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Mass transfer studies on the dehydration of supercritical carbon dioxide using dense polymeric membranes

Andrew Shamua,b, Henk Miedema, Sybrand J. Metza, Zandrie Bornemanb,c, Kitty Nijmeija,b,c,*

a Wessus, Centre of Excellence for Sustainable Water Technology, Oosterweg 9, 8911 MA Leeuwarden, The Netherlands
b Membrane Materials and Processes, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands
c Dutch Institute for Fundamental Energy Research (DIFFER), De Zaale 20, 5612 AJ Eindhoven, The Netherlands

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ABSTRACT

Continuous drying processes using supercritical CO2 (scCO2) as a water extraction agent require 24/7 operational dehydration units for scCO2 regeneration. Dehydration units using dense polymeric membranes are considered a cost effective, sustainable alternative to the current zeolite-based units. The focus of previous studies on the membrane-based dehydration of scCO2 was always on the membrane itself whereas boundary layer effects, e.g., concentration polarization, were not taken into account. To quantify the boundary layer effects, simulations were performed using three different membrane materials: SPEEK, Nafion® 117, and PEBAX® 1074. Process conditions during the simulations ranged from 8.0 to 18.0 MPa and 40 to 100 °C. Even though the three types of membranes examined differ in their H2O permeability and H2O over CO2 selectivity, in all cases 80% of the total mass-transfer resistance can be assigned to concentration polarization effects, making it the dominant parameter for water transport. Despite high but differing intrinsic water permeabilities of all three membranes materials, the H2O flux through the membrane is significantly reduced by concentration polarization down to similar levels. This makes it necessary to use larger membrane areas, that result in higher CO2 fluxes. As a consequence, material selection is predominantly based on the ability to reject CO2. Optimization of process conditions other than membrane material is briefly discussed.

1. Introduction

Supercritical CO2 (scCO2) is frequently used in industrial processes for e.g. the drying of fruits and vegetables to extent shelf life [1]. Due to its supercritical state, it has high densities values typical for liquids and simultaneously low viscosities characteristic for gases [2]. Moreover as drying is performed at relatively low temperatures and under oxygen free conditions, vitamins, pigments and proteins are preserved ensuring the nutritional value and the dried products keep their color, shape, structure and texture [3]. Although performed under pressure, scCO2 drying is a very mild process.

Fig. 1 displays the typical outline of such an industrial drying process using scCO2. Dry scCO2 enters the extraction unit, extracts the water from the product and leaves the unit as a humidified stream. This stream is then regenerated in a dehydration unit before it is re-injected into the extraction unit for the next water extraction cycle. Typical fluid temperatures and pressures are in the range of 45 °C and 13.0 MPa [3], which is beyond carbon dioxides critical values of T = 31.04 °C and p = 7.38 MPa [2].

Currently, columns packed with adsorbents such as zeolites are applied to dehydrate the scCO2. The enclosed adsorbents extract water from the scCO2 until they are fully saturated. Temperatures up to 260 °C are needed to reactivate the zeolite by water desorption [4]. While this energy demanding reactivation step is carried out, a second zeolite packed column is switched in to continue the scCO2 dehydration. The required reactivation energy and the additional zeolite column make the scCO2 drying process economically less attractive. Lohaus et al. [4] showed with their model, based on Scholz et al. [5], that a shift towards a membrane-based dehydration process, where a second dehydration unit and reactivation steps are obsolete, could reduce the dehydration costs up to 20%. Even though Lohaus et al. simulated and discussed water vapor concentration profiles and the driving force profiles along the membrane unit, the combined mass transfer of the skin layer material, its porous support and the feed- and permeate boundary layers were not taken into account in their analysis. Each of these stacked layers is very different constituted, especially under highly pressurized scCO2 conditions, where the fluids density and viscosity are very different to those in conventional gas separation applications. It stands to

* Corresponding author at: Membrane Materials and Processes, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands.
E-mail address: d.c.nijmeijer@tue.nl (K. Nijmeijer).

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reason that in the special case of exposure to scCO₂ the contribution of each single layer contributes differently to the total water transport resistance and thus to the water permeance.

Composite membranes, consisting of a thick porous support and a thin selective, water permeable, skin layer, can withstand transmembrane pressures of more than 10.0 MPa. Due to polarization effects in the boundary layers, evoked by severe scCO₂ conditions, the overall selectivity and permeability can be very different from those of the membrane (or skin layer) itself. Therefore, polarization effects need to be included in any analysis of mass transfer resistances during membrane transport.

Metz et al. [6] concluded that concentration polarization effects, enhanced by the relatively low H₂O diffusion across the feed gas boundary layer, compromise the water vapor permeability and H₂O/CO₂ selectivity already at low feed pressures. At constant temperature and increasing pressure, molecules start gathering more densely, leading to a reduced mean free path of motion, an increased molecular collision resulting in a lower diffusion coefficient. The relationship between the declining diffusion coefficient and increasing fluid density was also pointed out by Magalhães et al. [7]. Considering the high fluid density under scCO₂ conditions, up to 200 times higher compared to the low pressure experiments of Metz [6], it is expected that concentration polarization effects become even more dominant. Scholz et al. [5] analyzed non-ideal effects during gas permeation, including concentration polarization, the pressure drop along the flow channels and the Joule-Thomson effect. Even though we focused exclusively on the effect of concentration polarization, allowed maximum pressure drops along the flow channels are implicitly accounted for. Because of applying a sweep gas (in contrast to Schulz et al. [5]), the Joule-Thomson effect has been ignored during our simulations.

