Gas separation properties of crosslinked and non-crosslinked carboxymethylcellulose (CMC) membranes

S.I. Miremadi\textsuperscript{a}, N. Shafabadi\textsuperscript{b}, S.A. Mousavi\textsuperscript{b,*} and M.S. Amini-Fazi\textsuperscript{b}

\textsuperscript{a} Department of Energy Engineering, Sharif University of Technology, Tehran, Iran.
\textsuperscript{b} Department of Chemical & Petroleum Engineering, Sharif University of Technology, Tehran, P.O. Box: 11155-363, Iran.

Received 10 June 2012; received in revised form 19 February 2013; accepted 30 April 2013

\textbf{KEYWORDS}

Membrane; Carboxymethylcellulose; Gas separation; Gas permeability; Permselectivity.

\textbf{Abstract.} In this study, crosslinked and non-crosslinked carboxymethylcellulose (CMC) membranes were prepared with different concentrations of polymer. Then, the permeability of pure CO\textsubscript{2}, N\textsubscript{2}, and CH\textsubscript{4} was measured through these membranes in dry state to investigate the influence of polymer concentration and applied feed pressure on permeability and permselectivity. The permeability of CO\textsubscript{2} through membranes was higher than the other gases. A comparison of permeabilities revealed that the permeability of N\textsubscript{2}, CO\textsubscript{2}, and CH\textsubscript{4} increased on an average of 33, 40 and 20 percent, respectively, by increasing the feed pressure from 6 to 10 bar. Increasing CMC concentration from 1.2 to 3.0 wt\%, the permeability of N\textsubscript{2}, CO\textsubscript{2}, and CH\textsubscript{4} decreased on an average of 25, 12 and 19 percent, respectively. Also, the CO\textsubscript{2}/CH\textsubscript{4} and CO\textsubscript{2}/N\textsubscript{2} permselectivities increased 9 and 18 percent, respectively, with an increment in CMC concentration from 1.2 to 3 wt\%. The crosslinked CMC membranes with the same polymer concentrations were also prepared to investigate the effects of crosslinking reaction on permeability and permselectivity. The ATR-FTIR test was applied, and the peak at about 1108 cm\textsuperscript{-1} confirmed the presence of crosslinker groups. The comparison of gas permeation test results for crosslinked and non-crosslinked CMC membranes showed that the gas permeability decreased and its permselectivity increased due to crosslinking reaction. According to Robeson’s plots, the prepared CMC membranes would have potential for commercialization.

\copyright 2013 Sharif University of Technology. All rights reserved.

1. Introduction

The separation and capture of CO\textsubscript{2} from flue gas and natural gas streams is an important process in industry. Also, the removing of CO\textsubscript{2} during steam reforming process of hydrocarbons is very important to produce high purity hydrogen [1]. The most common technology for CO\textsubscript{2} removal is amine absorption [2]. Membrane separation technology is an alternative approach with less energy consumption and lower capital cost [3-5]. In addition, the membrane process does not involve sorbent regeneration and there is no secondary waste product [6]. Moreover, Membrane-based separation processes have simple operating procedures versus amine absorption [7].

Many research activities have been made for preparation of novel membranes from various types of polymers. High CO\textsubscript{2} permeability, good selectivity in favor of CO\textsubscript{2} and mechanical and thermal stabilities of membrane should be concerned in preparation of an efficient membrane. Most of the researches have discussed about improving gas separation properties of membranes by:
(i) Changing chemical composition of materials;

(ii) Effectively controlling of membrane structure by controlling of preparation conditions.

Adding new bulky, electronegative and polar group into the macromolecules is an effective way to improve selectivity of the membrane [8]. Hydrogel compounds, due to their physical-chemical characterizations, have good potential for preparation of the membrane.

