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Separation of Bulk Carbon Dioxide-Hydrogen Mixtures by Selective Surface Flow Membrane

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Abstract. The separation performance of carbon dioxide-hydrogen mixtures by a nanoporous carbon membrane called selective surface flow membrane is described. The membrane selectively permeates CO_2 from H_2 and a H_2 enriched gas is produced at the feed gas pressure. Extensive experimental data for the separation using feed gas pressures from 0.24 to 1.13 MPa and CO_2 compositions from 5 to 75 (mol%) in H_2 are reported. The data can be empirically correlated using a simple equation with a single adjustable-parameter. The adjustable parameter is found to be a linear function of the feed gas CO_2 partial pressure.

The membrane separates CO_2-H_2 mixture very efficiently even at a low total feed gas pressure (~0.4 MPa). The membrane area required for a given separation decreases drastically with increasing feed gas pressure in the range of 0.24–0.92 MPa and then it becomes insensitive to the feed gas pressure.

Keywords: selective surface flow, nanoporous carbon membrane, gas separation, carbon dioxide, hydrogen

Introduction

A nanoporous carbon membrane called Selective Surface Flow (SSF^{TM}) membrane has been developed by Air Products and Chemicals, Inc. (Rao et al., 1992; Rao and Sircar, 1993). It consists of a thin layer (2–3 μm) of a nanoporous (6–7 Å pore diameter) carbon matrix supported on a macroporous (<1 μm pore diameter) tubular alumina support. It is produced by coating the bore side of the tubular support with a poly vinylidene chloride latex film and then carbonizing the polymer by heating in an inert atmosphere. Only one coat of the polymer and a single heating step are used. The details of the carbonizing conditions and the pore characteristics of the membrane are given elsewhere (Rao et al., 1992; Rao and Sircar, 1993, 1996; Anand et al., 1997).

The membrane separates gas mixtures by an adsorption-surface diffusion-desorption mechanism (Rao and Sircar, 1993). The gas mixture to be separated is passed through the bore side of the membrane at a super-ambient pressure level (P^H) while keeping the permeate side at a near-ambient pressure level (P^L). Certain components of the feed gas mixture are selectively adsorbed on the pore walls of the carbon membrane, followed by their selective surface diffusion on the pore walls to the low pressure side where they are desorbed into the permeate gas phase. Consequently, the membrane produces a gas stream enriched in the less selectively adsorbed components of the feed gas mixture as the high pressure effluent gas while a gas stream enriched in the more selectively adsorbed components of the feed gas is produced as the low pressure effluent gas. This is often desirable because the less selectively adsorbed components, which are recovered at the feed gas pressure, form the product gas in many practical applications.

Adsorbates having larger molecular size, higher polarizability and larger permanent polarily are selectively adsorbed on the membrane walls and they selectively permeate through the membrane. This is, in contrast, with the characteristics of most polymeric membranes where the smaller molecules of a gas mixture preferentially permeate through the membranes by a solution-diffusion mechanism. The separation mechanism of the SSF membrane provides high permeance with high permselectivities of the adsorbed components while requiring relatively low feed gas pressures (0.24–1.5 MPa). Typical polymeric membranes, on the other hand, exhibit a reciprocal relationship between permeance and permselectivity of the permeated gas and they require relatively larger feed gas pressures (>1.5 MPa) for practical operation. These advantages of the SSF membrane have led to many separation concepts of practical interest such as hydrogen recovery from refinery and chemical waste gases and fractionation of hydrocarbon mixtures (Rao et al., 1995; Anand et al., 1995).

Previously reported nanoporous carbon membranes (Koresh and Soffer, 1983; Jones and Koros, 1994) were produced by carbonizing thermosetting polymeric materials such as polyacrylonitrile, cellulose acetate, polyimides, etc. These membranes, however, separated gas mixtures based on the differences in the molecular sizes of the components. The smaller molecules of the feed gas mixture diffused through the membrane producing a low pressure permeate stream enriched in these components, while the larger molecules were enriched in the high pressure side. Thus, these carbon molecular sieve (CMS) membranes exhibited a very different separation characteristics than the present SSF membranes.