During the dehydration process of scCO₂ and when moving from the feed bulk to the permeate bulk solution, the water vapor (and CO₂) passes four layers in series: the feed boundary layer, the active skin layer, the porous membrane support and the permeate boundary layer, as depicted in Section 2.1 Transport model. The three highly water vapor permeable and H₂O/CO₂ selective membrane materials: SPEEK, Naftion® 117 and PEBAX® 1074, were included in this study. The aim of this simulation study is to delineate the contribution of each of these layers to the overall mass transport resistance. Recommendations for membrane material selection as well as process conditions to optimize the membrane-based dehydration will be discussed.

2. Theory

The membrane design considered in this study contains multiple flat sheet membranes arranged in parallel and separated by feed and permeate channels (Fig. 2). Ideally, the membrane is highly permeable for H₂O but not for scCO₂. As a result, humid scCO₂ that enters the feed channel, gets dehydrated and exits the feed channel as a dry scCO₂ stream ready for its reuses as an extraction agent whereas the humidified air is emitted into the environment.

2.1. Transport model

The system analyzed in this study is schematically depicted in Fig. 3. The product drying, hydrated scCO₂ is the bulk feed solution from which the water is transported via the feed boundary layer, (selective) skin layer of the membrane, porous support of the membrane, permeate boundary layer into the bulk permeate solution.

Assuming well-stirred conditions in the bulk solutions, the overall mass transfer resistance $R_{ov}$ as well as the overall mass transfer coefficient $k_{ov}$ can be represented by four mass flow resistances in series:
including the mass transfer coefficient of the stagnant fluid boundary layer at the feed side \( k_f \), the selective skin layer \( k_m \), the porous support \( k_p \) and the stagnant fluid boundary layer at the permeate side \( k_p \), all with the unit m/s.

### 2.1.1. Mass transfer coefficient of the skin layer

There are two expressions describing the flux of H\(_2\)O and CO\(_2\) across the selective skin layer in Fig. 3, the first in terms of permeability \( P_i \):

\[
 J_i = \frac{P_i}{R} \Delta f_i \tag{2}
\]

where \( l \) represents the thickness of the skin layer (m) \( P_i \) the permeability coefficient, expressed in Barrer (1 Barrer = \( 7.5 \times 10^{-10}\) m\(^3\)(STP)/m\(^2\)(s)(Pa)) and \( \Delta f_i \) the driving force (Pa), being derived from the components fugacity of the supercritical and gaseous bulk phases of the feed and permeate side, respectively.

The second expression gives the flux in terms of mass transfer coefficient \( k_i \).

\[
 J_i = k_i \frac{V_{\text{STP}}}{R} \Delta f_i \tag{3}
\]

where \( J_i \) is the flux (m\(^3\)(STP)/m\(^2\)(s)), \( k_i \) is the mass transfer coefficient (m/s), \( \Delta f_i \) the process driving force (Pa), \( T \) the temperature (K), \( R \) the ideal gas constant \( (J/(\text{mol}\cdot\text{K})) \) and \( V_{\text{STP}} \) the molar volume at standard temperature and pressure (m\(^3\)(STP)/mol).

Combining Eqs. (1) and (2) correlates \( k_i \) and \( P_i \):

\[
 k_i = \frac{P_i}{R} \frac{V_{\text{STP}}}{T} \tag{4}
\]

The \( k_m \) values for H\(_2\)O and CO\(_2\) can be calculated using Eq. (4) and from the data in Table 1, showing the H\(_2\)O permeability and H\(_2\)O over CO\(_2\) selectivity for three types of membranes: SPEEK, Nafion® 117 and PEBAX® 1074. We selected these three types due to their extremely high permeabilities towards water vapor [6] and their high H\(_2\)O over CO\(_2\) selectivity compared to other currently existing membrane types. Further, Nafion® 117 and PEBAX® 1074 are commercially used for various drying applications [8,9]. SPEEK and PEBAX® 1074 on the other hand, have proven in months-long experiments to dehydrate flue gas under harsh corrosive conditions [10].

