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\textsubscript{2}, CO, and CO\textsubscript{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 polyamide hollow fibre module with 3000 hollow fibres. Permeability values were established at 1380 Barrer for H\textsubscript{2}, 23 Barrer for CO, and 343 Barrer for CO\textsubscript{2}. The measured selectivities differ from the ideal ones: the ideal H\textsubscript{2}/CO\textsubscript{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\textsubscript{2}, 34\% CO, and 50\% CO\textsubscript{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\textsubscript{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\textsubscript{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\textsubscript{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\textsubscript{2}, CO, CO\textsubscript{2}, and minor amounts of CH\textsubscript{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\textsubscript{2}/CO separation – the effect of the operating pressure was described for H\textsubscript{2}:CO ratios of 3:1, 5:1 and 7:1 and showed that permeance increased with a higher H\textsubscript{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\textsubscript{2} and CO\textsubscript{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\textsubscript{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\textsubscript{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\textsubscript{2}, 6\% O\textsubscript{2}, and 80\% N\textsubscript{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\textsubscript{2} and CH\textsubscript{4} separation. Based on simulations, applications of the spacers in the inter-fibre space was recommended to increase the CO\textsubscript{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 \( \text{H}_2-\text{CO}-\text{CO}_2 \) and ev. \( \text{CH}_4 \) 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 \( \text{H}_2-\text{CO}-\text{CO}_2 \) 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 \( T_M \).

The composition of each flow is measured using a gas analyser that switches between flows following a circuit that can maintain module temperature between pressure level.) The pressure conditions (permeate and retentate pressure) are defined within the unit interface and are maintained constant using an inline gas module that allows a module exchange. The unit is connected to the supply of 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 \( \text{H}_2 \), 30–45 \( \% \) mol for CO and 35–55 \( \% \) mol for \( \text{CO}_2 \).

The model mixture was tested at approximately constant temperature \( T_M = 22 \degree \text{C} \) (with a deviation smaller than 1°C). The feed gas flow rate was maintained at 100 NL h\(^{-1}\) (4.644 mol h\(^{-1}\)). The pressure conditions were defined by the permeate pressure varying at levels \( p_F = 1 \) bar, \( p_R = 2.5 \) bar and \( p_P = 4 \) bar. The total pressure difference ranged from 0.45 to 8 bar. 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 1 \( \% \) for all three components (\( \text{H}_2 \), CO and \( \text{CO}_2 \)) and their mixtures.

Values acquired from experiments consist of pressure for each branch (permeate \( p_F \), 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]:

\[
P_i = \frac{n_i}{S \cdot \Delta p_i} W,
\]

\[W = \text{ideal behaviour’s deviation.}
\]
where \( P_i \) is the permeability of the component in [mol m\(^{-1}\) s\(^{-1}\) bar\(^{-1}\)], \( n_i \) is the molar flow in [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 [m\(^2\)], and \( \Delta p_i \) 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:

\[
1 \text{ Barrer} = 3.35 \times 10^{-11} \text{ mol m}^{-1} \text{ s}^{-1} \text{ bar}^{-1}. \quad (2)
\]

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

For a better comparison with the literature, stage cut \( \theta \) 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 [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 [mol s\(^{-1}\)] and \( n_{i,R} \) is the molar flow of component \( i \) in the retentate in [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 \( P_i \) of pure components were measured. The values were averaged across all process conditions involved in the study (molar flow equal to 4.644 mol h\(^{-1}\), pressure differences ranging from 1 to 10 bar, permeate pressure from 1 to 10 bar, and temperature around 20–22°C). Table 1 shows the measured permeability values for H\(_2\), CO and CO\(_2\).

<table>
<thead>
<tr>
<th>Components</th>
<th>( H_2 )</th>
<th>CO</th>
<th>CO(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Permeability (Barrer)</td>
<td>1380 ± 62</td>
<td>23 ± 1</td>
<td>343 ± 11</td>
</tr>
</tbody>
</table>

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. [9] and Huang et al. [4], along with the permeance values of our study, are shown in Table 2.

