Matrimid Polyimide Membranes for the Separation of Carbon Dioxide from Methane

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ABSTRACT: Three types of polyimide membranes viz., Matrimid, Kapton and P84, were prepared by solution casting and solvent evaporation method to study the permeation of CO_2 and CH_4 gases. Barrier properties were investigated as a function of feed pressure for pure gases and feed composition for the binary mixtures of CO_2 and CH_4. Kapton polyimide, prepared by imidization of polyamic acid, showed an increase in permeability, but reduction in selectivity, due to the occurrence of plasticization at higher feed CO_2 concentrations. Matrimid was found to exhibit the highest permeability and was studied in greater detail, due to the feasibility in its scale-up into a hollow fiber modular configuration for commercial application. Matrimid was characterized by Fourier transform infrared (FTIR) spectroscopy and X-ray diffractometry (XRD) to assess the intermolecular interactions and to understand the separation profiles. The effect of feed flow was evaluated by studying the permeation behavior of flat sheet membrane in dead-end operation mode with the hollow fiber module operated in crossflow feed mode. For pure gases, Matrimid hollow fiber membrane exhibited a CO_2 permeability of 12.7 Barrers with a CO_2/CH_4 selectivity of 40 at the feed pressure of 20 bar. At the same pressure, for binary mixture feed of 5 mol % CO_2 in methane, the module gave a permeability of 7.4 Barrers with a selectivity of 21. The total binary mixture permeability was determined at the feed CO_2 concentrations varying from 0 to 20 mol % to demonstrate the preferential sorption of CO_2 in Matrimid membrane. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 1585–1594, 2007

Key words: polyimide membrane; gas permeation; CO_2/CH_4 separation; selectivity

INTRODUCTION

In recent years, membranes are widely used in gas separation studies due to many proven advantages over the traditional separation methods.[1–3] Among the many polymers studied for gas separations, polyimides show an impressive potential in terms of industrial viability due to their high gas permeability, high intrinsic permselectivity, good mechanical strength, and chemical stability as compared with other conventional membranes.[3,4] Polyimides are indeed the good alternatives for polysulfone and cellulose acetate polymers, which are currently being used in gas separation research. Aromatic polyimides are the polycondensation products of dianhydride and diamine. While studying the structural manipulation of homopolymers, many

routes have been developed to systematically vary the dianhydride and diamine components.[5–7] The incorporation of bulky groups in dianhydride moieties tend to stiffen the polymer backbone and reduce the intrasegmental movements, thus enhancing the selectivity. However, when bulky groups are introduced in diamine moieties, permeability increases at the expense of declining selectivity.[8,9]

Matrimid is originally developed for use in microelectronics industry[10] as well as in gas separation problems. Matrimid polyimide is a soluble thermoplastic polyimide, consisting of 3,3′-4,4′-benzophenone tetracarboxylic dianhydride (BTDA) and diaminophenylindane (DAPI).[11] The polyimide formed is a mixture of 6-amino and 5-amino isomers of DAPI, which is fully imidized during the manufacturing process. It is soluble in a wide variety of common organic solvents such as $N,N′$-dimethylacetamide (DMAc), N-methylpyrrolidone (NMP), $N,N′$-dimethyl formamide (DMF), chloroform and methylene chloride. It is believed that the phenylindane ring system is the reason for its extremely high solubility.[11] P84 is a copolyimide of BTDA and 80% methyl phenylene diamine + 20% methylene diamine.[12] Kapton polyimide is a soluble thermoplastic polyimide prepared by the polycondensation reaction of pyromellitic anhydride and $P,P′$-diamino diphenyl ether.[13] Research efforts in using these polymers

have been growing steadily because of their favorable physicomechanical and chemical properties by utilizing versatile combinations of dianhydrides and diamines. Aromatic polyimides have excellent thermal stability at high temperatures under inert atmosphere and have been the extensively investigated membranes in CO_2 separations.[14–17] Kapton based membranes have been investigated for the separation of supercritical CO_2 from hydrocarbons[18,19] and He/N_2, H_2/N_2 separations at high temperatures.[20]

Natural gas streams vary widely depending upon the geographical location. The CO_2 content of these streams is generally less than 10% and some natural gas fields contain as much as 70% of CO_2 at pressures up to 5000 psi. While methane is the principal hydrocarbon present in natural gas streams, a mixture of ethane, propane, and butane content may be as high as 20%; 500 trace aromatic and paraffinic compounds may be present.[21] Propane and butane are known to plasticize the polyimide membranes,[22,23] but small amounts of aromatic hydrocarbons ($\leq$600 ppm) will cause a significant performance decline of polyimide membranes.[24] The principal objective of the present study is to quantify the effect of varying feed CO_2 concentration, pressure gradient, and mode of feed flow. Single gas permeation studies have been performed and compared with the binary mixture permeation to study the coupling between permeating species. Polyimides of interest are highly susceptible to plasticization and hence, it was studied in greater detail with the Kapton polyimide membrane. Among the polyimides tested, Matrimid has shown a maximum potential for scale-up due to its feasibility in fabricating the defect-free hollow fiber membranes. The performance of Matrimid hollow fiber module was investigated in crossflow pattern under different test conditions and compared with the dead-end mode of feed flow in a permeability cell installed with the flat sheet Matrimid membrane.

EXPERIMENTAL

Materials

Matrimid and P84 polymers in powder form were supplied by the University of Twente, The Netherlands. Hollow fiber Matrimid module was supplied by Permionics Membranes Pvt., Vadodara, India. Polyamic acid was supplied by ABR Organics, Hyderabad, India. Tetrahydrofuran (THF), DMAc and 1,4-dioxane solvents were purchased from s.d. Fine Chemicals, Mumbai, India.

