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Effects of Minor Components in Carbon Dioxide Capture Using Polymeric Gas Separation Membranes

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Abstract: The capture of carbon dioxide by membrane gas separation has been identified as one potential solution to reduce greenhouse gas emissions. In particular, the application of membranes to CO_2 capture from both pre- and post-combustion strategies is of interest. For membrane technology to become commercially viable in CO_2 capture, a number of factors need to be overcome, one being the role of minor components in the process on membrane performance. This review considers the effects of minor components in both pre- and post-combustion use of polymeric membranes for CO_2 capture. In particular, gases such as SOx, NOx, CO, H_2S, NH_3, as well as condensable water and hydrocarbons are reviewed in terms of their permeability through polymeric membranes relative to CO_2, as well as their plasticization and aging effects on membrane separation performance. A major conclusion of the review is that while many minor components can affect performance both through competitive sorption and plasticization, much remains unknown. This limits the selection process for membranes in this application.

Keywords: Gas separation, membranes, polymeric, plasticization, carbon dioxide, sulfur dioxide, nitric oxide, carbon monoxide, hydrogen sulphide, ammonia, water, hydrocarbons

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INTRODUCTION

Anthropogenic induced climate change is driven by increasing atmospheric carbon dioxide levels (1), caused by the world's dependence on fossil fuels. Currently, there is significant effort being directed towards developing technologies that will reduce CO_2 emissions to the atmosphere (2). In particular, the capture of carbon dioxide from large point sources, such as power plants, is recognised as a viable option, since it allows storage opportunities, such as geo-sequestration. Currently, there are three main strategies for CO_2 capture from fossil fuel based power plants (3, 4). Post-combustion is where CO_2 capture occurs after combustion from the exiting flue gas. Pre-combustion occurs where fossil fuels are reformed into "synthesis gas" (syngas) comprising primarily of hydrogen and carbon monoxide, carbon dioxide and water in a reducing environment. This is then further converted to more hydrogen through the water shift reaction. CO_2 is then separated from hydrogen before combustion. Finally, in oxy-fuel combustion air is replaced by oxygen in the combustion process which produces a flue gas of mainly H_2O and CO_2, which is readily captured. A number of CO_2 capture technologies exist (3, 5), of which only reversible solvent absorption has been commercially proven. This review paper focuses on polymeric membrane gas separation as a potential CO_2 capture technology; in particular the role minor components in the feed gas might have on membrane performance.

Membranes separate one or more gases from a feed mixture and generate a specific gas rich permeate. Two characteristics dictate membrane performance, permeability; that is the flux of a specific gas through the membrane, and selectivity; the preference of the membrane to pass one gas species and not another (6–8). There are five possible mechanisms for membrane separation: these are schematically represented in Figure 1. Knudsen separation is based on the difference in the mean path of gas molecules through the porous membrane due to collisions with the pore walls, and therefore separation is based on molecular weight. Molecular sieving relies on size exclusion to separate gas mixtures. Pores within the membrane are of a carefully controlled size

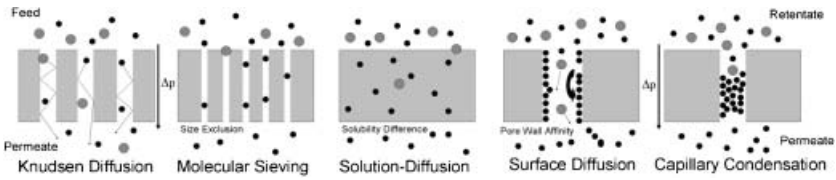

Figure 1. Schematic of membrane gas separation mechanisms.

Table 1. Kinetic diameter (9) and critical temperature (12) of various molecules found in CO_2 capture.

