Development of carbon membrane for CO\textsubscript{2}/N\textsubscript{2} and CO\textsubscript{2}/CH\textsubscript{4} separation

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Carbon membranes were prepared using stainless steel supports and evaluated for the separation of two mixtures, i.e. CO\textsubscript{2}/N\textsubscript{2} and CO\textsubscript{2}/CH\textsubscript{4}. The effect of several operating variables, including temperature, pressure and precursor concentration was examined. In this study, carbon membranes were synthesized using a sucrose precursor. Sucrose was subjected to pyrolysis in the temperature range 300–700°C, leading to the complete formation of carbon structure. The gas separation characteristics of the produced membranes were estimated by evaluating CO\textsubscript{2}, CH\textsubscript{4} and N\textsubscript{2} permeation. The highest selectivity obtained for CO\textsubscript{2}/CH\textsubscript{4} and CO\textsubscript{2}/N\textsubscript{2} was 1.64 and 1.41 respectively. The emphasis towards CO\textsubscript{2}/CH\textsubscript{4} and CO\textsubscript{2}/N\textsubscript{2} separation is due to their importance and direct relevance to the gas industry processes.

Keywords: Carbon membrane, greenhouse gases, pyrolysis temperature, separation mechanism, sucrose precursor.

Industrial activities have led to an excessive increase of greenhouse gas (GHG) emission levels in the atmosphere\textsuperscript{1}. Despite the fact that more energy resources from other non-fossil sources are being used in the industrial sector, fossil fuels are still considered as the main source\textsuperscript{2}. CO\textsubscript{2} is a major GHG, and plays a significant role in climate change. The existing power plants worldwide are the main source and emit around 2 billion tonnes of CO\textsubscript{2} per year\textsuperscript{2–5}. Therefore, the recovery of CO\textsubscript{2} from large emission sources is a difficult task confronting many developing countries. The separation of CO\textsubscript{2} from CH\textsubscript{4} and N\textsubscript{2} is important to be implemented in many industry-related processes, including natural gas sweetening, oil recovery enhancement, biogas upgrading and gas purification from landfill.

The identification of a separation/capture technology which would fulfil the needs of separation processes, with minimum energy consumption, is key and has attracted the attention of many researchers. Currently, the processes used for CO\textsubscript{2} separation are absorption, adsorption and cryogenic separation\textsuperscript{3–8}. The conventional amine-based absorption technology is the most popular for CO\textsubscript{2} capture, as it is capable of achieving 90% of CO\textsubscript{2} capture from flue gas\textsuperscript{3}. This is due to the fast kinetics along with the strong chemical reaction obtained\textsuperscript{3,9}. Yet, absorption technology requires a significant amount of energy (4–6 MJ/kgCO\textsubscript{2}) due to the significant energy ingested in the regeneration step\textsuperscript{9–11}. On the other hand, membranes are a relatively novel separation technology and are considered to be a promising alternative to fulfil this task due to their simplicity, energy efficiency and as also being eco-friendly\textsuperscript{12–14}. Nowadays, membranes are being studied for many separation applications, including CO\textsubscript{2} emissions capture from fossil fuel-based flue-gas streams\textsuperscript{15–20}. They can consist of different material types, including organic (polymeric) and inorganic (carbon, zeolite, ceramic or metallic) with different structures, i.e. porous or non-porous\textsuperscript{19–21}. Carbon membranes have been used in gas separation since 1970s, but the development of these types of membranes is yet to be studied\textsuperscript{22–25}. Carbon membranes are produced by a pyrolysis procedure (heat-treatment process) using different types of precursors\textsuperscript{26}. Yet, many precursors have not been explored and utilized\textsuperscript{27}. In the present study, a simple sucrose precursor was used to produce carbon membranes through the pyrolysis process. Sucrose was chosen due to its natural resource and the fact that it can be produced without the extensive use of energy\textsuperscript{28}. These membranes were subjected to CO\textsubscript{2} separation to determine their performance and effectiveness.

Experimental work

A thin carbon layer was prepared and supported using a porous stainless steel disc to provide mechanical strength. Before performing pyrolysis, the precursor solution was applied over the stainless steel support and left overnight to dry at room temperature. The sucrose solution was acquired by dissolving different amounts of sucrose in water to produce different concentrations by weight, i.e. 1 : 1, 2 : 1 and 3 : 1 ratios (sucrose : water). Pyrolysis was performed at 300°C and a heating rate of 2.5°C/min with soak time of 60 min using nitrogen as an inert gas. Table 1 lists the mass of carbon obtained.