Membrane preparation

All the polyimide membranes were prepared by solution casting–solvent evaporation technique. The struc-

tures of the three polyimides are presented in Figure 1. A 12 wt % of solution was prepared by dissolving Matrimid in a mixture of THF and 1,4-dioxane for 4–5 h under constant stirring. The solution was cast as a membrane on a clean glass plate and allowed to dry at ambient temperature. After drying, the membrane was peeled off from the glass plate and dried under vacuum at an elevated temperature of 60°C for 6 h. Membrane thickness was measured by micrometer screw gauge at different positions of the sheet film. These values were around 50 $\pm$ 1.0 μm. The membranes obtained were yellowish in color.

P-84 membrane was prepared from a 10% (w/v) solution in a mixed solvent system consisting of 80% 1,4-dioxane + 20% DMF (N,N'-dimethyl formamide). The film thus formed after solution casting on a clean glass plate and complete solvent evaporation was post-treated in a water bath for 30 min followed by solvent exchange in a bath containing isopropanol for about 30 min to remove the residual solvent. The membrane was then dried in an oven at 60°C for 3 h.

Kapton polyimide membrane was prepared from a 12% (w/v) solution of polyamic acid in DMAc (Fig. 2). The shelf life of polyamic acid solution was 2 months in a refrigerator, but only 10 days if stored outside, where the degradation becomes more rapid. It is ensured that viscosity of the polyamic solution was below 2.5 dL/g to avoid the formation of brittle films. The 12% (w/v) polyamic acid solution was cast at room temperature on a clean glass plate, which was kept in an oven at 60°C for 2–3 h. The oven temperature was raised to 80°–100°C and maintained for 3 h. Imidization was again carried out at 160°C for 3 h in an oven after which the temperature was further raised to 210°C and maintained for 6 h to obtain about 80% imidization. To achieve 100% imidization, the oven temperature was raised to 300°C for 6 h in N_2 atmosphere. For this study, imidization was restricted to 80% to allow the sufficient permeation of gas molecules.

Fourier transform infrared spectroscopy

Fourier transform infrared (FTIR) spectral measurements were performed on a Matrimid membrane using the Nicolet spectrophotometer (Model Impact 410, Milawaukee, WI) using KBr pellet method. Each sample was finely ground with KBr to prepare pellets under a hydraulic pressure of 400 kg and spectra were scanned between 500 and 4000 cm^{-1}.

XRD studies

A siemens D5000 (Germany) powder X-ray diffractometer was used to study the solid-state morphology of the Matrimid membrane. X-rays of 1.5406 Å wavelength was generated by a CuK-∞ source. The angle
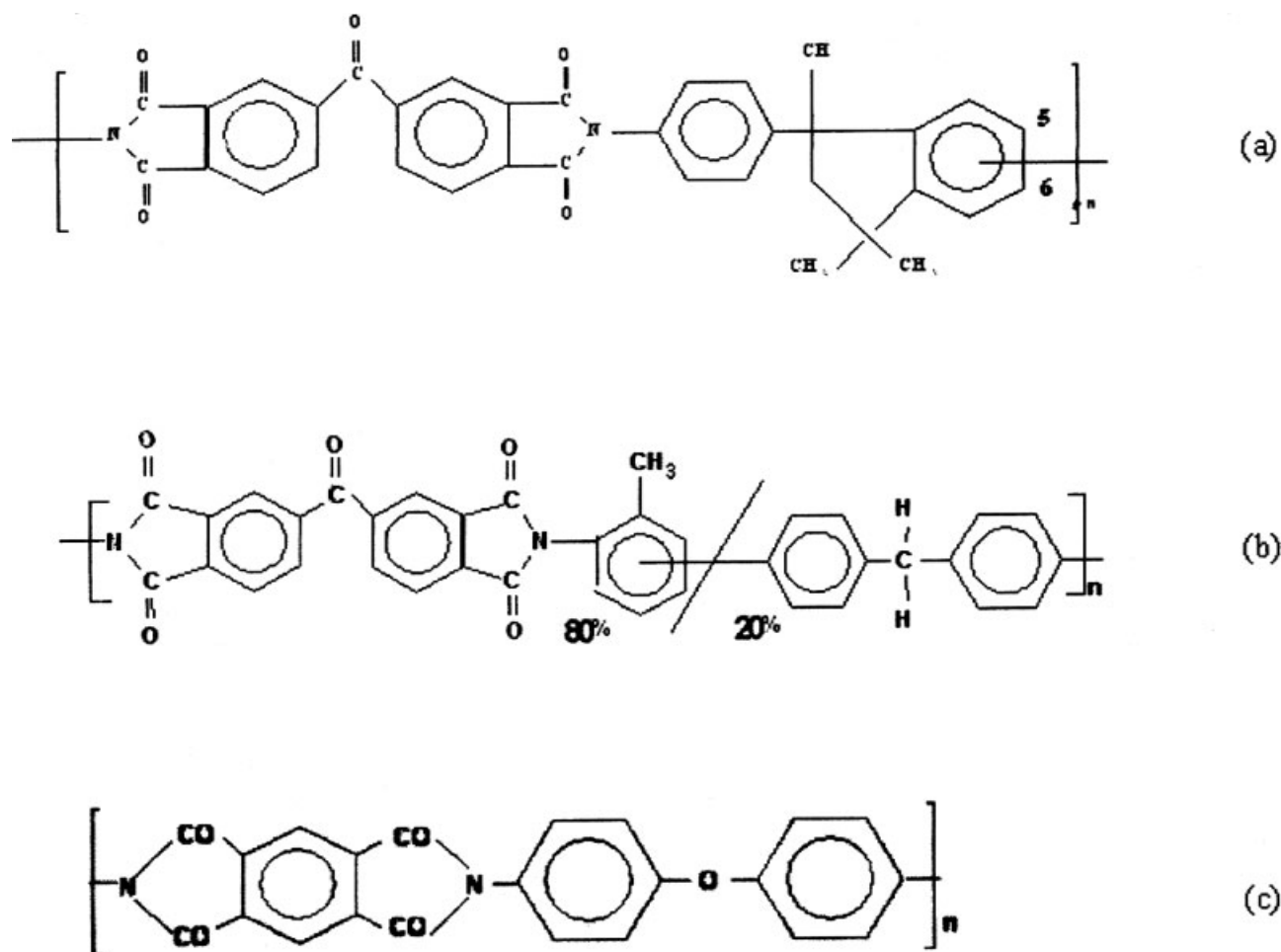
Figure 1 Chemical structures of (a) Matrimid, (b) P84, and (c) Kapton polyimide.

of diffraction (2θ) was varied from 0° to 65° to identify the changes in crystal structure and intermolecular distances between intersegmental chains of the polymer matrix.