Gas	Kinetic Diameter (Å)	Critical Temperature (K)
H_2	2.89	33.2
N_2	3.64	126.2
CO	3.76	132.9
Ar	3.40	150.8
O_2	3.46	154.6
NO	3.17	180
CH_4	3.8	190.6
CO_2	3.3	304.2
HCl	3.2	324.6
C_3H_8	4.3	369.8
H_2S	3.6	373.2
NH_3	2.6	405.6
SO_2	3.6	430.8
NO_2		431.4
SO_3		491
C_6H_{14}		507.4
C_6H_6	5.85	561.9
H_2O	2.65	647.3
Hg		1750

relative to the kinetic diameter of the gas molecule. This allows diffusion of smaller gases at a much faster rate than larger molecules. The kinetic diameter of a gas is defined as the intermolecular distance of closest approach for two molecules colliding with zero initial kinetic energy (9). This is dependent on the molecular size, shape, as well as dipole-dipole interactions. Table 1 lists the kinetic diameter of a range of species present in the various CO_2 capture strategies. Surface diffusion depends on the migration rate of adsorbed gases along the pore walls of porous membranes (10). The rate of surface diffusion, and therefore separation, is dependent on the strength of the association between gases and the pore surface. Capillary condensation is an extension of surface diffusion; low vapour pressures causes partial condensation within the pores (11). Thus, the condensed component diffuses more rapidly through the pore, leading to separation.

The solution-diffusion mechanism occurs in non-porous membranes, such as polymerics, where gas permeation is described by the solubility of specific gases within the membrane and their diffusion through the dense polymer matrix. Hence, separation is not just diffusion dependent but also reliant on the physical-chemical interaction between the various gases and the polymer. The relationship between permeability, diffusivity and solubility is described by (8, 13):

$$P = DS \tag{1}$$

where P is the permeability coefficient (cm^3 (STP) cm $cm^{-2}\,s^{-1}\,cmHg^{-1}$, or Barrer ($10^{-10}\,cm^3$ (STP) cm $cm^{-2}\,s^{-1}\,cmHg^{-1}$)). D is the diffusion coefficient ($cm^2\,s^{-1}$) which represents the mobility of the gas through the membrane, and S the solubility coefficient (cm^3 (STP) $cm^{-3}\,cmHg^{-1}$). The permeability is related to the gas permeation rate through the membrane, or flux (Q), the surface area of the membrane (A), the thickness of the membrane (l) and the fugacity difference across the membrane (Δf), which is the driving force for separation:

$$\frac{P}{l} = \frac{Q}{A\Delta f} \tag{2}$$

For ideal gases, Δf can be replaced with the partial pressure difference across the membrane, Δp. Similarly, if the membrane thickness is not accurately known, it is usual to present performance data as gas permeance, P′ (cm^3 (STP) $cm^{-2}\,s^{-1}\,cmHg^{-1}$, or GPU ($10^{-6}\,cm^3$ (STP) $cm^{-2}\,s^{-1}\,cmHg^{-1}$):

$$P' = \frac{P}{l} \tag{3}$$

The ideal selectivity (α) of one gas, A, over another gas, B, is defined as:

$$\alpha = \frac{P_A}{P_B} \tag{4}$$

Polymeric membranes are further classified as rubbery or glassy, dependent on their operating temperature relative to the glass transition temperature (T_g) of the polymer (14). Rubbery membranes, operating above the glass transition temperature, are able to rearrange on a meaningful time scale and are usually in thermodynamic equilibrium. Therefore, gas solubility within the rubbery polymer matrix follows Henry's Law and is linearly proportional to the partial pressure, or fugacity, f(14):

$$C_D = K_D f \tag{5}$$

where C_D is the concentration of gas in the polymer matrix and is proportional through the Henry's Law constant (K_D).