Table 1 shows that higher concentrations have an accumulated amount of carbon mass due to their higher viscous properties. For further comprehension, the membranes were evaluated for CO\textsubscript{2}/N\textsubscript{2} and CO\textsubscript{2}/CH\textsubscript{4} permeation using a membrane gas unit (Convergence Inspector Neptunus). The experiments were performed at 25°C using feed...
pressure ranging from 5 to 15 bar and a feed flow rate of 100 \,1 \h^{-1}. The flux and selectivity of the carbon membrane were estimated using eqs (1) and (2) respectively. Usually, the permeability units used in membrane studies are the gas permeation unit (GPU) and Barrer.

\[
P_{i\text{GPU}} = \frac{Q_i}{\Delta p \cdot A}, \quad (1)
\]

\[
\alpha_{A/B} = \frac{P_A}{P_B}, \quad (2)
\]

where \( P_i \) is the flux, \( Q_i \) the volumetric flow rate of the gas, \( \Delta p \) the transmembrane pressure drop, \( A \) the surface area of the membrane and \( \alpha_{A/B} \) is the separation factor/selectivity.

**Results and discussion**

The images obtained from a scanning electron microscopy (SEM), (JEOL, JSM-IT300) show carbon formation over the stainless steel support with thickness of around 36 \,\mu\m (Figure 1). An electron-dispersive X-ray (EDX) spectrometer fitted with an INCA \times\ act detector was utilized for additional characterization (Figure 2), indicating that the main components in the membrane are carbon, silica and alumina. Table 2 shows the performance of the membranes with different feed pressures and sucrose concentrations. It can be observed from the results that feed pressure is proportional to the fluxes and inversely proportional to selectivity, which illustrates the trade-off relation between these variables. With regard to precursor concentration, the solution concentration has significant influence on the overall performance in terms of flux and separation factor. Sucrose concentration is proportional to selectivity and inversely proportional to the flux. This is observed up to a certain limit (3 : 1), where the viscosity of the solution is very high and does not assist in the formation of a coherent carbon film. As a result, the membrane with the highest concentrated solution does not follow the pattern of the other three concentrations. Thus it was concluded that the 3 : 1 concentration resulted in the highest selectivity of CO\textsubscript{2}/CH\textsubscript{4}, and hence it was taken for further analysis. Different pyrolysis temperatures were considered and evaluated to optimize the entire preparation procedure. Also, the membrane with 3 : 1 concentration was subjected to different pyrolysis temperatures, i.e. 300\textdegree–700\textdegree\C (Table 3). As can be noted from the results, there is a decrease in the CO\textsubscript{2} and CH\textsubscript{4} fluxes with increase in the pyrolysis temperature. This may be due to the fact that higher pyrolysis temperature results in the narrowing of the pore structure, leading to an increase in membrane selectivity\textsuperscript{29,30}.

Table 3 clearly indicates that the membrane prepared at 600\textdegree\C shows the best performance. This could be related to the coherent formation of carbon at this pyrolysis temperature. Therefore, the membrane prepared at 600\textdegree\C was taken for further analysis performed using different feed pressures (5–15 bar) and different gases, i.e. CO\textsubscript{2}, CH\textsubscript{4} and N\textsubscript{2} (Figures 3 and 4). Both CO\textsubscript{2}/CH\textsubscript{4} and CO\textsubscript{2}/N\textsubscript{2} followed the same performance pattern. However, the membrane was less selective to CO\textsubscript{2}/N\textsubscript{2} due to similar molecule size of CO\textsubscript{2} and N\textsubscript{2} that will lead to more penetration of N\textsubscript{2} rather than CH\textsubscript{4}, resulting in less selective performance. In other words, the permeability trend was inversely proportional to the kinetic diameter of these gases (CO\textsubscript{2} < N\textsubscript{2} < CH\textsubscript{4}). This indicates the more rapid passing of gases with small-sized molecules through the membrane than the large ones, revealing that the permeation

| Table 1. Weight of carbon membrane during preparation (1 : 1, 2 : 1 and 3 : 1 sucrose : water ratio) |
|-----------------|-------|-------|-------|
| Membrane        | Carbon layer (weight in g) |       |
| Stainless steel disc | 31.92 | 31.94 | 31.93 |
| Stainless steel disc + sucrose | 36.01 | 36.56 | 37.89 |
| Membrane after pyrolysis | 31.96 | 32.03 | 32.03 |
| Mass of carbon | 0.04  | 0.09  | 0.1   |

**Figure 1.** SEM images of (a) surface view and (b) edge view of carbon membrane with 3 : 1 concentration at magnification of 20 and 50 \,\mu\m respectively.