Permeability measurements-continuous flow method

In the present study, continuous flow method was used to carry out permeability experiments for sheet membrane in a dead-end mode of feed flow. The feed component permeates through the membrane into a flowing stream of inert gas in the permeate chamber. The stream flowing towards permeate side was then analyzed to determine the component concentration. The continuous flow method was preferred because the measurement of low and high permeation rates can be easily done by varying the carrier gas flow rate to bring the concentration of penetrant in the permeate stream within the detectable range of gas chromatography. For the hollow fiber module with a cross-flow mode, a wet gas-meter was used to directly measure the high permeate flow rates.

Experiments with flat sheet membranes

The schematics of gas separation system used for permeability studies is presented in Figure 3. A stainless steel (SS 316) permeability cell of 42 cm² was incorporated into the manifold to house the circular sheet membrane. Permeability of the gases through the polyimide membranes was measured at 30°C. Permeate line was evacuated by vacuum pump (Toshniwal, Mumbai, India). In the dead-end mode of permeation, pure feed gas or binary mixture was introduced slowly into the upper chamber by means of a mass flow controller (MFC) keeping the outlet control valve closed until the dial gauge indicated the desired pressure. The pressure was kept constant by throttling the regulator of the cylinder. Inert nitrogen gas was used to sweep the permeated gas to SS 316 gas sample container (100 mL capacity) for consequent analysis. Experiments were repeated thrice to check for reproducibility, typically within 1% error. Flow rate of the carrier gas was controlled and kept constant using a needle valve, which was measured by a soap-bubble meter connected to the end of the permeate line. The permeate stream was
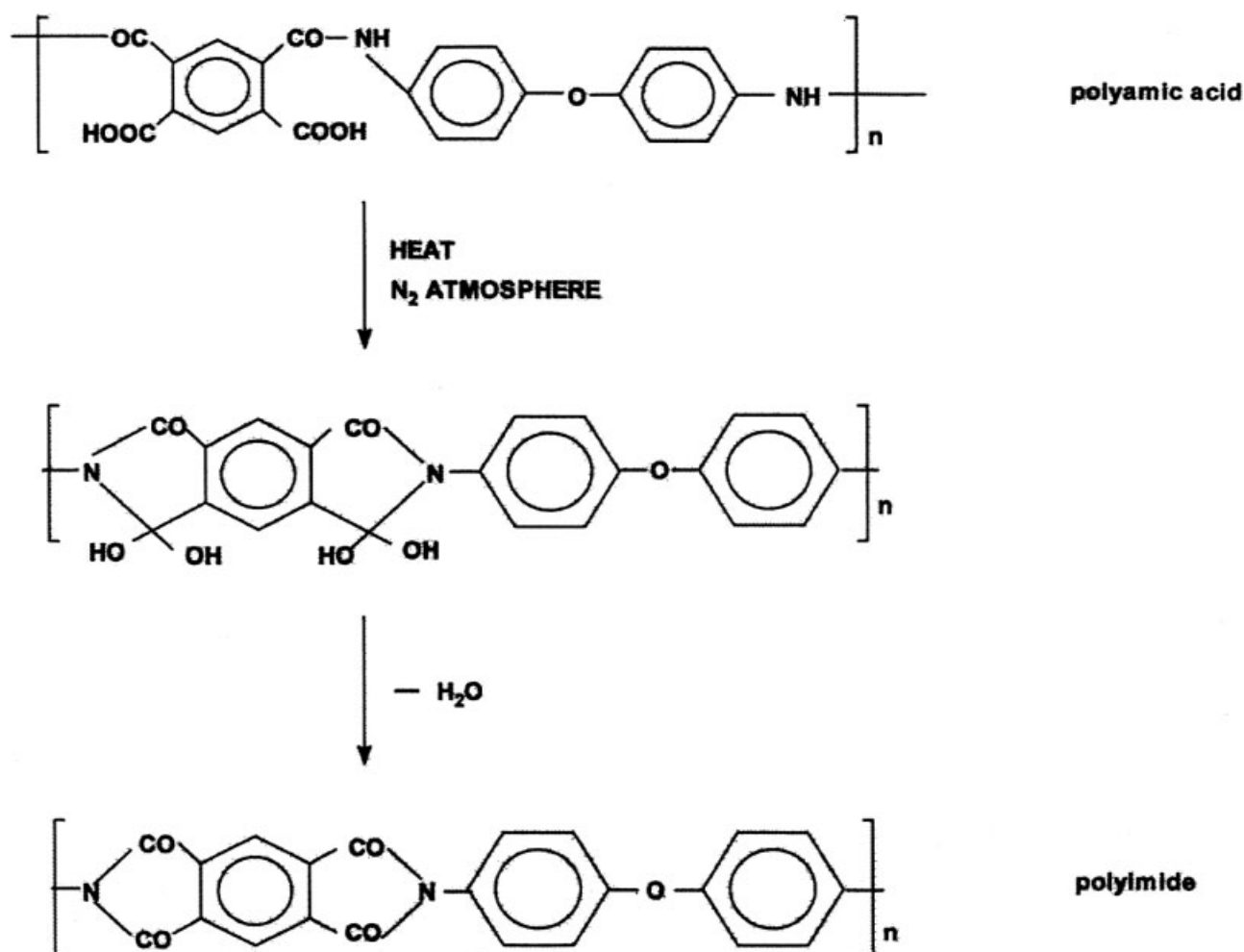
Figure 2 Schematic representation of the conversion of polyamic acid to polyimide.

collected after 3 h of equilibration of the membrane with the feed gas. The sample collection duration was 4–6 h.