The purpose of the present work is to report on the separation characteristics of bulk CO_2-H_2 mixtures under various operating conditions using the SSF membrane. Carbon dioxide is selectively adsorbed and permeated through the SSF membrane because of (a) its larger polarizability (26.5×10^{-25} cm^3) than H_2 (7.9×10^{-25} cm^3) and (b) its larger permanent quadrupole moment (4.3×10^{-26} esu cm^2) than H_2 (0.6×10^{-25} esu cm^2) (Prausnitz et al., 1986). The kinetic diameters of CO_2 and H_2 are, respectively, 3.30 and 2.92 Å (Breck, 1973). The CMS membranes, in contrast, selectively permeate the smaller H_2 molecules from a mixture with CO_2.

Experimental Methods and Data Analysis

Figure 1 is a schematic diagram of the apparatus used for evaluating the separation performance of a CO_2-H_2 mixture by the SSF membrane. A single SSF membrane tube (30 cm long, 0.56 cm i.d., 0.165 cm thick support wall) was mounted in a cylindrical membrane holder (2.3 cm i.d. and 40.0 cm long). The holder was fitted with high pressure gas inlet and effluent outlet lines in the bore side of the membrane as well as with a low pressure effluent outlet line in the permeate side. The feed gas flow rate into the membrane at pressure P^H was measured using a rotameter (RM) which was calibrated using a wet test meter (WTM). The flow rates of both the high and low pressure effluent gases were measured using wet test meters. The low pressure effluent gas was withdrawn in a direction counter-current to that of the feed gas flow. The feed gas mixtures were premixed. The effluent gas compositions were measured by a gas chromatograph (GC). A back pressure regulator was used in the high pressure effluent line to maintain a constant value of P^H, which was varied between 0.24 and 1.15 MPa during the test runs. The low pressure side of the membrane was maintained at a constant value of 0.1 MPa ($= P^L$) for all tests. The system temperature was ambient (25 ± 3°C).

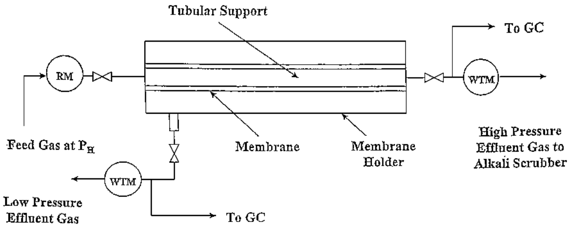

Figure 1. Schematic diagram of the experimental apparatus.

The experiments were conducted by varying the feed gas mole fractions of CO_2 ($y^F_{CO_2}$) between the values of 0.05 and 0.75 at different feed gas pressures. The effluent gas flow rates and compositions were measured after steady-state operations were established, which typically took 0.5 hour of operation.

The partial pressures of CO_2 and H_2 (both high and low pressure sides) vary along the length of the membrane under steady-state operation. Consequently, the amounts of CO_2 and H_2 adsorbed on the membrane pore walls at both the high and low pressure sides as well as their surface diffusivities vary along the membrane length. As a result, the CO_2 permeance and permselectivity are functions of the membrane length. These functionalities are not known. We, therefore, chose to describe the separation performance of the SSF membrane in terms of overall H_2 recovery (α_{H_2}) and CO_2 rejection (β_{CO_2}). The H_2 recovery is defined as the ratio of the molar flow rates of H_2 in the high pressure effluent gas stream to that in the feed gas stream. The CO_2 rejection is defined as the ratio of the molar flow rates of CO_2 in the low pressure effluent gas stream to that in the feed gas stream.

The separation performance data will be given in terms of β_{CO_2} as functions of α_{H_2} for different feed gas conditions. High rejections of CO_2 at high recoveries of H_2 are the desired separation properties. This mode of description of the separation performance of the SSF membrane represents the practical separation characteristics by the membrane.

The other key variable to define the separation performance of the membrane is the equivalent feed gas space velocity, given by the ratio of the geometric transport area of the membrane (A) to the feed gas flow rate (F) as functions of H_2 recovery (α_{H_2}). Low (A/F) for a given α_{H_2} is also a desired property. That reduces the area requirement for a given feed flow rate.