### 2.1.2. Mass transfer coefficient of the porous support layer

The flux through the porous support layer is a combination of diffusion-promoted flow and viscous flow [13]. At low pressures, as present at the permeate side, and high concentration gradients, the viscous flow is small compared to the diffusion-promoted flow, and is therefore neglected [13]. The mass transfer coefficient of the porous support is described by the reduced Dusty gas model [14]:

\[
 k_{i,p} = \frac{D_{\text{comb},i} \tau}{\tau_{\text{supp}}} \neg \neg \neg \neg \tag{5}
\]

where \( D_{\text{comb},i} \) is the combined diffusion coefficient (m\(^2\)/s), \( \tau_{\text{supp}} \) the porous support thickness (m), \( \epsilon \) the support porosity (\( \cdot \)) and \( \tau \) the support tortuosity (\( \cdot \)), approximated by Iversen et al. [15]

\[
 \tau = \frac{(2-\epsilon)^2}{\epsilon} \frac{\epsilon}{\frac{1-\epsilon}{\epsilon}} \tag{6}
\]

Table 2 lists the transport characteristics of the composite membrane used in this simulation study. The selected values for pore size, porosity and thickness of both dense and porous support layer of the membrane are all based on specifications of commercially available composite membranes [14].

With the support porosity, tortuosity and thickness known, Eq. (5) just requires the input of \( D_{\text{comb},i} \) (m\(^2\)/s). This parameter, in turn, is composed of two separate diffusion coefficients, \( D_{\text{Abb}} \) the binary diffusion coefficient (m\(^2\)/s) and \( D_{\text{Knudt}} \), the Knudsen diffusion coefficient (m\(^2\)/s) [14]:

### Table 1

H\(_2\)O permeability and H\(_2\)O/CO\(_2\) selectivity of SPEEK, Nafion® 117 and PEBAX® 1074 membranes. The H\(_2\)O/CO\(_2\) selectivity has been derived from the H\(_2\)O and CO\(_2\) permeabilities. Data for SPEEK has been obtained from [10] (CO\(_2\)) and [6] (H\(_2\)O), data for Nafion® 117 from [11] (CO\(_2\)) and [12] (H\(_2\)O) and for PEBAX® 1074 from [10].

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Abbreviation</th>
<th>H(_2)O permeability (Barrer)</th>
<th>CO(_2) permeability (Barrer)</th>
<th>H(_2)O/CO(_2) selectivity (( \cdot ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfonated polyetheretherketon</td>
<td>SPEEK</td>
<td>61,000</td>
<td>0.11</td>
<td>554,545</td>
</tr>
<tr>
<td>Perfluorosulfonic acid/Polytetrafluoroethylene copolymer</td>
<td>Nafion® 117</td>
<td>410,000</td>
<td>2.8</td>
<td>146,429</td>
</tr>
<tr>
<td>Polyamide-12-b-ethylene oxide</td>
<td>PEBAX® 1074</td>
<td>200,000</td>
<td>122</td>
<td>1639</td>
</tr>
</tbody>
</table>
The Knudsen diffusion coefficient is determined according to,

\[ D_{Knud,i} = \frac{1}{D_{Knud,0} + \frac{1}{D_{AB}}} \]  

(7)

where \( r_p \) is the pore radius of the porous support layer (m) and \( M_i \) is the molecular weight of the component \( i \) (kg/mol), \( T \) is the considered temperature (K) and \( R \) is the ideal gas constant (J/(mol K)).

As for the used sweep gas (dry air), we just consider the most abundant component in air, \( N_2 \) interacting with the permeating \( H_2O \), thus present in the binary diffusion equation. Following Massman [16], the binary diffusion coefficient is expressed by the (empirical) relation:

\[ D_{AB} = D_{AB,0} \left( \frac{P}{P_0} \right)^{1.84} \]  

(9)

where \( D_{AB,0} \) is the binary diffusion coefficient (m²/s) at 0.1013 MPa and 273.15 K (2.178 \( \times 10^{-5} \) m²/s for the \( H_2O \)/Air system), \( P \) the actual pressure (Pa), \( P_0 \) 0.1013 MPa, \( T \) the actual temperature (K) and \( T_0 = 273.15 \) K.

### 2.1.3. Mass transfer coefficient of the boundary layers

Starting point for the mass transfer coefficient at the boundary layer at the feed side is the Sherwood number (\( Sh \)), under turbulent conditions defined by [17]:

\[ Sh = 0.023 \cdot Re^{0.8} \cdot Sc^{0.33} \left( \frac{d_h \cdot k_{BL,i}}{D_{AB}} \right) \]  

(10)

Here \( d_h \) is the hydraulic diameter of the boundary layer (m) and \( k_{BL,i} \) is the mass transfer coefficients over the stagnant fluid boundary layer (m/s). The dimensionless Reynolds (\( Re \)) and Schmidt (\( Sc \)) numbers are defined as [18]:

\[ Re = \frac{\rho \cdot v \cdot d_h}{\mu} \]  

(11)

and

\[ Sc = \frac{\mu}{\rho \cdot D_{AB}} \]  

(12)

with \( \rho \) the fluid density (kg/m³), \( v \) the fluid velocity (m/s), \( \mu \) the dynamic viscosity (Pa s), \( d_h \) the hydraulic diameter (m) being twice the channel height and \( D_{AB} \) the continuum diffusion coefficient (m²/s).