Experiments with Matrimid hollow fiber module

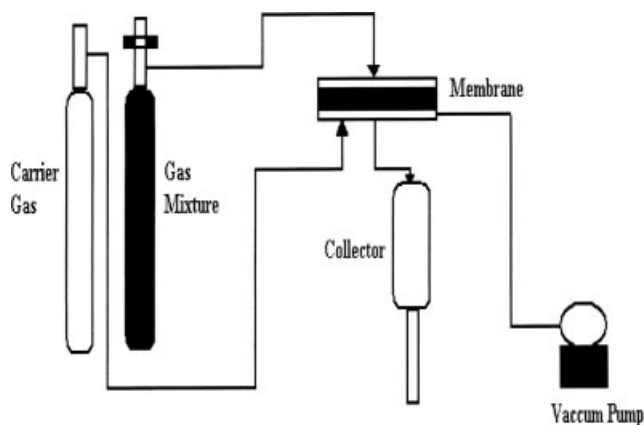Matrimid polymer (25% wt) was dissolved in a mixture of *n*-methyl-2-pyrrolidone NMP (55%) and meth-

Figure 3 Schematic of laboratory gas separation unit.

anol (20%) for spinning of hollow fibers of 1 m length each by the phase inversion technique at the laboratory of Permionics Membranes Pvt., Vadodara, India. The fibers were shredded to the module size and heated in an oven to 200°C for 5 min before assembling in a stainless steel housing. The characteristics of hollow fiber module shown in Figure 4 have an effective membrane area of 0.3 m^2, a skin thickness of 0.5 μm, and a maximum operating pressure of 20 bar. For studies with hollow fiber membrane module, the retentate valve was kept partially open to facilitate the continuous flow of feed gas at the rate of 50–100 mL/min across the membrane surface in hollow fibers. The retentate rate was adjusted accordingly to achieve a constant stage cut of 10–15% through the membrane at increasing pressures. Permeate rate was directly measured using a wet-gas meter in place of soap-bubble meter. The permeate outlet valve was kept open to the atmosphere to allow it for a continuous flow out to avoid any increase in permeate pressure. Samples were drawn from a silicone septum arrangement at a sample point in the permeate line instead of collecting in a sample bottle. The composi-
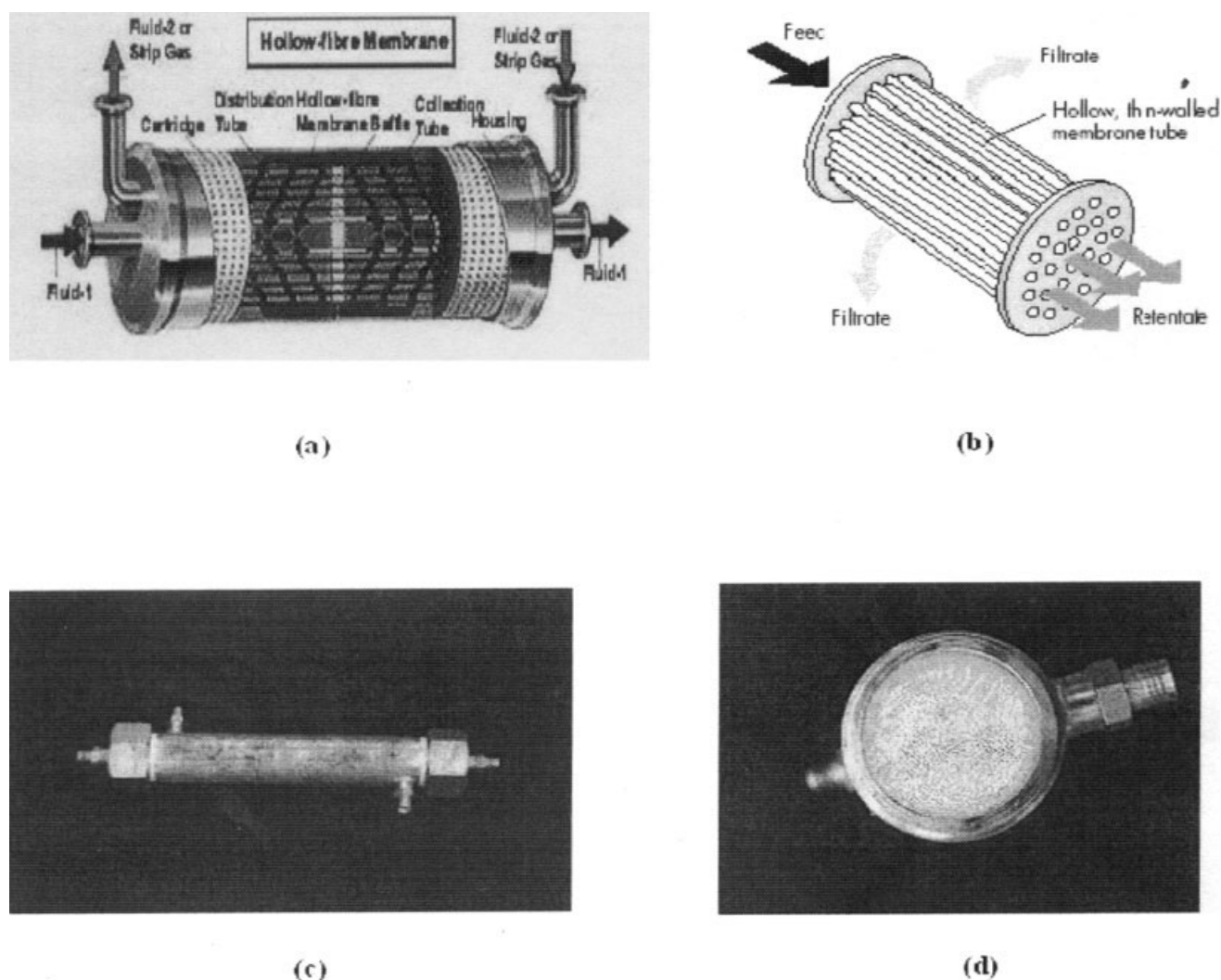
Figure 4 Matrimid module (a) schematic of module with housing, (b) inside view of the module, (c) photograph of actual module, and (d) cross-sectional view.

tion of feed and permeate streams were determined by gas chromatography.