Hydrogels are hydrophilic polymer networks with incredibly absorption properties. Production of Soft Contact Lenses (SCLs) [9], food packaging [10], wound dressings [11], drug delivery [12] and humidification or dehumidification of gases are the most common applications of hydrogel materials. Hydrogels, due to their hydrophilic functional groups (see Figure 1), allow the passage of some types of molecules, while rejecting many others. There are many studies on possible use of hydrogel membrane for gas separation processes [13-16]. Feng et al. studied the role of water content in water-swollen hydrogel membranes (e.g. PVA, CMC, Chitosan). According to their investigations, comparing of hydrogel membranes in swell and dry states showed that the gases permeabilities through these membranes in dry state were lower than the swell state [6]. The ability to swell in water is an advantage of hydrogels, despite the poor mechanical properties of swollen hydrogels [16]. Tanaka et al. reported the weak mechanical strength of wet hydrogel membranes against dry ones [17]. Xing and Ho remarked that increasing the crosslinking degree of the membrane slightly decreased the CO₂ permeability [18]. Wijmans explained the importance of operational condition on membrane performance [19]. Many investigations have been made to show the influence of operational conditions, such as applied pressure [20,21]. Based on these reports, increasing pressure difference increases the permeability of membrane. In addition, in manner of capturing CO₂ from flue gas containing acid gases as impurities, water would cause reduction of membrane performance and stability [22].

The aim of this work is to prepare a hydrophilic membrane and then investigate the influence of preparation condition and applied pressure difference on membrane performance in case of CO₂ separation. Carboxymethylcellulose (CMC) is a hydrogel material with excellent hydrophilic property. CMC is a cellulose derivative with carboxymethyl groups bound to some of the hydroxyl groups of the glucose monomers that has high hydrophilic properties and intensive polarity, because of its hydroxyl and carboxylate groups. With respect to the hydrophilic property of CMC, it seems that CMC could be a suitable candidate for separation of gases with high interaction with polar groups, such as CO₂. As mentioned before, these membranes could have very good potential in some applications such as gas sweetening.

Hence, a set of non-crosslinked and crosslinked CMC membranes were prepared at different conditions, and then the permeability of pure CO₂, N₂ and CH₄ was measured through these membranes in dry state. The effects of preparation condition and feed pressure on these membrane performance were discussed.

2. Materials and methods

2.1. Materials

The polysaccharide carboxymethyl cellulose (CMC) with a Degree of Substitution (D.S). 0.52, was purchased from Merck. Distilled water was used as solvent. N₂ and CO₂ gases with 99.99% purity (Roham Gas Corp., Tehran, Iran), and ultra high purity CH₄ (Air Products Co.) were used in permeation experiments. Glutaraldehyde (25 wt. % in H₂O) was purchased from Sigma-Aldrich as crosslinking agent. All of materials were analytical grade.

2.2. Membrane preparation method

The CMC polymer were dissolved in distilled water at ambient temperature. The CMC powder was added into water slowly. The produced solution was decanted into a glass petri dish at room temperature, and dried for one day in a dust-free chamber. The decant process should have been done as quickly as possible to obtain uniform films. Finally, dried film was easily detached from the plate. A set of CMC membranes were prepared from solution mixtures of CMC polymer with different compositions. Table 1 shows the preparation conditions of CMC membrane.

The dry CMC membranes were crosslinked by immersion for 24 hours at room temperature in crosslinking solution (2 wt. % of Glutaraldehyde in water). At the end of crosslinking reaction period, the membranes were taken out of solution and washed out with distilled water.

2.3. Gas permeation test

Nitrogen, methane, and carbon dioxide permeabilities of the prepared membranes were measured using a constant pressure/variable volume method at room temperature.
Table 1. The preparation conditions of CMC membranes.

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Solvent volume</th>
<th>Amount of CMC (gr)</th>
<th>Polymer concentration</th>
<th>Crosslinking condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50 cc</td>
<td>0.6</td>
<td>1.20%</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>50 cc</td>
<td>0.8</td>
<td>1.60%</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>50 cc</td>
<td>1.2</td>
<td>2.40%</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>50 cc</td>
<td>1.5</td>
<td>3.00%</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>50 cc</td>
<td>0.6</td>
<td>1.20%</td>
<td>Immersion in 2 wt% of GA solution</td>
</tr>
<tr>
<td>6</td>
<td>50 cc</td>
<td>0.8</td>
<td>1.60%</td>
<td>Immersion in 2 wt% of GA solution</td>
</tr>
<tr>
<td>7</td>
<td>50 cc</td>
<td>1.2</td>
<td>2.40%</td>
<td>Immersion in 2 wt% of GA solution</td>
</tr>
<tr>
<td>8</td>
<td>50 cc</td>
<td>1.5</td>
<td>3.00%</td>
<td>Immersion in 2 wt% of GA solution</td>
</tr>
</tbody>
</table>