Glassy membranes operate below the glass transition temperature and therefore polymer rearrangement is on an extraordinarily long time scale, meaning the membrane never reaches thermodynamic equilibrium. Hence, the polymer chains are packed imperfectly, leading to excess free volume in the form of microscopic voids (14). Within these voids gases

adsorb, increasing the solubility. Therefore, the total concentration of absorbed gas within a glassy membrane (C) can be described by:

$$C = C_D + C_H \tag{6}$$

where C_H is the standard Langmuir adsorption relationship

$$C_H = \frac{C'_H f}{(1 + bf)} \tag{7}$$

C'_H is the maximum adsorption capacity while b, is the ratio of rate coefficients of adsorption and desorption, or Langmuir affinity constant, defined as:

$$b = \frac{C_H}{(C'_H - C_H)f} \tag{8}$$

Hence, the dual-mode sorption for glassy membranes is written as:

$$C = K_D f + \frac{C'_H b f}{(1 + bf)} \tag{9}$$

If the coefficients D_D and D_H are the diffusion coefficients for the polymer matrix and free volume respectively, the permeability of a pure gas is given by:(15)

$$P = K_D D_D \left[1 + \frac{D_H}{D_D} \cdot \frac{C'_H b}{K_D(1 + bf)}\right] \tag{10}$$

When multiple gas species are present, competition restricts both the solubility within the polymer matrix and amount adsorbed in the Langmuir free volume. Hence, for a binary mixture of gases A and B, the permeability of gas A becomes (16, 17):

$$P_A = K_{DA} D_{DA} \left[1 + \frac{D_{HA}}{D_{DA}} \cdot \frac{C'_{HA} b_A}{K_{DA}(1 + b_A f_A + b_B f_B)}\right] \tag{11}$$

Similarly, the permeability of gas B is:

$$P_B = K_{DB} D_{DB} \left[1 + \frac{D_{HB}}{D_{DB}} \cdot \frac{C'_{HB} b_B}{K_{DB}(1 + b_A f_A + b_B f_B)}\right] \tag{12}$$

Each parameter has the same definition as in the single gas case with the subscript denoting whether it is a property of gas A or B. The permeability of both gas A and B is reduced compared to the single gas case (Equation 10), and is heavily dependent on the relationship between b, the affinity constant,

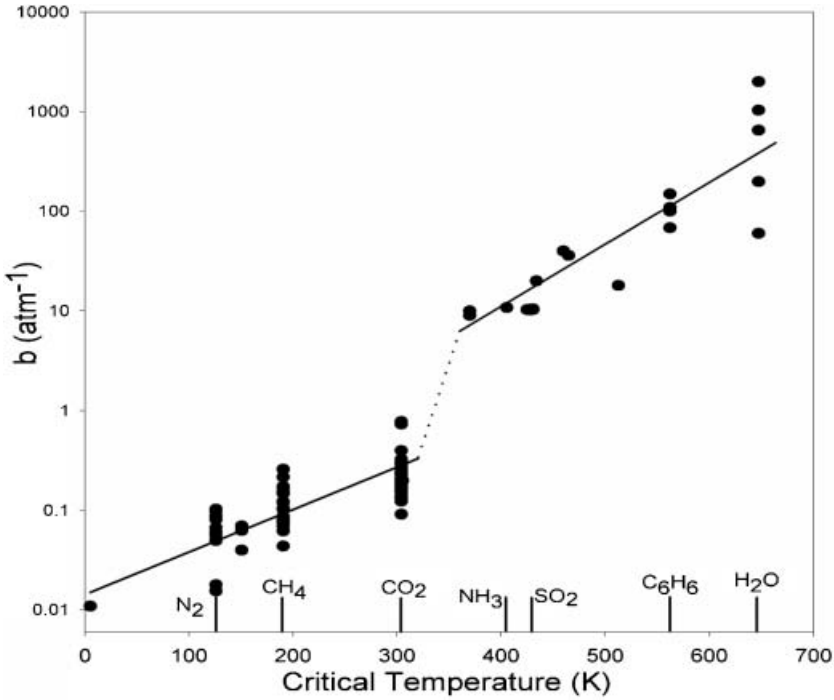

Figure 2. Langmuir affinity constants (b) for a range of gases in various polymeric membranes relative to gas critical temperature (18–27).