The permeabilities are expressed in Barrers (1 Barrer = 10^{-10} cm^3 (STP) cm cm^{-2} sec^{-1} cmHg^{-1}). Flux was calculated using eq. (1). The partial pressure difference across the membrane was determined using eq. (2), wherein P_H represents feed side pressure, P_L the permeate side pressure, x_i and y_i the feed and permeate mole fractions of CO_2, respectively. Permeability, K was calculated using eq. (3) where l represents the membrane thickness (μm). The selectivity for pure gases (α^*) and mixtures (α) respectively, were calculated using eqs. (4) and (5):

Flux (J) = Permeate flow rate /

$$\text{Membrane area [cc/(cm}^2 \text{ sec)]} \quad (1)$$

$$\Delta P = P_H x_i - P_L y_i \quad \text{(cmHG)} \quad (2)$$

$$\text{Permeability (K)} = \left(\frac{\text{Flux} \times l}{\Delta P} \right) \quad \text{(Barrers)} \quad (3)$$

Selectivity based on pure gas permeability ratio(α^*)
$$= K_{CO_2}/K_{CH_4}$$

$$(4)$$

$$\text{Mixed gas selectivity}(\alpha) = y_i(1 - x_i)/x_i(1 - y_i) \quad (5)$$

Analytical procedure

Feed and permeate samples were analyzed using Nucon Gas Chromatograph (Model 5765, Mumbai, India) installed with thermal conductivity detector (TCD) using a Haysep 'Q' column. The oven temperature was maintained at 50°C (isothermal), while injector and detector temperatures were maintained at 150°C each. The sample injection size was 0.5 mL and

pure hydrogen was used as a carrier gas at a pressure of 0.9 kg/cm^2. The GC response was calibrated for this particular column and conditions with the known binary feed mixture compositions. The calibration factors were fed into the software to obtain the correct analysis for the unknown samples.

RESULTS AND DISCUSSION

FTIR studies

The chemical structure of Matrimid monomer unit is given in Figure 1. FTIR spectrum of Matrimid is shown in Figure 5. A band at 3061 cm^{-1} indicates the presence of aromatic C—H stretching vibrations, while the aromatic bending vibration is present at 716 cm^{-1}. Bands observed at 2961 and 2854 cm^{-1} show the presence of aliphatic C—H stretching vibrations, whereas the aliphatic C—H bending vibration is indicated at 1387 cm^{-1}. Asymmetric and symmetric C=O stretching vibrations are represented, respectively, by the bands observed at 1780 and 1738 cm^{-1}. The C—N stretching vibration is shown by a band at 1387 cm^{-1}, while the C=C stretching vibration of aromatic ring is represented by a band at 1617 cm^{-1}. The study shows that polar sites in the membrane matrix could aid the preferential interaction and solubility of CO$_2$ gas molecules.

XRD studies

Figure 6 shows the wide-angle X-ray diffractogram of Matrimid polyimide membrane. The X-ray pattern of Matrimid shows sharp peaks at 2θ of 14° and 27.5°. However, relatively small peaks were observed at 2θ of 2°, 3.5°, 5.5°, 10°, and 18.5°, indicating that the polymer was semicrystalline in nature. The semicrystalline membrane is expected to yield high selectivity at a moderate permeation rate.
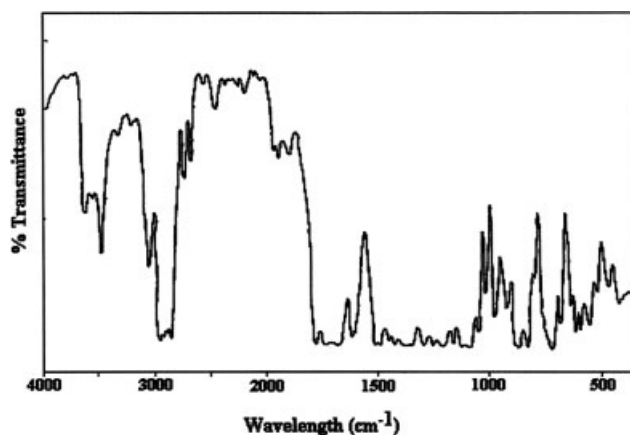
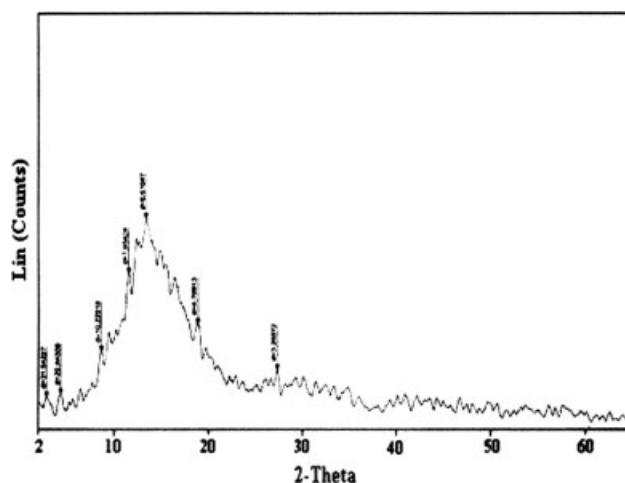

Figure 5 FTIR Spectra of Matrimid membrane.

Figure 6 X-ray diffractogram of Matrimid membrane.