Each gas was fed from high pressure cylinders to a stainless steel membrane cell. The membranes were fastened between cell plates by nuts and bolts. The feed pressure was regulated with 6, 8 and 10 bar, and permeates were collected at atmospheric pressure. The gas permeability of each membrane in their dry state was determined from the following equation [6,8]:

\[
P = \frac{q l}{\Delta p A}
\]

(1)

where \(P\) is the gas permeability in barrer (1 barrer = \(1 \times 10^{-10}\) cm²(STP) cm/(cm² s cmHg)), \(q\) is the permeation flowrate (cm³(STP)/s), \(l\) is the membrane thickness (cm), \(\Delta p\) is the pressure difference between feed and permeate sides (cmHg), and \(A\) is the effective membrane area (cm²).

The ideal gas selectivity, \(\alpha_{A,B}\) (permselectivity), of pair gases \(A\) and \(B\) was calculated by the following equation:

\[
\alpha_{A,B} = \frac{P_A}{P_B}
\]

(2)

where \(P_A\) and \(P_B\) are the gas permeabilities of \(A\) and \(B\) gases, respectively.

Reproducibility and repeatability of the data were checked randomly in some occasions, and a maximum variability of 17% demonstrated a fair level of reproducibility and repeatability in the experimentation.

2.4. ATR-FTIR test method

The ATR-FTIR spectra were obtained on a Fourier Transform Infrared spectrometer (EQUINOX 55, Bruker, Germany). The Attenuated Total Reflectance accessory (ATR) was mounted into the sample compartment. The internal reflection crystal, made of zinc selenide (ZnSe), had a 45° angle of incidence to the IR beam. Spectra were acquired at a resolution of 2 cm⁻¹, and the measurement range was 4000-700 cm⁻¹. All experiments were performed in triplicate at ambient temperature, 25 ± 2°C.

3. Results and discussion

Permeability of non-crosslinked CMC membranes with respect to \(N_2\), \(CH_4\) and \(CO_2\) gases were studied at different feed pressures, and the results are summarized in Table 2. According to these results, carbon dioxide and nitrogen have the highest and lowest permeabilities, respectively. These results can be discussed by the condensability and kinetic diameter of the applied gases. Table 3 shows the condensability and kinetic diameter of \(N_2\), \(CH_4\) and \(CO_2\). According to Table 3, Carbon dioxide has the highest permeability due to its low kinetic diameter and high condensability. The permeability of \(CH_4\) is always higher than that of \(N_2\), in spite of its bigger molecular size. The reason of this

Table 2. Gas permeability of CMC membranes at different feed pressures.

<table>
<thead>
<tr>
<th>Permeability (Barrer)</th>
<th>Feed pressure = 6 bar</th>
<th>Feed pressure = 8 bar</th>
<th>Feed pressure = 10 bar</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMC concentration</td>
<td>(N_2)</td>
<td>(CH_4)</td>
<td>(CO_2)</td>
</tr>
<tr>
<td>1.20%</td>
<td>1.041</td>
<td>2.947</td>
<td>8.901</td>
</tr>
<tr>
<td>1.60%</td>
<td>0.979</td>
<td>2.687</td>
<td>8.706</td>
</tr>
<tr>
<td>2.40%</td>
<td>0.826</td>
<td>2.442</td>
<td>8.254</td>
</tr>
<tr>
<td>3.00%</td>
<td>0.776</td>
<td>2.290</td>
<td>7.809</td>
</tr>
</tbody>
</table>
matter should be the higher condensability of CH₄ in comparison with N₂.

The gas permeability depends on some physicochemical factors of membrane structure, such as the presence of electronegative and polar groups in the polymer backbone and bulky or polar side-groups linked to the main chain of the polymer [7, 14, 16, 23, 24]. In case of CMC membranes, the presence of polar carboxyl groups bonded to some hydroxyl groups of glucose monomers (shown in Figure 1) enhances the solubility of CO₂ due to the increased interaction between this gas and the polymer. This fact helps CO₂ molecules to have higher permeability through CMC membranes.

