate. The permeate pressure causes

coefficients in exponent decrease to half with increase of permeate pressure from 1 bar to 4 bar – exponent coefficients for H₂ decreasing from average of 0.81 bar⁻¹ for $p_P = 1$ bar to 0.36 bar⁻¹ for $p_P = 4$ bar, the coefficients for CO₂ decreasing from average 0,75 bar⁻¹ for $p_P = 1$ bar to 0.37 bar⁻¹ for $p_P = 4$ bar.

The decrease in exponent coefficient can be caused by multiple effects among which hollow fibres compression is the most probable. Another reason might be the decrease in sorption and diffusion coefficients with increasing pressure. The problematics of the parametrisation will be the subject of the further study. The presented paper proves existence of direct dependency on components recovery on pressure difference along with highlighting some parameters affecting the parameters of the approximation being feed gas concentration and mainly permeate pressure.

Another effect that can be observed on the presented data is that with increasing p_P the differences between components recovery (for CO₂ and H₂) seem to decrease and the coefficients become closer. This phenomenon must be further studied as it was not the subject of this study.

Nomenclature

A – exponent coefficient in approximation, bar ⁻¹	p_0 – approximation coefficient, bar
c_F – concentration in feed gas, %mol	P_i – permeability of component i, Barrer
F – feed flowrate, mol h ⁻¹ , NI h ⁻¹	R_i – i-component recovery, -
L – length of the module, m	S – total area of the module, m ²
m_F, m_P, m_R – mass flow of gas in feed, permeate and retentate, respectively, g s ⁻¹	T_F, T_P, T_R – temperature in feed, permeate and retentate, respectively, °C
M_i – molar weight of component i, g mol ⁻¹	T_M – mean temperature of the measurement, °C
n_i – molar flow of component i, mol s ⁻¹	Δp – pressure difference, bar
p_F, p_P, p_R – pressure in feed, permeate and retentate branch, respectively, bar	θ – stagecut, -

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