Permeability studies

Table I displays pure gas permeabilities of the three polyimide membranes as well as the corresponding CO$_2$/CH$_4$ selectivities at 40 bar pressure. Kapton polyimide gave the lowest permeability of 8.5 Barrers, but the highest selectivity of 85. Literature shows Kapton membranes to be highly selective for different gaseous mixtures including He/N$_2$ and H$_2$/N$_2$.[20] On the other hand, Matrimid exhibited the highest permeability of 63 Barrers at a moderate selectivity of 17.5. The P84 membrane exhibited intermediate results between those of polyimide and Matrimid membranes. The selectivity of 33.4 for P84 correspond well with the reported data of Barsema et al.,[25] who obtained a selectivity of 45 for CO$_2$/N$_2$ system. CH$_4$ is marginally more permeable than the relatively inert N$_2$ gas and hence, the CO$_2$/CH$_4$ selectivity was a trifle lower. Studies with binary mixtures expectedly produced a decrease in both membrane parameters as displayed by Table II. This discrepancy is believed to arise from the coupling effect, gas phase nonideality, competitive sorption and changes in free volume.[26–28] The observed reduction in CO$_2$ selectivity is most likely due to coupling effect between the two gases, resulting in dragging of CH$_4$ molecules through transfer of momentum from the permeating CO$_2$ molecules. CO$_2$ permeability decreases, since the presence of CH$_4$ is believed to reduce the solubility coefficient of CO$_2$ due to competition for occupation of the unrelaxed volume, i.e., Langmuir sorption sites in the glassy polymer.[29] The presence of CO$_2$ increases the solubility of methane by contributing to an increase in polymer free volume, which is generally low during permeation of pure methane.[30] Therefore, a comparison of Matrimid performance given in Tables I and II shows that CH$_4$ permeability for mixed gas is higher than that observed in case of pure gas.

TABLE I
Pure Gas Permeabilities and Ideal Selectivities of Three Types of Flat Sheet
Polyimide Membranes (Pressure 40 bar)

S. no.	Membrane type	Permeability (K) (Barrers[a])		Ideal selectivity K_{CO_2} / K_{CH_4}
		CO_2	CH_4	
1.	Matrimid	63.2	3.6	17.5
2.	P84	14.4	0.43	33.4
3.	Kapton	8.5	0.10	85.0

[a] 1 Barrer = 10^{-10} [cc (STP) cm/cm^2 s cmHg].

Table II shows the performance of three membranes over the important feed CO_2 concentration range of 5 mol % to 2 mol % at a feed pressure of 40 bar. Natural gas mixtures generally have CO_2 content in the range of 5–7 mol %, which must be brought down to the pipeline specification of ≤2 mol %. Matrimid revealed the highest average permeability of 21.0 Barrers for CO_2, but a relatively low selectivity of 4.1, possibly due to the dead-end mode of feed flow in the permeability cell. On the other hand, the P84 membrane gave the reasonable values of permeability and selectivity of 4.4 Barrers and 20.0, respectively. The corresponding observations with Kapton polyimide membrane were 1.5 Barrers and 50.8, respectively.

Further experiments with Kapton membrane were carried out at 40 bar feed pressure by varying the feed composition from 1 to 20 mol % CO_2 (see data displayed in Fig. 7). The permeability of gas increased from 0.85 to 2.8 Barrers, whereas the mixed gas selectivity reduced from 71.3 to 18.6, in contrast to a selectivity of 85 for pure gases (as seen in Table I). Ideally, the selectivity of a membrane should be constant irrespective of the feed stream composition. But in a real practical situation, a reduction in selectivity is observed that can be attributed to the swelling induced plasticization of Kapton membrane by the preferential absorption of CO_2 gas molecules, which enhances the permeability of CH_4 component. With increasing CO_2 concentration, the degree of membrane swelling will increase, leading to a more unrestricted passage of CH_4 molecules to the permeate side. A detailed explanation is already provided before. Thus, the membrane

is suitable for processing mixtures with CO_2 concentrations ≤5%. In view of high permeability of Matrimid membrane, besides difficulties faced in scaling up of the other two polymeric membranes because of defects and cracking of membrane support layers, further studies were taken up with the Matrimid hollow fiber module membrane system fabricated at Permionics Membranes Pvt., Vadodara, India. This system was operated in the crossflow mode with a flowing feed as per the procedure described in the experimental section.

Effect of feed pressure

Figures 8 and 9 exhibit pure gas permeabilities of CO_2 and CH_4 as well as the corresponding permeability ratio as a function of feed pressure, which was varied from 2 to 20 bar for hollow fiber module. The CO_2 permeability increased from 12.5 to 14.7 Barrers, whereas CH_4 permeability improved marginally from 0.22 to 0.26 Barrers as shown in Figure 8. However, the selectivity increased from 56.8 to nearly 60 as shown in Figure 9. These observations can be explained on the basis of increasing plasticization of the membrane by the preferentially sorbed CO_2 gas with increasing pressure.[14] On the other hand, the saturated CH_4 molecule does not have a substantial interaction with the membrane and therefore, any improvement in its permeability is only marginal. Hence, the selectivity to CO_2 is greater for pure gases, since there is no scope for the competitive sorption of CH_4 or coupling effect, which are seen in case of binary mixtures.