Eq. (8), taken of Massman [16], was used to determine \( D_{AB} \) for the low pressure permeate side, whereas a model developed by Magalhães et al. [7] was used to determine \( D_{AB} \) of the two component system \( H_2O \)/\( CO_2 \) at the feed side. Actually, our experimental conditions fall beyond the range in which Lito’s model has been validated. However, given the fact that the model has been successfully applied to almost five hundred binary systems in the gas, liquid or \( scCO_2 \) state for a wide range of pressures and temperatures, we feel confident that application here is justified as well.

Calculation of \( Re \) and \( Sc \) requires knowledge of the density and dynamic viscosity, also under \( scCO_2 \) conditions. Table 3 shows values obtained from literature, for air and water (0.1 MPa and 45 °C) and \( scCO_2 \) (13.0 MPa and 45 °C), including the references. Worth to note, we found at least one website that allows the calculation of these parameters under a given set of experimental conditions. An example is given by [19] and [20]. The values obtained from this website were always in very close agreement with the values published in [21,22].

Table 2 shows a number of process parameters used in and obtained from the simulation being: fluid pressure, fluid channel height, cross flow velocity and others. The (maximum) pressure drop for the feed and sweep gas stream were set at 0.15 MPa and 5000 Pa, respectively to exclude any significant changes in both fluid properties due to their compression. These two pressure values were used as boundary conditions for the adjustment of the fluid channel height at each side of the membrane. Listed fluid velocities in Table 4 resulted directly from the simulations. In addition, \( t \) contains the calculated \( Re \) and \( Sh \) numbers. The first is essential to justify the use of Eq. (10) as it demands the condition of turbulent flow to be fulfilled [17]. With a \( Re \) number of > 20,000, this is certainly the case.

As shown in Table 4, with a \( Re \) value of 2160, the flow regime at the permeate side of the membrane is laminar, implying Eq. (10) cannot be used. Instead two Sherwood numbers, differing in their boundary conditions, thus in their values, are used to describe the mass transport at laminar conditions, according to Skelland et al. [23]. In case of a uniform penetrant concentration along the permeate side \( Sh \) equals 7.60 whereas \( Sh \) is 8.23 in case of a uniform penetrant flux along the fluid-membrane interface. For the system considered here, we face an intermediate regime. Following Beusher et al. [13], the average of both \( Sh \) values (i.e., 7.92) was used.

Once \( Sh \) is known, \( k_{BL,i} \) is calculated according to:

\[ k_{BL,i} = \frac{D_{AB} \cdot Sh}{d_h} \]  

(13)

### 2.1.4. Calculation of driving force and fluxes

With all the individual mass transfer coefficients determined, Eq. (1) allows the calculation of the overall mass transfer coefficient for component \( i, k_{i,m} \). Apart from \( k_{BL,i} \), calculation of fluxes requires calculation of the driving forces. The driving force \( \Delta f_i \) for water vapor and \( CO_2 \) is given by the logarithmic mean difference of the components fugacity at the feed and permeate side:

\[ \Delta f_i = \frac{(f_i^F - f_i^P) - (f_i^F - f_i^P)}{\ln\frac{f_i^F}{f_i^P} - \ln\frac{f_i^F}{f_i^P}} \]  

(14)

where \( f_i^F \) and \( f_i^P \) are the fugacities of the components in the feed and retentate stream and \( f_i^F \) and \( f_i^P \) are the fugacities of the components in

<table>
<thead>
<tr>
<th>Process parameter</th>
<th>Value</th>
<th>Process parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Process temperature</td>
<td>45 °C</td>
<td><strong>Table 2</strong> Process parameters for the composite membrane used for the simulations.</td>
<td></td>
</tr>
<tr>
<td>Pore size of the porous support</td>
<td>0.1 μm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Porosity of the support</td>
<td>0.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thickness porous support</td>
<td>120 μm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thickness of the skin layer</td>
<td>1 μm</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### 2.2. Results

The results of Table 3 show the effects of varying the process parameters. The varying process parameters are the process temperature, pressure, and sweep gas flow rate. The most significant effect on the separation performance was seen when the process temperature was increased. The results show that the permeate flux increases with increasing process temperature. This is due to the increase in the driving force, which is the logarithmic mean difference of the components fugacity at the feed and permeate side. The results also show that the selectivity decreases with increasing process temperature. This is due to the increase in the permeate flux, which decreases the concentration difference between the feed and permeate side.

<table>
<thead>
<tr>
<th>Fluid</th>
<th>Density ( \rho ) = [kg/m³]</th>
<th>Dynamic viscosity ( \mu ) = [Pa s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>1.10</td>
<td>19.43 ( \times 10^{-6} )</td>
</tr>
<tr>
<td>( scCO_2 )</td>
<td>693.7</td>
<td>55.57 ( \times 10^{-6} )</td>
</tr>
<tr>
<td>( H_2O )</td>
<td>990.2</td>
<td>59.61 ( \times 10^{-5} )</td>
</tr>
</tbody>
</table>

### 2.3. Discussion

The results show that the separation performance is strongly dependent on the process parameters. The most significant effect on the separation performance was seen when the process temperature was increased. This is due to the increase in the driving force, which is the logarithmic mean difference of the components fugacity at the feed and permeate side. The results also show that the selectivity decreases with increasing process temperature. This is due to the increase in the permeate flux, which decreases the concentration difference between the feed and permeate side.
the sweep gas and permeate stream (Pa). At low pressures, apparent at the permeate side, gases behave fairly ideal and their partial pressure equals their corresponding fugacity.