and fugacity. The Langmuir affinity constant is generally proportional to the critical temperature of the gas (14), a measure of a compound's condensability, and values for molecules encountered in CO_2 capture are provided in Table 1, with corresponding measured Langmuir affinity values in Figure 2. For example, water has a very high critical temperature compared to N_2 and CO_2. This means water is more condensable within the free volume and correspondingly a higher Langmuir affinity constant is observed. Hence, the presence of water even in trace amounts may dominate observed gas permeabilities, because even though the partial pressure is low, water will successfully compete for sorption sites in the membrane.

A wide range of membranes have been designed to be highly selective for CO_2 over N_2 (which is required for post-combustion), and to a lesser extent over H_2 (necessary for pre-combustion), while also providing high CO_2 permeabilities. Pre-combustion operates under high pressure, which is favourable for membrane gas separation, however the trade-off being the high temperature of the gas, $\sim$350°C. Generally, polymeric membranes cannot operate at such temperatures, due to problems such as loss of structural integrity. Therefore, for polymeric membrane separation in

pre-combustion flue gas, generally cooling is required. Conversely, in post-combustion, the flue gas is at low temperature, however, pressure is also low, limiting the driving force for gas separation. Therefore, compressors or vacuum systems may be required. These options affect the costs of membrane gas separation and therefore their economic viability compared to other CO_2 capture technologies, such as solvent absorption (28).

Alongside the major gases a range of minor components are present. In post-combustion, SOx, NOx, and water are also present in flue gases (3); while in pre-combustion syngas, there exists, H_2S, CO, NH_3, water and hydrocarbons (3). In addition, O_2 is present, residual of combustion, along with Ar, due to its presence in air. Also depending on the fuel, heavy metals, such as mercury and arsenic, may exist as well as halogens, such as fluorine and chlorine, in their acidic form (29, 30). The concentration of these minor components varies considerably and is dependent on the fuel, temperature and pressure of combustion or syngas reformation, as well as the amount of oxygen present. Potential concentrations of some of these minor components are provided in Table 2. Other processes than power generation have the possibility for CO_2 capture, such as cement production, refineries, as well as from blast furnaces, in which the minor components have a different composition. For example, from iron blast furnaces, both H_2 (59 mol %), CO (5 mol %) and H_2S (0.5 mol%) (31) are in higher concentrations than those reported in Table 2. Thus for membrane gas separation CO_2 capture the effects of minor components have to be considered on a case by case basis.

The presence of minor components in the membrane gas separation process may compete with CO_2 for separation and therefore decrease permeability, as well as degrade the membrane, altering separation performance. Furthermore, the permeabilities of these minor components are of interest, because of the possibility of generating component rich permeate or retentate streams, dependent on membrane selectivity. Hence, this review will cover the reported permeabilities and selectivities of a range of minor components in pre- and post-combustion gas relative to CO_2, as well as their influence on membrane gas separation performance in CO_2 capture. The minor gas components considered

Table 2. Concentration range of minor components in untreated CO_2 capture (ppm) (3, 35).

	SOx	NOx	CO	H_2S	NH_3	Water	Hydrocarbons
Precombustion	0	0	300–4000	500–1000	0–1500	Saturated	0–100
Postcombustion	1000–5000	100–500	~10	0	0	Saturated	0

are SOx, NOx, CO, H_2S, NH_3 and Ar; these are followed by the condensable components, water and hydrocarbons, and a brief discussion on the effects of other minor components. Oxygen permeability is not reviewed here, since a number of excellent reviews (32–34) on O_2 permeability through polymeric membranes exist. In general, oxygen has a lower permeability through CO_2 selective polymeric membranes due to lower solubility. The review concludes with a discussion on the factors that influence membrane choice, and future research directions in relation to minor components.