Figures 2, 3 and 4 show the effect of feed pressure on the N₂, CH₄ and CO₂ permeabilities, respectively. Increasing feed pressure can increase the amount of gas molecules on the membrane surface. This phenomenon leads to more gas molecules available to interact with polar groups of CMC polymer chain. Based on these figures, the permeability of all three gases were increased by increasing the feed pressure. The permeability of methane evidently changes with feed pressure, because of its high condensability and consequently high solubility.

According to solid lines in Figure 5, a comparison of gas permeabilities through membranes prepared at different concentrations revealed that the permeability of each gas decreased as polymer concentration increased. With respect to the direct relationship of gas permeation and membrane free volume [15, 24], indirectly, it can be concluded that an increment in concentration of CMC polymer decreases the free volumes in membrane, and the membrane with more free volumes shows higher diffusivity. As the amount of polar groups at membrane surface does not change with polymer concentration, the solubility of gases is relatively constant, and hence the difference in gas

<table>
<thead>
<tr>
<th>Gas</th>
<th>Kinetic diameter (Å)</th>
<th>Condensability (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon dioxide</td>
<td>3.3</td>
<td>195</td>
</tr>
<tr>
<td>Methane</td>
<td>3.8</td>
<td>149</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>3.64</td>
<td>71</td>
</tr>
</tbody>
</table>

Figure 2. Permeability of pure nitrogen gas through non-crosslinked CMC membranes.

Figure 3. Permeability of pure methane gas through non-crosslinked CMC membranes.

Figure 4. Permeability of pure carbon dioxide gas through non-crosslinked CMC membranes.

Figure 5. Gas permeability of crosslinked (dashed lines) and non-crosslinked (solid lines) CMC membranes at 8 bar feed pressure.
permeability of membranes should be related to the diffusivity effects.

Considering the small difference of N₂ and CH₄ permeabilities, it can be concluded that the diffusivity effect is small due to high kinetic diameters of these gases. But, the considerable difference of CO₂ permeability at different concentrations of polymer reveals that the polymer concentration and consequently free volumes of membrane have important effect on CO₂ diffusivity, because of its low kinetic diameter.

The results of gas permeability through membranes with different CMC concentrations for other feed pressures (6 bar and 10 bar) are similar to that of the 8 bar.

The permselectivity values of CO₂/CH₄ and CO₂/N₂ of non-crosslinked CMC membranes at 6, 8 and 10 bar feed pressure are reported in Figure 6. These data show that permselectivity of the CO₂/N₂ and CO₂/CH₄ increased considerably by increasing the CMC concentration. As mentioned before, by increasing the CMC concentration, the diffusivity of CO₂ increased more than the other gases.

The effect of feed pressure on CO₂/N₂ and CH₄/N₂ permselectivity of CMC membranes is shown in Figure 7. The CH₄/N₂ permselectivity is approximately constant with an increment in the feed pressure in the range of 6 to 10 bar. However, the CO₂/N₂ permselectivity increased from 8.80 to 9.65 in this range of feed pressure. These observations were made from the fact that the pressure had no significant effect on the permeability of N₂ and CH₄, while the permeability of CO₂ increased with pressure, as shown in Figure 4.

There are numerous hydroxyl groups on the chain of CMC polymer that has the potential to react with glutaraldehyde (GA) to form crosslinked membrane. The products of crosslinking reaction have complex structures and are considered to form interpenetrated-interconnected networks [25].

![Figure 6. CO₂/N₂ (dashed lines) and CO₂/CH₄ (solid lines) permselectivities of non-crosslinked CMC membranes at different feed pressures.](image)

![Figure 7. CO₂/N₂ and CH₄/N₂ permselectivity of non-crosslinked CMC membrane with 1.6% polymer concentration.](image)

![Figure 8. ATR-FTIR spectral data of crosslinked and non-crosslinked CMC membranes with 2.4% polymer concentration.](image)

The ATR-FTIR spectral data of crosslinked and non-crosslinked CMC membranes with 2.4% polymer concentration are shown in Figure 8 to confirm the crosslinking reaction. The ATR-FTIR spectrum of both crosslinked and non-crosslinked membranes showed bands at about 3367 and 3266 cm⁻¹, because of O-H groups. Also, there were bands at about 1587, 1413 and 1053 cm⁻¹ due to asymmetric and symmetric stretching of the carboxylate groups, and stretching vibrations of C-O-C groups, respectively.