Supercritical conditions are typified by high pressure and high temperature therefore the apparent fugacity was used instead of the partial pressure to describe the (non-ideal) fluid. The model developed by Spycher et al. [24] was used to determine the H2O and CO2 fugacity in the feed stream. The water activity of the supercritical feed stream entering the membrane module was assumed to be unity, implying a feed stream saturated with water. Assuming a dehydration of the feed solution of 85%, the water activity of the retentate was set at 0.15. The CO2 fugacity in the feed was considered to be constant.

The Antoine equation [6] was used to convert the dew point temperature of the sweep gas (of +3°C and 0.3 MPa) to its corresponding water vapor fugacity, assuming a sweep gas exit stream of 60% relative humidity. The CO2 fugacity at the permeate side was considered to be negligible small compared to that of the feed side. By implication, the CO2 driving force is essentially insensitive to the CO2 fugacity of the permeate stream.

With both \( k_{\text{fl}} \) and \( \Delta f_i \) known, Eq. (15) gives the flux \( J_i \) (in \( \text{m}^3(\text{STP})/\text{m}^2 \text{s} \)) of component \( i \):

\[
J_i = k_{\text{fl}} \frac{V_{\text{STP}}}{R \cdot T} \Delta f_i
\]

(15)

2.2. Selectivity

The H2O over CO2 selectivity of the membrane \( S_{\text{fl}} \) is defined as the ratio of the permeability coefficients:

\[
S_{\text{fl}, \text{H}_2\text{O}/\text{CO}_2} = \frac{P_{\text{H}_2\text{O}}}{P_{\text{CO}_2}}
\]

(16)

The overall mass transfer coefficient (and resistance) for H2O and CO2 transport includes not only the membrane itself but also both boundary layers (Eq. (1)). In analogy to Eq. (16), the ratio of the overall mass transfer coefficient for H2O and CO2 \( S_{\text{fl}, \text{H}_2\text{O}/\text{CO}_2} \) is given by:

\[
S_{\text{fl}, \text{H}_2\text{O}/\text{CO}_2} = \frac{k_{\text{fl}, \text{H}_2\text{O}}}{k_{\text{fl}, \text{CO}_2}}
\]

(17)

Due to e.g. concentration polarization effects, the selectivity predicted by \( S_{\text{fl}, \text{H}_2\text{O}/\text{CO}_2} \) can significantly deviate from the selectivity represented by \( S_{\text{fl}, \text{H}_2\text{O}/\text{CO}_2} \). Finally, according to Eq. (3), the ratio of the flux of H2O and CO2 over the membrane \( S_{\text{p}, \text{H}_2\text{O}/\text{CO}_2} \) is given by:

\[
S_{\text{p}, \text{H}_2\text{O}/\text{CO}_2} = \frac{k_{\text{p}, \text{H}_2\text{O}} \cdot \Delta P_{\text{H}_2\text{O}}}{k_{\text{p}, \text{CO}_2} \cdot \Delta P_{\text{CO}_2}}
\]

(18)

3. Results and discussion

3.1. Delineating the overall mass transport resistance for water

Simulations were performed for three polymer membranes: SPEEK, Nafton® 117 and PEBAX® 1074, all with their distinctive properties as listed in Tables 1 and 2. SPEEK and Nafton® 117 are glassy polymers at room temperature and show exceptionally high H2O/CO2 selectivities compared to the elastomeric polymer PEBAX® 1074, whereas PEBAX® 1074 and Nafton® 117 show a water vapor permeability of 3 and 6 times higher than SPEEK, respectively.

Fig. 4 shows the calculated mass transfer resistance of the layers displayed in Fig. 3, with either the implementation of a SPEEK, Nafton® 117 or PEBAX® 1074 membrane.

Irrespective the membrane type used, the feed boundary layer forms by far the highest mass transfer resistance, comprising about 80% of the overall mass transfer resistance. Apparently, even the diminishing effect of high turbulence (Re = 20,800), as observed by Metz [6], cannot compensate the aforementioned feed boundary layer. To this end we concluded that the high fluid density substantially reduces the free path of motion of the water molecules and with that diffusive mass transport.

The second largest contributor to the overall mass transport resistance is the permeate boundary layer. Although the hydraulic diameter of the permeate canal, is about 9 times larger than those of the feed canal and its flow profile is laminar, it contributes for about 10% of the total mass transport resistance. Given the much lower fluid density at the permeate side, this outcome underlines the dominant effect of fluid density on the boundary layer resistance.

The porous support layer of thickness 120 μm contributes minor to the overall mass transfer resistance.