TABLE II
Performance of Flat Sheet Polyimide Membranes for CO_2/CH_4 Binary Gas Mixtures
of Composition in the Range 5–2% CO_2 (Pressure 40 bar)

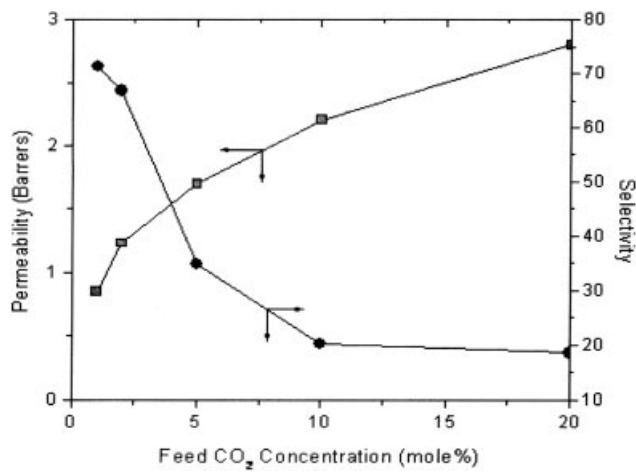| S. no.	Membrane type	Average permeability (K) (Barrers)		Average selectivity K_{CO_2} / K_{CH_4}
		CO_2	CH_4	
1.	Matrimid	20.8	5.1	4.1
2.	P84	4.40	0.22	20.0
3.	Kapton	1.5	0.03	50.8

Figure 7 Plasticization of Kapton polyimide membrane with increasing feed CO_2 concentration (feed pressure 40 bar).
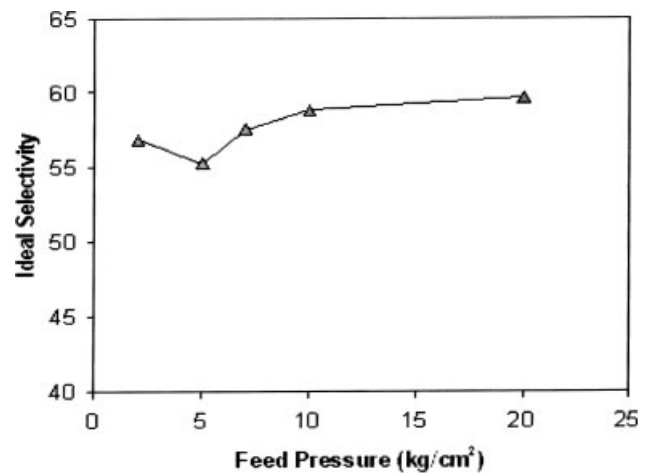

Figure 9 Effect of feed pressure on ideal selectivity of Matrimid Hollow fiber membrane operated in crossflow mode.

Effect of feed composition and flow pattern

Figure 10(a,b) depict the effect of binary mixture feed composition, which was varied from 2 to 20 mol % CO_2 on the performance of Matrimid membrane at the pressure of 20 bar. The Matrimid hollow fiber module was operated in crossflow mode, with a continuous flow of feed through the hollow fibers and a simultaneous removal of the permeate in a perpendicular direction. The results obtained are compared with the observations for flat sheet Matrimid membrane cell operated in a dead-end mode (stagnant feed). Figure 10(a) shows that permeability for flat sheet membrane ranged from 11.4 to 43.9 Barrers, whereas that of the module varied from 3.1 to 12.6 Barrers. High permeability in a flat sheet cell with the retentate valve in fully closed position is due to the aggressive transport of gas molecules, which do not

have any opening to exit from the system other than penetrating the membrane. Thus, when the system is operated in dead-end mode, both CO_2 and CH_4 molecules are forced to diffuse through the membrane, thereby contributing to an increase in the overall permeability. Figure 10(b) reveals that the selectivity of flat sheet membrane varies from only 2.2 to 12.6 at 20% feed concentration. Corresponding values of 8.1–33.5 for the hollow fiber module were much higher, suggesting that the concentration polarization of CH_4 molecules near the membrane surface is minimized due to the continuous movement of feed across the membrane.[31]
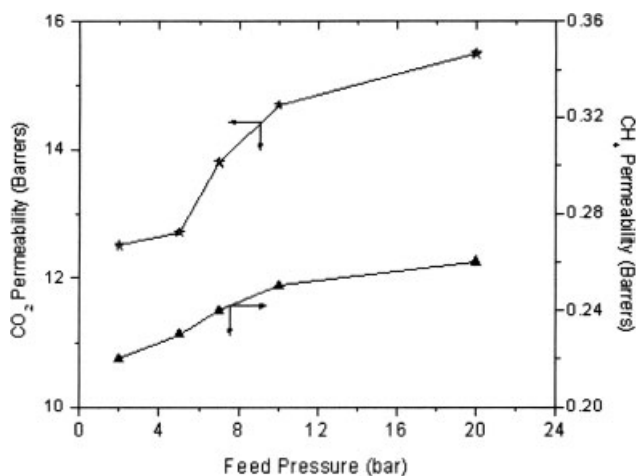

Figure 8 Effect of feed pressure on permeabilities of pure CO_2 and CH_4 gases through Matrimid hollow fiber module operated in crossflow mode.
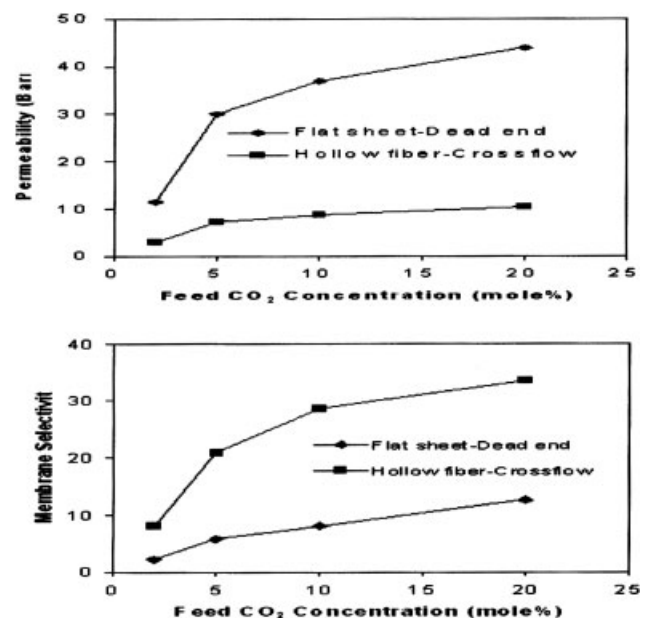