There are numerous hydroxyl groups available on the macromolecular chains of CMC that may react with glutaraldehyde. These hydroxyl groups may give either semiacetal or acetal type rings, but the semiacetals are less stable than the acetals [25]. As shown in Figure 8, the peak at about 1108 cm⁻¹ in crosslinked CMC membrane indicates that the C-O groups are inserted to polymer chains due to reaction between hydroxyl groups available on CMC chains and glutaraldehyde. Figure 9 shows this reaction mechanism.

The effect of crosslinking reaction has not been clearly determined, yet. However, a majority of literature reports suggest that crosslinking reduces gas permeability [15, 16, 19], and this should be considered as a result of formation of interpenetrated-interconnected
networks. The formation of these interpenetrating networks resulted in decreasing the pore size of membrane, and subsequently, the gas permeation is reduced.

The effect of crosslinking reaction on gas permeation of CMC membranes was shown in Figure 5. Also, formation of C-O-C groups in polymer chains intensify polarity of network, and the solubility of CO₂ increased due to enhanced interaction between CO₂ and crosslinked CMC membrane. Consequently, the CO₂/N₂ and CO₂/CH₄ permselectivities increased as shown in Figure 10.

Figures 11 and 12 show CO₂/CH₄ and CO₂/N₂ permselectivities versus permeability of CO₂ for 8 bar feed pressure, respectively. According to Figures 11 and 12, the data for all samples were placed below the Robeson’s upper bound. The Robeson’s plots show the maximum obtained permselectivities versus permeabilities of commercial membranes for different pair gases [26]. Therefore, according to proximity of data samples to the upper bound of Robeson’s plots, the prepared CMC membranes would be a potential candidate for commercial use.

4. Conclusions

A set of membranes were prepared based on carboxymethylcellulose (CMC) and in a variety of polymer concentrations (1.2%, 1.6%, 2.4% and 3.0%). In addition, the crosslinked CMC membranes with the same polymer concentrations were made to investigate the effect of crosslinking. The occurrence of crosslinking reaction was determined by ATR-FTIR test.

The permeability of CO₂, N₂ and CH₄ through each membrane was measured at 6, 8 and 10 bar of feed pressure. The permeability of CO₂ through each membrane was evidently higher than the permeabilities of other gases. Also, permeability of gases were increased with the feed pressure. The permeability of CO₂ increased more than the other gases with increasing the pressure. In other hand, gas permeability decreased as CMC concentration increased.

The permselectivity of the CO₂/N₂ and CO₂/CH₄ increased considerably by increasing the CMC concentration. By comparing CO₂/N₂ and CH₄/N₂ permselectivity of CMC membranes, it was
concluded that the pressure had no significant effect on the permeability of N<sub>2</sub> and CH<sub>4</sub>, but the permeability of CO<sub>2</sub> increased with pressure.

The crosslinking reaction reduced the permeability of gases through crosslinked membranes, but enhanced the solubility of CO<sub>2</sub> in membrane. Consequently, the CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> permselectivities were increased.

Eventually, according to Robeson's plots, prepared CMC membranes would have potential for commercialization.

References


**Biographies**

**Seyed Iman Miremadi** received his BS degree in Chemical Engineering from Sharif University of Technology, Tehran, Iran, in 2011. Currently, he is an MS student in Energy Engineering at the same University. His research interests are gas separation and membranes properties.

**Navid Shafiaabadi** received his BS degree in Chemical Engineering from Sharif University of Technology, Tehran, Iran, in 2011. Now, he is an MS student in Chemical Engineering at the same University. His research interest is process simulation and control.

**Seyyed Abbas Mousavi** received his BS degree in Chemical Engineering from Sharif University of Technology, Tehran, Iran, in 1999 and his MS and PhD degrees in Polymer Engineering from the same University in 2001 and 2007, respectively. His current research interests are in the areas of membrane preparation for gas separation, water treatment, waste water treatment and micro and ultrafiltration processes. Now, he is an assistant professor of Polymer Engineering at Sharif University of Technology.

**Mohammad Sadegh Amini-Fazl** received his BS degree in Chemistry from Tabriz University in 2003 and his MS degree in Polymer Chemistry from Sharif University of Technology, Tehran, Iran, in 2005. Now, he is a PhD student in Polymer Engineering at Iran Polymer and Petrochemical Institute. His research interest is polymer synthesis.