MINOR GAS COMPONENTS

Sulfur Oxides (SOx)

Polymeric Membranes

Combustion of sulfur containing fuels, such as coal, results in the production of SO_2 and SO_3 in trace amounts, the combination of which is commonly referred to as SOx (36). Their emission is a major environmental problem, leading to acid rain. During the 1970s when sulphur emissions became regulated, research was conducted into using membranes as an alternative to scrubbing technologies (36). The lack of large-scale industrial trials of membrane desulfurization hindered the development of this technology. However, the similar chemical properties SO_2 shares with CO_2 means that much of the membrane research undertaken for desulfurization is considered the forebear of current CO_2 membrane capture technologies. The permeation of SO_2 for a number of polymeric membranes is provided in Table 3 and plotted against selectivity over CO_2 in Figure 3. The permeabilities quoted, irrespective of gas, are for dense homogeneous membranes, unless otherwise stated in the relevant table. Quoted selectivity values are generally ideal, that is the ratio of the two pure gas permeabilities. Selectivities observed under mixed gas conditions can be significantly lower because of competitive sorption in the membrane and these values are noted in the relevant tables.

Many of these polymeric membranes have been reported for their potential in CO_2 capture, and it is immediately clear that they provide a SO_2 / CO_2 selectivity in the range of 5–40. SO_2 has a larger kinetic diameter than CO_2 so this selectivity is not diffusion related. Further, both are acidic gases and therefore will have similar associations with the polymer. Rather, the increased permeability of SO_2 can be explained through the higher critical temperature, leading to a greater affinity constant (Figure 2) and higher loading in the Langmuir free volume sites.

Table 3. Permeability and selectivity of SO_2 for a range of polymeric membranes (* indicates thin composite membrane).

Membrane	SO_2 Permeability (barrer)	SO_2 / CO_2	Ref.
Cellulose hydrate	37.8	148	(37)
Cellulose Nitrate	1.76	0.83	(38)
Cellulose triacetate *	270	48	(39)
Dimethyl silicone *	11500	4.6	(39)
Dimethyl silicone Peroxide cured	43630		(40)
Ethyl Cellulose	263	2.3	(38)
Nylon 11	6.58		(41)
Buna N on Nylon *	800	20	(39)
Polyacrylate	1700	41	(39)
Polyamide	21.1		(42)
Polycarbonate	22.4		(41)
Chlorinated Polyether	$<10^{-15}$		(43)
Polyethylene Glycol		13–15	(44)
Polyethylene glycol	4100	44	(45)
Polyethylene	34		(46)
Polyethylene Glycol	81300		(47)
Poly methyl methacrylate	2.6		(43)
Polypropylene	6.18		(42)
Polyvinyl chloride	412		(48)
Polyvinyl fluoride	15.5		(49)
Polyvinylidene fluoride	3.2		(49)
Poly (amide-6-b-ethylene oxide)	1000	7.6	(50)
Silastic LS-63	1262		(51)
Silastic LS-63 (Fluoro)	3180		(52)
Tecsil (silicone rubber)	11800		(42)
TFE Teflon	11.4		(53)
TFE Teflon	5.1		(43)
FEP Teflon	2.6		(54)
FEP Teflon	2.3		(55)
FEP Teflon	2.4		(56)
Cellulose acetate-butyrate	720	18	(39)
Cellulose triacetate- Polyacrylate53 *	311	7.37	(57)
Cellulose triacetate-Polyacrylate58 *	125	5.553	(57)
Cellulose triacetate-Polyacrylate59 *	178	5.74	(57)
Polyacrylate 1% Polyethylene glycol	1680	16.9	(39)
Polyacrylate 5% Polyethylene glycol	1930	16.9	(39)
Polyacrylate 10% Polyethylene glycol	1980	19.4	(39)
Polyacrylate 25% Polyethylene glycol	3210	28.4	(39)
Polyacrylate 50% Polyethylene glycol	5160	40.3	(39)
Polyacrylate 5% sulfolane	1860	21.8	(39)
Polyacrylate 10% sulfolane	1520	18.1	(39)
Polyacrylate 25% sulfolane	2150	20.1	(39)
Polyacrylate 50% sulfolane	4470	23.3	(39)

Table 3. Continued.