Figure 10 Comparison of separation characteristics of flat sheet membrane operated in dead-end mode with hollow fiber module in cross flow mode (pressure 20 bar).
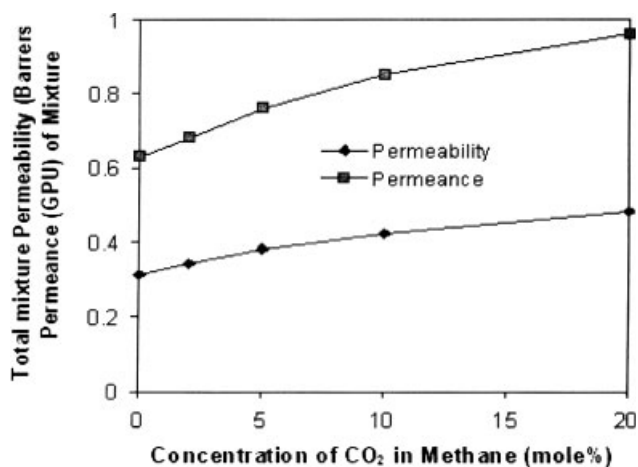
Figure 11 Effect of CO_2 concentration on total permeability/permeance of binary mixture (pressure 10 bar, 1 GPU = 10^{-6} cm^3(STP)/cm^2 s cmHg).

The general enhancements in membrane performance for both the modes of feed flow are attributed to a greater degree of sorption of CO_2 gas molecules in the membrane arising from its increasing availability at higher feed concentrations. Gas transport through homogeneous dense polymeric membrane follows the solution-diffusion principle.[32] CH_4 molecules do not undergo any significant changes in sorption due to the lack of any interaction with Matrimid membrane. This effect is further illustrated in Figure 11, wherein the total binary mixture permeance and permeability are plotted as a function of CO_2 concentration in CH_4. At 0% CO_2 concentration, the mixture permeability is 0.31 Barrers, which increased to 0.34 Barrers at 2% CO_2 and finally to 0.48 Barrers at 20% CO_2 feed concentration.

Comparison of present data with the literature

Table III compares the results obtained in the present study with the single gas permeabilities and selectiv-

ities reported in the literature for Matrimid and its modified forms as well as other polyimides. Most of the measurements reported are between temperatures of 25 and 35°C and pressure of 10 and 20 bar. Table III shows that carbon molecular sieves derived from P84 and Matrimid membranes exhibit very high permeabilities at the selectivities comparable to that observed in the present study, whereas the 6FDA-based polyimide membranes gave a relatively lower permeability or lower selectivity. The pure CO_2 permeability of 14.7 Barrers and CO_2/CH_4 selectivity of 59.6 exhibited by hollow fiber module used in the present study was even better than the results shown by the mixed matrix materials of Matrimid as well as Matrimid/polyethersulfone dual layer hollow fiber membrane.

CONCLUSIONS

Three types of polyimide membranes were prepared and tested for the enrichment of CH_4 gas from CO_2/CH_4 binary mixtures. Experiments with single gases revealed that Kapton polyimide membrane gave the highest selectivity, but Matrimid membrane was the most permeable. A similar trend was observed for binary mixtures containing with P84 polyimide membrane exhibiting reasonable results, which are intermediate to the other two polyimide membranes. The permeability and selectivity of the binary mixtures are comparatively lower than found for pure gases due to the coupling effect between CO_2 and CH_4 gases, which resulted in an increased permeability of the latter. The Kapton polyimide membrane was plasticized at higher feed CO_2 concentrations, resulting in a loss of selectivity. Sheet membrane was characterized by FTIR and XRD followed by detailed permeation studies with the upscalable membrane in the form of a hollow fiber module. For pure gases, increasing feed pressure caused the membrane to be

TABLE III
Comparison of Present Work with Literature on Matrimid and Other Polyimide Membranes

S. no.	Membrane	Operating conditions		Permeability (K) (Barrers)		Ideal selectivity α^*	Ref.
		Temp (°C)	Pressure (bar)	CO_2	CH_4	K_{CO_2} / K_{CH_4}	
1.	Untreated Matrimid film	35°C	20	9.0	0.24	37.5	14
2.	Matrimid/C_{60} mixed matrix	23°C	25	5.1	0.15	34.0	15
3.	6FDA-mPD	35°C	3.7	11.0	0.19	58.0	1
4.	Crosslinked Matrimid	35°C	20	5.0	0.16	31.0	12
5.	Matrimid/CMS mixed matrix	35°C	3.5	10.6	0.23	46.7	18
6.	6FDA-DAM-DABA 2 : 1	35°C	10	133.0	4.6	28.9	2
7.	CMS derived from P84	35°C	10	499	5.6	89	3
8.	CMS derived from Matrimid	35°C	10	611	10	61	17
9.	Matrimid/PES dual layer	22°C	18	11.0	0.67	16.3	16
10.	Matrimid hollow fiber	30°C	20	14.7	0.24	59.6	Present work

CMS, carbon molecular sieve; 6FDA, 4,4′-hexafluoroisopropylidene diphthalic anhydride; mPD, *m*-phenylene diamine; DAM, diaminomesitylene; DABA, diamino benzoic acid.

plasticized by the preferentially interacting CO_2 gas, and subsequently, selectivity; however, increase in CH_4 sorption was not as pronounced. Improved results were obtained with the hollow fiber module operated in crossflow mode as opposed to flat sheet Matrimid membrane in a dead-end mode due to the minimization of concentration polarization of CH_4 molecules near the membrane surface. The increasing sorption of CO_2 gas molecules in the Matrimid membrane was demonstrated by observing an enhancement of total mixture permeability with the concentration of CO_2 in the feed mixture increasing from 0 to 20%. The results of the present work, especially selectivity values, correlated well with the literature data. For scale-up and commercialization purposes, the hollow fiber membrane exhibited promising results even at low feed CO_2 concentrations.

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