<table>
<thead>
<tr>
<th>Components</th>
<th>( P/W_i ) measured</th>
<th>( P/W_i )</th>
<th>( P/W_i )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( H_2 )</td>
<td>61.40 ± 2.80</td>
<td>241.0</td>
<td>97.10</td>
</tr>
<tr>
<td>CO</td>
<td>1.00 ± 0.03</td>
<td>8.7</td>
<td>1.28</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>15.20 ± 0.50</td>
<td>67.0</td>
<td>31.10</td>
</tr>
</tbody>
</table>

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. [9] for similar conditions. Values in [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\textsubscript{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\textsubscript{2}/CO\textsubscript{2} and CO\textsubscript{2}/CO selectivities. As seen in the figures below, with increasing stage cut, the measured selectivities decrease both for H\textsubscript{2}/CO\textsubscript{2} and CO\textsubscript{2}/CO.

![Figure 2. Ideal and measured selectivity for H\textsubscript{2}/CO\textsubscript{2}.](image)

**Figure 2.** Ideal and measured selectivity for H\textsubscript{2}/CO\textsubscript{2}.

![Figure 3. Ideal and measured selectivity for CO\textsubscript{2}/CO.](image)

**Figure 3.** Ideal and measured selectivity for CO\textsubscript{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\textsubscript{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\textsubscript{2}:He) mixture and from 3.58 to 0.49 for the 3:1 (CO\textsubscript{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\textsubscript{2}:CO\textsubscript{2} in our study (ratio 16:50 ∼ 1:3) correspond very well to the data presented for He:CO\textsubscript{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\textsubscript{2}, CO\textsubscript{2}) decrease. However, for CO\textsubscript{2}, a slight maximum can be seen around stage cut θ = 0.40 for p\textsubscript{P} = 1.2 bar, of approximately 66 %mol, around stage cut θ = 0.45 for p\textsubscript{P} = 2.5 bar of approximately 62.5 %mol, and around stage cut θ = 0.5 for p\textsubscript{P} = 4 bar, of approximately 60.5 %mol. This observation implies that the CO\textsubscript{2} concentration in the permeate flow decreases with increasing permeate pressure.

![Figure 4. H\textsubscript{2} concentration in the permeate flow at stage cut.](image)

**Figure 4.** H\textsubscript{2} concentration in the permeate flow at stage cut.

![Figure 5. CO\textsubscript{2} concentration in the permeate flow at stage cut.](image)

**Figure 5.** CO\textsubscript{2} concentration in the permeate flow at stage cut.

A similar trend of decreasing H\textsubscript{2} and CO\textsubscript{2} concentrations when separating a ternary gas mixture containing 45 %mol H\textsubscript{2}, 40 %mol CO\textsubscript{2}, 15 %mol CH\textsubscript{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 CO₂ and from 41%mol to 32%mol for H₂ 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 (H₂) 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 H₂ is four times higher than the permeability of CO₂. Figure 6 shows data for all three components (H₂, CO, and CO₂) for permeate pressure $p_P = 2.5$ bar. The described dependencies can be observed.

![Component recovery for H₂, CO and CO₂ for permeate pressure $p_P = 2.5$ bar.](image)

Another observed effect is the effect of the permeate pressure. The two more permeable components, H₂ and CO₂, 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 CO₂ in the ternary mixture of H₂:CO₂:CO (in ratio 45:40:15, respectively) as the published data follow the trend. However, the data for H₂ 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).

![Hydrogen H₂ recovery on total pressure drop.](image)

![Carbon dioxide CO₂ recovery on total pressure drop.](image)

![Carbon monoxide CO recovery on total pressure drop.](image)

### 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 H₂ and CO₂ separation, as the permeabilities of the pure components reach 1380 ± 62 Barrer for H₂ and 343 ± 11 Barrer for CO₂. The permeability of CO reached 23 ± 1 Barrer. The ideal selectivity (computed as the ratio of pure component permeabilities) for H₂/CO₂ and for CO₂/CO differ from the measured selectivities – the measured selectivities $\alpha_{H₂/CO₂}$ and $\alpha_{CO₂/CO}$ decrease with increasing stage cut and drop to 1/3 of the ideal selec-
tivity for $\alpha_{H_2/CO_2}$ 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 $\theta$ 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 66.2% 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 [m$^2$]
- $T_F, T_P, T_R$: temperature in feed, permeate, and retentate, respectively [$^\circ$C]
- $T_M$: mean measurement temperature [$^\circ$C]
- $W$: thickness of wall of the fibres [$\mu$m]
- $\Delta p$: pressure difference [bar]
- $\theta$: stage cut [-]

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