For all three membrane types, the layer showing the lowest mass transfer resistance is the dense, skin layer itself. This is a rather atypical outcome for a gas separation process as, in general, the thickness of the skin layer is the mass transfer limiting parameter. Our finding results directly from the combination of the exceptionally high water vapor permeability of these fairly thin skin layers and the scCO2 condition, resulting in a high feed boundary layer resistance. Consequently, even though Nafton® 117 is six times more permeable for water vapor than SPEEEK, it will only marginally improve the overall water permeance.

3.2. H2O feed boundary resistance and fluid density as function of pressure and temperature

Given the high feed boundary resistance as outlined in the previous section, here we investigate strategies to lower this resistance by changing temperature and/or pressure. Fig. 5 displays the feed boundary resistance and fluid density in relation to feed pressure (left panel) and temperature (right panel). Values in Table 3 refer to process conditions of 13.0 MPa and 45°C. To be consistent, the process temperature for the pressure profile was set at 45°C whereas the process pressure for the temperature profile was set at 13.0 MPa. As for the effect of pressure (left panel of Fig. 5), fluid density and boundary layer resistance change in parallel as both parameters are affected by the reduction in free path of motion with increasing pressure. Both parameters increase till a pressure of around 11.0 MPa, after which the increase slightly flattens off. The temperature profile (right panel) also shows boundary resistance and fluid density change in parallel. This parallel change suggests that the effect of temperature is indirect and via the fluid density, which again leads, according to Magalhães et al. [7], to a reduction in free path of motion, and with that to a declined species diffusivity within the fluid-membrane interface.

Both fluid density and feed boundary layer resistance decrease with temperature, with a flattening starting at a temperature around 70°C. Pressure or temperature variation near the supercritical point results in...
a more pronounced change in fluid density (and thus boundary layer resistance) due to its higher compressibility at this point [24]. This might be the root of the inflection points of the density and boundary layer resistance in the pressure profile.

As evident from Fig. 5, reducing the feed pressure from 13.0 MPa to 8.5 MPa while increasing the temperature from 45 °C to 100 °C would significantly diminish the boundary layer resistance with a factor 6 and thus improve the overall water vapor transport across the system. Despite the beneficial effects for the water vapor transport, the lower density leads to higher volume flow rates.

In analogy to Fig. 4 for H₂O, Fig. 6 shows the relative contribution of each transport layer to the overall mass transfer resistance for CO₂. Compared to Fig. 4, differences are striking. Firstly, not only are the overall mass transfer resistances for CO₂ much higher than those for H₂O, values for the three membranes vary widely.

The calculated mass transfer resistances for CO₂ are 9300, 403,500 and 10,269,800 s/m for PEBAX® 1074, Naﬁon® 117 and SPEEK, respectively. Note that for PEBAX® 1074, showing the lowest CO₂ density leads to higher volume flow rates.
resistance, the value of 9300 s/m is already about 15 times the overall resistance for water vapor transport (Fig. 4). Secondy, due to the high scCO₂ concentration, the feed boundary layer resistance for CO₂ is non-existent (and for that reason not shown in Fig. 6). The consequence of this is that the CO₂ mass transfer resistance is dictated for more than 99% by the skin layer.

### 3.3. Selectivity

Fig. 7 shows the H₂O over CO₂ membrane selectivity (SM), the ratio of the overall mass transfer resistance for H₂O and CO₂ (SOV) and H₂O/CO₂ flux ratio (SF), calculated for all three selected membrane materials. As shown by Eq. (16), the membrane selectivity reflects the ratio of the permeability for H₂O and CO₂. The relatively high H₂O over CO₂ membrane selectivity of SPEEK and Naflon® 117, in the range of 10^5–10^6, arises from the combined effect of a high water vapor permeability and a very low CO₂ permeability, see also Table 1. Even though the H₂O permeability of PEBAX® 1074 is comparable to that of SPEEK and Naflon® 117, the permeability for CO₂ of 122 Barrer is 2 to 3 orders of magnitude higher than for SPEEK and Naflon® 117, resulting in H₂O over CO₂ membrane selectivity of just 10^3.

As obvious from Fig. 7, the ratio of the overall mass transfer coefficient SOV for H₂O and CO₂ is for all three membranes lower than the membrane selectivity SM being solely based on the permeability ratio of the selective skin layer material itself. The reason is the dominance of the feed boundary layer resistance in the overall H₂O mass transfer resistance. In our simulations this effect is independent of the type of membrane. Therefore, differences in the overall mass transfer resistance between the three membrane types shown in Fig. 7 reflect more than anything else the differences in their CO₂ permeability as this parameter dominates the overall CO₂ mass transfer resistance.