Membrane	SO_2 Permeability (barrer)	SO_2 / CO_2	Ref.
Polyvinylidene fluoride 18% sulfolene	430	215	(58)
Poly vinylidene fluoride 8.2% sulfolane		30–100 SO_2/N_2	(59)
Poly tetrafluoroethylene-co-ethylene	2.6	1.32	(53)

Composite membranes consist of copolymers that have glassy and rubbery segments. The glassy segments form the structural frame and provide the mechanical support. The rubbery segment generally forms continuous microdomains within the membrane and the flexible nature of the structure allows the transportation of gas, which leads to greater permeability when compared with the glassy segment. For composite membranes based on polyacrylate (glassy) with either poly ethylene glycol or sulfolane (rubbery) segments, increased permeability of SO_2 corresponds with an increasing quantity of rubbery polymer (Table 3). It

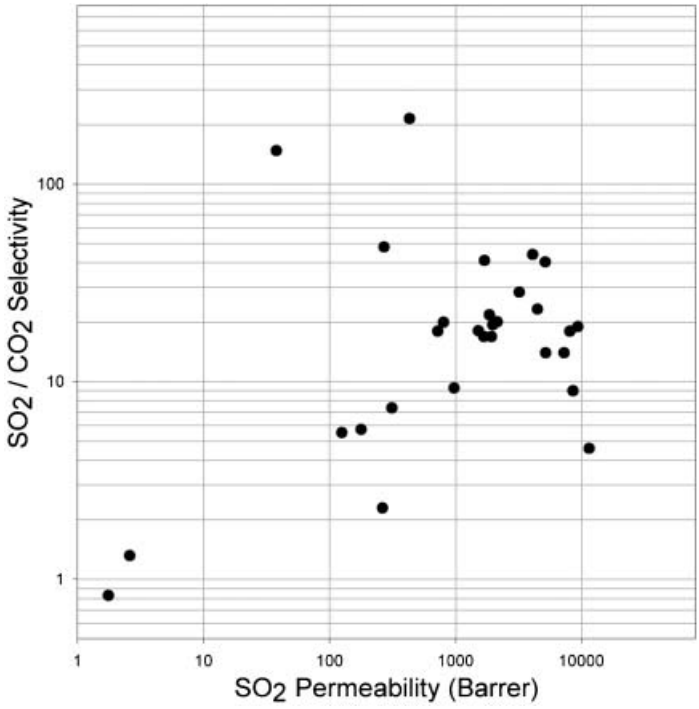

Figure 3. SO_2 permeability within polymeric membranes and selectivity relative to CO_2.

is thought that the rubbery segments increase the transportation rate of gases through the generation of microdomains. Importantly, the selectivity of SO_2 over CO_2 also increases, which indicates that this mechanism is more significant for the more condensable gas.

Facilitated Transport Membranes

Facilitated transport membranes rely on a chemical reaction occurring between the gas of interest and a component of the polymeric membrane (carrier) (60, 61). The reacted species is readily carried across the membrane, whereas diffusion of the nonreactive gases is inhibited. The driving force remains the partial pressure difference across the membrane; however, the carrier increases both the permeability and selectivity through increased loading in the membrane. For CO_2 selective facilitated transport membranes, the active carrier is generally basic, taking advantage of the acid-base relationship to increase CO_2 loading. These membranes generally have much higher permeabilities and selectivity compared to the polymeric membranes discussed in the previous section.