All gas flow rates and compositions for the membrane system can be expressed in terms of the variables α_{H_2}, β_{CO_2}, F and $y^F_{CO_2}$ by carrying out mass balances:

High Pressure Side Effluent

$$\frac{P}{F} = \sum y_i^F(1-\beta_i); \quad y_i^P = \frac{y_i^F(1-\beta_i)}{\left[\sum y_i^F(1-\beta_i)\right]} \tag{1}$$

Low Pressure Side Effluent

$$\frac{W}{F} = 1 - \sum y_i^F(1-\beta_i); \qquad y_i^W = \frac{y_i^F\beta_i}{\left[1-\sum y_i^F(1-\beta_i)\right]} \tag{2}$$

where P and y_i^P, are, respectively, the molar flow rate and mole fraction of component i in the high pressure product effluent. W and y_i^W are the corresponding properties of the low pressure effluent. It should be noted that ($\alpha_i + \beta_i = 1$). The summations in Eqs. (1) and (2) are over both components ($i = 1, 2$).

It should be emphasized here that the separation performance of a SSF membrane of a given length (L) and area (A) can be completely described by defining the feed gas composition (y_i^F), its flow rate (F) and the variables β_i and (A/F) as functions of α_i. Experimental performance data for the SSF membrane (β_i and A/F as functions of α_i) are needed for given values of y_i^F, P^H and P^L. The conventional procedure used for design of a polymeric membrane (Ruthven and Sircar, 1997) by specifying the pure gas permeabilities of the components of the feed gas mixture (which are assumed to be constants) along with the variables F, y_i^F, A, L, P^H and P^L cannot be employed for the case of SSF membranes because the local permeabilities of the components of the gas mixture substantially vary along the length of the membrane and they are complex functions of local gas phase compositions and pressures in the high and low pressure sides of the membrane. Satisfactory and reliable models to calculate mixed gas adsorption and surface diffusivities through nanoporous carbon matrix do not exist. The detailed pore structure of the SSF membranes are also not known.

Experimental Results

Figures 2, 3 and 4 show the CO_2 rejection (β_{CO_2}) against H_2 recovery (α_{H_2}) plots for feed gas pressures of 0.24, 0.44 and 1.13 MPa, respectively. Each plot describes the effect of feed gas CO_2 composition ($y^F_{CO_2} = 0.05$, 0.25, 0.50 and 0.75) at that feed gas pressure. The permeate gas pressures (P^L) were maintained at 0.11 MPa for each run. The feed gas flow rate (F) was varied at constant values of P^H and $y^F_{CO_2}$ in order to generate these performance curves. The curves of Figs. 2–4 are bounded by the limits ($\alpha_{H_2} = 0$, $\beta_{CO_2} = 100$) and ($\alpha_{H_2} = 100$, $\beta_{CO_2} = 0$), and a straight line through these limiting points represents the case of no separation. The overall and component mass balances closed within ±3% for each experimental run.

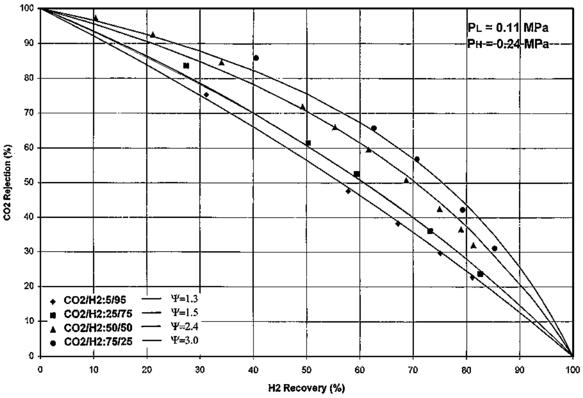

Figure 2. Carbon dioxide rejections as functions of hydrogen recoveries at a total feed gas pressure of 0.24 MPa and various feed gas mole fractions of CO_2.