Based on the SM and SOV values (all ≫ 1) shown in Fig. 7, all three membrane types favor H₂O transport over CO₂ transport. This picture changes however dramatically when including driving forces in the analysis and investigating the actual flux ratio of H₂O and CO₂ (S_F) across the system. The large difference between SOV and SF values is caused by the large difference in driving force for H₂O and CO₂. According to Spycher [24], water vapor-saturated CO₂ at the feed side of 13.0 MPa and 45°C has a CO₂ and H₂O fugacity of 6.76 MPa and 0.01 MPa, respectively. Given the virtually zero H₂O and CO₂ fugacity at the permeate side, this large difference in fugacity translates in a driving force for CO₂ that is almost 700 times (= 67.6/0.01) higher than the driving force for H₂O. As a result, S_F becomes < 1 for Naflon® 117 and PEBAX® 1074 membranes, implying that the membrane actually passes more CO₂ than H₂O. Only the SPEEK membranes permeates more H₂O than CO₂. In conclusion, this outcome shows that a very H₂O/CO₂ selective skin layer, as is the case for Naflon® 117 and PEBAX® 1074, does not necessarily lead to (desired) low CO₂ crossover and high H₂O fluxes over the membrane (S_F ≫ 1). Strong concentration polarizations effects and an unfavorable driving force ratio can severely reduce or even inverse the H₂O/CO₂ flux ratio. Given the membrane polymers included in this study as well as the process conditions, SPEEK would be the material of choice since even under the given scCO₂ conditions the SPEEK membrane shows a SF value of almost 10, indicating the H₂O flux is almost 10-times higher than the CO₂ flux. This means that during the dehydration process with SPEEK membranes the CO₂ loss is limited.

#### 3.3.1. Effect of skin layer thickness

The mass transfer over the feed boundary layer is dictating for the H₂O transport, while the selective skin layer controls the CO₂ mass transfer. Fig. 8 shows the effect of skin layer thickness on the overall mass transfer coefficient.

Increasing the skin layer thickness from 1 µm up to 250 µm increases SF. Up to 25 µm this increase is about 1.5 orders of magnitude. Above 25 µm it levels asymptotically approaching SM. The initial increase reflects the sensitivity of the overall mass transfer resistance for CO₂ towards skin layer thickness with the one for H₂O remaining essentially unaffected as for H₂O the feed boundary layer remains by far the dominant resistance.

However, upon a further increase of the skin layer thickness, the skin layer resistance towards H₂O transport becomes more pronounced, even to the point that it supersedes the feed boundary layer as the mass transfer limiting layer. As a result, for both H₂O and CO₂ the membrane resistance becomes the dominating term in the overall mass transfer resistance with the value of SOV asymptotically approaching that of SM.

Even though the behavior outlined above is valid for all three membrane types, they differ in detail. For SPEEK SM and SOV are already fairly the same at a skin layer thickness of 150 µm. In contrast, at the same skin layer thickness Naflon® 117 still demonstrates a significant discrepancy between these two parameters, whereas PEBAX® 1074 behaves immediately. This diverse behavior is rooted in differences in water permeability, 61,000 Barrer for SPEEK and 410,000 Barrer for Naflon® 117. As a consequence, when increasing the skin...
layer thickness, a SPEEK-based membrane becomes limiting towards the transport of H2O already at a much lower skin layer thickness than its Naﬁon® 117 counterpart.

To exemplify this in more detail, Fig. 9 displays the H2O/CO2 flux ratio and the H2O flux, both plotted for a SPEEK membrane of various thickness, and at a feed pressure of 13.0 MPa and temperature of 45 °C. A low skin layer thickness leads to severe CO2 losses. This effect is also pronounced by the low H2O/CO2 flux ratio. To compensate for this CO2 loss, CO2 reﬁll, is demanded therefore installing thicker membranes is preferred from the CO2 perspective. On the other hand, it might also not be cost-effective to install membranes with very thick skin layers. The substantially lower H2O ﬂux would demand a larger membrane area thereby inﬂating investment costs. Optimization of skin layer thickness resulting in total cost minimization is the focus of current investigation.

3.3.2. Driving force

As evident from Eq. (15), the H2O and CO2 ﬂux depends on the respective driving force. Consequently, the ﬂux ratio can not only be manipulated by parameters affecting (the ratio of) mass transfer resistances but also by those affecting (the ratio of) driving forces. In this section, we will explore the later in more detail in order to gain insight how to combine a high H2O ﬂux with a low CO2 crossover. Changing the ﬂuid properties by changing pressure and/or temperature affects the fugacities of CO2 and H2O and in addition latter’s solubility in CO2. Fig. 10 displays the ratio of isothermal driving force for H2O and CO2 in the H2O-saturated CO2 feed stream, each calculated using Eq. (14), as a function of ﬂuid pressure, and at various temperatures.

As shown in Fig. 10, the driving force ratio strongly depends on ﬂuid temperature, an effect related to the H2O solubility/fugacity enhancing effect of the temperature. In addition, pressure increase lowers the H2O and CO2 driving force ratio, an effect more pronounced at elevated temperatures and possibly caused by a disproportional increase of the CO2 fugacity with increasing pressure compared to the increase of H2O fugacity [24]. Increasing the process temperature from 45 °C to 70 °C, combined with a pressure reduction from 13.0 MPa to 10.0 MPa, enhances the H2O/CO2-driving force ratio almost a factor 3 (see Fig. 10), resulting in a similar increase of the H2O/CO2 ﬂux ratio. In effect, such a change in process conditions would result in a 75% reduction of CO2 loss while maintaining the H2O ﬂux.