**Figure 2.** EDX membrane with 3 : 1 concentration.
Table 2. Selectivity and permeability of the prepared membranes at pyrolysis temperature of 300°C

| Concentration | Feed pressure (bar) | Permeance (GPU) | Selectivity CO2/CH4 |
|---------------|---------------------|-----------------|---------------------|
| sucrase : water |                     | CO2             | CH4                 |
| 1 : 1         |                     | 290.71          | 236.35              | 1.23                |
|               | 5                   | 442.69          | 365.87              | 1.21                |
|               | 10                  | 460.37          | 390.15              | 1.18                |
|               | 15                  | 448.13          | 400.12              | 1.12                |
| 2 : 1         | 5                   | 283.07          | 199.35              | 1.42                |
|               | 7                   | 285.24          | 205.21              | 1.39                |
|               | 10                  | 290.56          | 213.65              | 1.36                |
|               | 15                  | 297.38          | 227.01              | 1.31                |
| 3 : 1         | 5                   | 224.05          | 150.37              | 1.49                |
|               | 7                   | 233.56          | 159.97              | 1.46                |
|               | 10                  | 240.96          | 167.33              | 1.44                |
|               | 15                  | 258.82          | 180.99              | 1.43                |

Table 3. Permeability and selectivity of the membrane with concentration 3 : 1 at different pyrolysis temperatures and feed pressure of 5 bar

| Pyrolysis temperature (°C) | Permeance (GPU) | Selectivity CO2/CH4 |
|----------------------------|-----------------|---------------------|
|                            | CO2             | CH4                 |
| 300                        | 224.05          | 150.37              | 1.49                |
| 400                        | 215.29          | 140.71              | 1.53                |
| 500                        | 218.11          | 135.47              | 1.61                |
| 600                        | 218.27          | 133.09              | 1.64                |
| 700                        | 216.04          | 132.54              | 1.63                |

The durability of the prepared membrane was tested and assessed. The membrane prepared at 600°C was subjected to pure CO2 feed at 25°C and 5 bar. The durability/repeatability test was conducted for 7 h at different intervals. In general, the preparation method of fabricating carbon membranes for CO2 separation yielded a stable performance during this period. This was evaluated by the variances (S²) deviation in the data (eq. (3)). The membranes were permeating CO2 within variances of 1.44. Other concentrations are expected to follow similar behaviours as they have been prepared using the same procedure.

\[
S^2 = \frac{\sum (X_i - \bar{X})^2}{n-1}
\]

Conclusion

The preparation of selective carbon membrane was achieved successfully using a sucrose precursor for CO2/
CH₄ and CO₂/N₂ separation applications. The pyrolysis temperature is an important factor in determining the performance of the membrane that is produced in terms of selectivity and permeability. The results obtained from this study indicate that selectivity of the carbon membrane is proportional to pyrolysis temperature. This can be attributed to the fact that higher pyrolysis temperatures lead to the formation of a dense layer with narrow interplanar spacing, resulting in small pore structure. This eventually minimizes any pinholes and defects on the surface. A comparison between the permeability of different gases, i.e. CO₂, N₂ and CH₄, led to the conclusion molecular sieving is the dominant separation mechanism. In the literature, more selective carbon membranes using polymeric precursors have been reported. However, the present overcomes the long process involved and toxic solvents used in the conventional precursors and preparation methods.

| Membrane               | Feed temperature (°C) | Selectivity  | Permeance CO₂ (GPU) | Reference               |
|------------------------|-----------------------|--------------|---------------------|-------------------------|
| Carbon                 | 25                    | 1.64         | 218.26              | Present study           |
| PDMS                   | 25                    | 32           | 110                 | 31                      |
| Pebax                  | 35                    | 18           | 13.5                | 32                      |
| Polyvinylamine         | 25                    | 23           | 81                  | 33                      |
| Poly(4-vinylpyridine)/silico | 35          | 29           | 92                  | 34                      |
| Polyallylamine         | 50                    | 15           | 112.5               | 35                      |

| Membrane               | Feed temperature (°C) | Selectivity  | Permeance CO₂ (GPU) | Reference               |
|------------------------|-----------------------|--------------|---------------------|-------------------------|
| Carbon                 | 25                    | 1.41         | 218.26              | Present study           |
| Oxydiphthalic anhydride| 35                    | 33.02        | 88.21               | 36                      |
| PSF                    | 25                    | 4.1          | 28                  | 37                      |
| POEM                   | 26                    | 2.1          | 1.6                 | 38                      |
| PVA                    | 25                    | 270          | 29                  | 39                      |
| PDMS                   | 25                    | 35           | 110                 | 31                      |

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