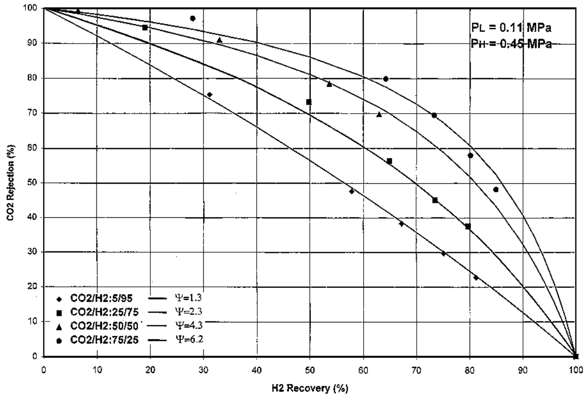

Figure 3. Carbon dioxide rejections as functions of hydrogen recoveries at a total feed gas pressure of 0.44 MPa and various feed gas mole fractions of CO_2.

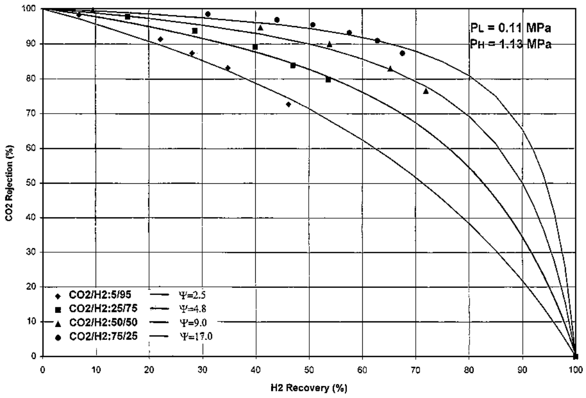

Figure 4. Carbon dioxide rejections as functions of hydrogen recoveries at a total feed gas pressure of 1.13 MPa and various feed gas mole fractions of CO_2.

It may be seen from these figures that CO_2 is preferentially permeated through the SSF membrane and the separation of bulk CO_2 from mixtures with H_2 improves as the partial pressure of CO_2 in the feed gas is increased. A significant separation of CO_2 from H_2 can be achieved even when the total feed gas pressure (P^H) is low ($\geq$0.24 MPa) as long as the composition of CO_2 in the feed gas is moderate ($y^F_{CO_2} \geq 0.5$). The CO_2 separation efficiency is substantially improved at higher feed gas pressures ($P^H \sim 1.13$ MPa).

The data of Figs. 2–4 are replotted in Fig. 5 in the form of β_{CO_2} against α_{H_2} at constant feed gas partial pressures of CO_2 ($p^F_{CO_2}$). It shows that β_{CO_2} can be described as smooth functions of α_{H_2} at constant $p^F_{CO_2}$ even though the individual points in the graph were obtained by measuring the performance of the membrane

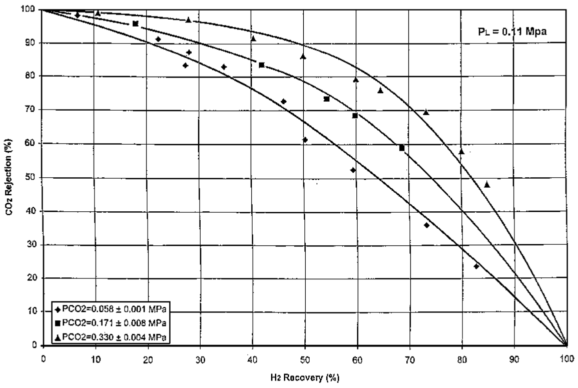

Figure 5. Carbon dioxide rejections as functions of hydrogen recoveries at different feed gas partial pressures of CO_2.