3.4. Summary of all discussed effects

The H2O/CO2 ﬂux ratio can not only be manipulated by choice of membrane material and skin layer thickness but also by the process pressure and temperature. Fig. 11 compiles the possible effects of these parameters on the (intrinsic) membrane selectivity (Sm), ratio of the overall mass transfer coefﬁcient (Swv) and ﬂux ratio (Sp). Given SPEEK as material of choice, three different dehydration systems are considered:

- System A with a skin layer thickness of 1 µm and a feed pressure and temperature of 13.0 MPa and 45 °C, respectively. This system represents the default state which is used as a benchmark for the other systems.
- System B with an increased skin layer thickness of 5 µm but the same feed pressure and temperature as in A, 13.0 MPa and 45 °C, respectively.
- System C with the same skin layer thickness as in B, 5 µm, but with a decreased feed pressure and an increased temperature of 10.0 MPa and 70 °C, respectively.

Since all three systems are SPEEK-based, the (intrinsic) membrane selectivity is the same. Regarding the ratio of overall mass transfer resistance (Swv), Fig. 11 shows an incremental increase when moving from system A to system B. The jump seen from system A to system B reﬂects the increase of skin layer thickness from 1 to 5 µm and the
resulting disproportional increase of CO₂'s the mass transfer resistance compared to those of H₂O, as discussed previously (Fig. 8). The difference between the S₉₅ values of system B and C is the result of the increased temperature, from 45 to 70 °C, and lower pressure, from 13.0 to 10.0 MPa (see Fig. 11). Both adjustments of the process conditions lower the density of the supercritical fluid and by that improving the diffusion of water across the feed boundary layer.

Finally, most relevant is of course how these considered parameters translate in the overall performance of the system, i.e., the H₂O/CO₂ flux ratio, indicated by the S₉₅ value. As shown in Fig. 7, the large difference in driving force for H₂O and CO₂ cancels out for most part the huge differences in S₉₅ and, to a slightly lesser extent, S₉₅ values, resulting in S₉ values ranging from approximately 5 × 10⁻³ (for PEBAX® 1074) to 8 (for SPEEK). As the driving forces in Fig. 11 for systems A and B are the same, the observed increase in S₉₅ and S₉ can solely be attributed to the effect of increased skin layer thickness, affecting predominantly the CO₂ permeance. As discussed in Fig. 10, lowering the feed pressure and increasing the feed temperature increases the H₂O/CO₂ driving force ratio, and thus H₂O/CO₂ flux ratio as well. This effect, in turn, is responsible for the difference shown between systems B and C. Comparing systems A and C, it can be concluded that increasing the skin layer thickness from 1 to 5 µm, while lowering the pressure from 13.0 to 10.0 MPa and increasing the temperature from 45 to 70 °C, increases the H₂O/CO₂ flux ratio up to almost 20 times.

4. Conclusions

The specific flow pattern across membranes depends on the geometry of the system. For that reason, here we consider the (relatively simple) mass transfer behavior of flat sheet membranes, depicted in Fig. 2. Despite their different geometry and more complex flow pattern, we nevertheless expect that conclusion can be (partly) extrapolated to outside-in hollow fiber membranes.

The system’s performance of a scCO₂ dehydration unit was assessed by implementing a polymeric membrane based on either SPEEK, Nafion® 117 or PEBAX® 1074, all three materials are combining a very high H₂O permeability with a high H₂O over CO₂ membrane selectivity. Apart from membrane material, the system’s performance, with the H₂O/CO₂ flux ratio as decisive criterion, was tested for skin layer thickness and the effects of feed pressure and temperature. One of the main findings of the analysis is that the feed boundary layer resistance is by far the principal term in the overall mass transfer resistance for H₂O. In contrast, the intrinsic membrane permeability towards CO₂ dominates the overall mass transfer resistance for CO₂. Together with the huge difference in driving force for CO₂ and H₂O this leads to H₂O/CO₂ flux ratios orders of magnitude lower than suggested by the S₉₅ values, based solely on the membrane permeability for H₂O and CO₂. In case of Nafion® 117 and PEBAX® 1074 the H₂O/CO₂ flux ratio even lies below unity making CO₂ instead of H₂O the dominant species in the permeate. Which means high CO₂ loss during the regeneration process, thus making the process CO₂ selective.

Because of the above and given the scCO₂ process conditions and driving forces, membrane selection is based on a low CO₂ permeance rather than on high H₂O permeance. This consideration defines SPEEK as the preferred material for this specific application. In addition to the chosen membrane material, the thickness of the skin layer has a profound effect on CO₂ permeance as well, balancing between high permeance/high CO₂ loss for a thin layer and low permeance/large required membrane areas for a relatively thick layer. Common sense predicts an optimum thickness in terms of operational and investment costs. In addition to membrane properties, process conditions will greatly affect the S₉₅ values. For a SPEEK membrane, increasing the skin layer thickness from 1 to 5 µm, lowering the feed pressure from 13.0 to 10.0 MPa and increasing the temperature from 45 to 70 °C, increases S₉ almost 20-fold. System optimization, including effects of skin layer thickness as well as feed pressure and temperature, is the focus of future research.

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