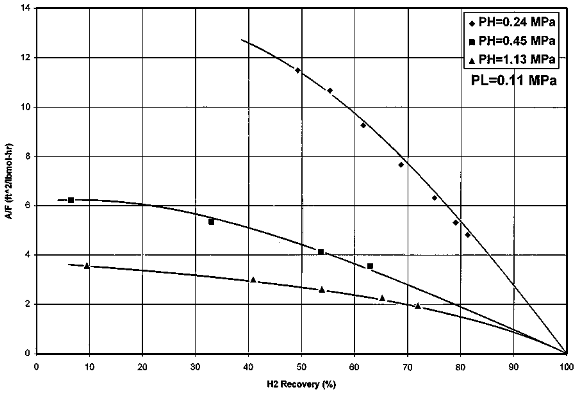

Figure 6. Plots of (A/F) as functions of α_{H_2} for different values of feed gas pressure.

at different constant total gas pressures using different feed gas CO_2 mole fractions. This shows that the separation performance of the SSF membrane for bulk CO_2-H_2 separation can be described by specifying the partial pressure of CO_2 in the feed gas.

Figure 6 shows an example of the plot of the variable (A/F) as functions of α_{H_2} at different feed gas pressures for a given feed gas composition (50% CO_2 + 50% H_2). Table 1 reports relative values of the parameter (A/F) as functions of total feed gas pressure (P^H) at two specific values of H_2 recovery ($\alpha_{H_2} = 50\%$ and 80%). It shows that the SSF membrane area required to process a CO_2-H_2 mixture of given flow rate rapidly decreases when the total feed gas pressure is increased. In particular, the value of the parameter (A/F) decreases substantially between feed gas pressures of 0.24 and 0.44 MPa. Then the change in the value of the parameter (A/F) with increasing P^H becomes less pronounced,

Table 1. Relative SSF membrane area requirement as functions of hydrogen recovery and feed gas pressure (feed CO_2 mole fraction = 0.5).

Feed gas pressure (MPa)	Relative membrane area	
	50% H_2 recovery	80% H_2 recovery
0.24	1.00	1.00
0.44	0.36	0.46
0.93	0.25	0.30
1.13	0.25	0.30

and practically no change in the value of (A/F) occurs when $P^H \geq 0.93$ MPa.

The performance of the SSF membrane for CO_2-H_2 separation was compared with that of a commercial cellulose acetate (CA) polymeric membrane. The ASPEN program was used to calculate the performance of the CA membrane. The permeabilities of CO_2 and H_2 through the CA membrane at 20°C were chosen to be 17.8 and 3.5 Barrers, respectively (Bandrup and Immergut, 1975), and the membrane thickness was assumed to be 1000 Å. The CA membrane permeates CO_2 over H_2 with a permselectivity (assumed constant) of 5.1 at 20°C. The steady-state performance calculations were made by assuming plug flow behavior in both high and low pressure sides of the membrane and using a membrane transport area equal to that of the SSF membrane. The feed gas mixture contained 50% CO_2 + 50% H_2 and the feed gas pressure was varied between 0.24 and 1.13 MPa. The permeate gas pressure was 0.11 MPa.

Table 2 compares the relative performances of SSF and CA membranes for CO_2-H_2 separation. It shows that the CA membrane potentially exhibits a slightly higher rejection of CO_2 than the SSF membrane for the same values of H_2 recoveries but the (A/F) values are an order of magnitude larger for the CA membrane than the SSF membrane. The difference in the β_{CO_2} values between the two membranes substantially decrease as the feed gas pressure is increased. An important property of the SSF membrane is that it offers a relatively smaller (A/F) value even when the feed gas pressure is fairly low.

Table 2. Relative performance for separation of CO_2-H_2 mixture by SSF and cellulose acetate membranes (Feed CO_2 mole fraction = 0.5).

Feed gas pressure (MPa)	α_{H_2}	β_{CO_2}		Relative membrane area	
		SSF	CA	SSF	CA
0.24	0.5	0.71	0.83	1.0	27.2
	0.8	0.35	0.42	1.0	29.0
1.13	0.5	0.92	0.96	1.0	15.0
	0.8	0.64	0.63	1.0	11.9

Empirical Representation of the Data

In absence of binary adsorption equilibrium and surface diffusion data for the CO_2-H_2 mixture on the SSF membrane, we empirically described the rejection-recovery plots of Figs. 2–4 by the following relationship:

$$\beta_{CO_2} = \frac{\psi(1 - \alpha_{H_2})}{1 + (\psi - 1)(1 - \alpha_{H_2})} \tag{3}$$

where ψ is an empirical parameter. It is a function of the partial pressure of CO_2 in the feed gas. The value of ψ is greater than unity for any separation to occur ($\beta_{CO_2} + \alpha_{H_2} = 1$ for $\psi = 1$). The higher the value of ψ, the better is the separation of CO_2 from H_2. Equation (3) exhibits the appropriate boundary conditions for the rejection-recovery plots. Equation (3) can be used to generate analytical equations describing the performance of staged SSF membranes (Parrillo et al., 1997).

The solid lines in Figs. 2–4 show the best fit of the experimental data by Eq. (3). The values of ψ for different feed gas mole fractions of CO_2 are given in the figure. It may be seen that the fit of the experimental data is very good. The value of the parameter ψ increases as $p^F_{CO_2}$ increases, which indicates better separation of CO_2 from H_2.

Figure 7 is an empirical correlation of the parameter ψ as a function of $p^F_{CO_2}$. It uses all data points reported in this work. Figure 7 shows that ψ is a linear function

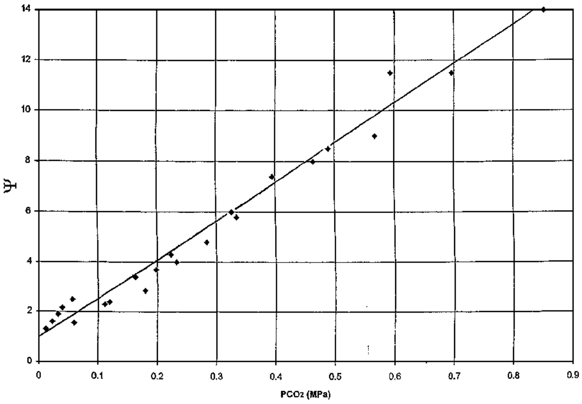

Figure 7. Dependence of the empirical parameter (ψ) on feed gas partial pressure of CO_2.

of $p^F_{CO_2}$ over a very large range of $p^F_{CO_2}$ ($\psi = 1$ when $p^F_{CO_2} = 0$ as required).

This demonstrates that the separation performance of the SSF membrane for CO_2-H_2 binary mixture can be adequately described by a simple empirical relationship (Eq. (3)) where the parameter ψ is a linear function of the feed gas partial pressure of CO_2. Obviously, ψ will also be a function of the system temperature.

Summary

The SSF membrane can be used to separate CO_2-H_2 gas mixtures. CO_2 is selectively permeated through the membrane, thereby producing a H_2 enriched gas at the feed gas pressure. The degree of separation of CO_2 by the membrane improves as the partial pressure of CO_2 in the feed gas is increased. However, the membrane exhibits substantial separation of CO_2 even when the total feed gas pressure is low (~0.44 MPa). The membrane area needed to process any given feed gas flow rate drastically decreases as the feed gas pressure is increased, until a feed gas pressure of ~0.93 MPa is reached. No further decrease in the membrane area is observed beyond that pressure level. The membrane area requirement is a function of the hydrogen recovery.

An empirical correlation (Eq. (3)) can be used to describe the CO_2 rejection-H_2 recovery characteristics of the SSF membrane using a single adjustable parameter (ψ). The parameter ψ can be correlated as a linear function of the feed gas CO_2 partial pressure.

Nomenclature

A	Membrane area
F	Feed gas flow rate
P	High pressure product flow rate
P^H	Pressure in the high pressure side of membrane
P^L	Pressure in the low pressure side of membrane
p_i	Partial pressure of component *i*
W	Low pressure product flow rate
y_i	Mole fraction of component *i*

Greek Letters

α_i	Recovery of component *i* in high pressure effluent
β_i	Rejection of component *i* in low pressure effluent
ψ	Parameter defined by Eq. (3)

Superscripts

F	Feed gas
P	High pressure effluent
W	Low pressure effluent

Subscript

i	Component *i*

Acknowledgments

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