In facilitated transport, the acid-base relationship between an active carrier and CO_2 will also increase the SO_2 loading in the membrane due to the similar chemistry (Figure 4). Permeability and selectivity for a range of facilitated transport membranes are provided in Table 4, and show that SO_2/CO_2 selectivities are similar to those observed for standard polymeric membranes, irrespective of the facilitated carrier. Hence, in facilitated transport membranes the active carrier increases the SO_2 permeability in conjunction with CO_2.

Other Effects of SO_2

In addition to the permeability and selectivity of polymeric membranes to SO_2, its presence within polymeric membranes can lead to plasticization,

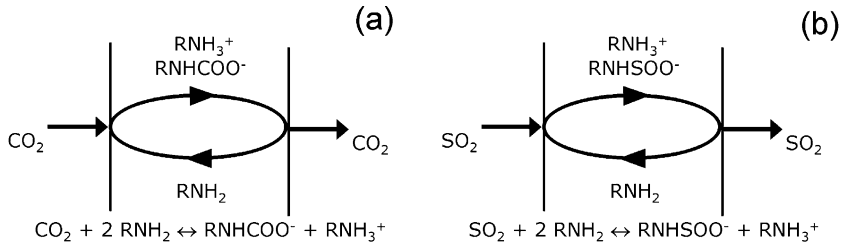

Figure 4. Schematic of facilitated transport mechanism based on amine carriers for both CO_2 (a) and SO_2 (b).

Table 4. SO_2 permeability through facilitated transport membranes.

Membrane	Carrier	SO_2 Permeability (Barrer)	SO_2 / CO_2	Ref.
Polyethylene Glycol	Diethanolamine		13	(44)
Polyethylene Glycol	Diethanolamine		140 SO_2/N_2	(63)
Polyethersulfone	Ionic liquid EMIM BF4	9350	19	(64)
Polyethersulfone	Ionic liquid BMIM BF4	8070	18	(64)
Polyethersulfone	Ionic liquid BMIM PF6	5200	14	(64)
Polyethersulfone	Ionic liquid HMIM BF4	7280	14	(64)
Polyethersulfone	Ionic liquid BMIM Tf2N	8560	9	(64)
Poly vinylidene fluoride	NaOH (wet)	2000	2000 SO_2/N_2	(62)

EMIM BF4: ethyl methyl imidazolium tetrafluoroborate, BMIM PF6: butyl methyl imidazolium hexafluorophosphate, HMIM BF4: hexyl methyl imidazolium tetrafluoroborate, BMIM Tf2N: butyl methyl imidazolium bis triflyl amide.

which produces a more rubbery material (65–67), and increases the diffusivity of penetrants. Plasticization is dependent on the amount of gas dissolved within the polymeric matrix, and through Henry's Law (Equation 5) is therefore heavily dependent on the partial pressure. Plasticization is generally represented by highly non-ideal permeability behaviour with increasing partial pressure. This occurs for polyvinylidene in the presence of SO_2, Figure 5, where the permeability is not constant with changing pressure differential (58). Indeed in this case, non-ideal behaviour is over two orders of magnitude greater for SO_2 compared to CO_2, implying SO_2 has a stronger plasticization effect on polyvinylidene, most likely due to its more condensable nature (Table 1). This behaviour has also been observed in polyacrylate and cellulose triacetate (39). However, plasticization is a strongly pressure dependent phenomenon and only occurs in these examples at high partial pressure, which are not observed for SO_2 in flue gas. Therefore, SO_2 will have only a minor plasticization affect on polymeric membranes compared to CO_2, which is present at higher partial pressures.

In an industrial process stream, high levels of water vapour are often present. The mixture of SO_2 and water allows for the generation of sulfuric acid, especially within the free volume of polymeric membranes. Table 5 shows the permeability of SO_2 through cellafan and polyvinyl chloride under different relative humidity conditions (48). For cellafan, a

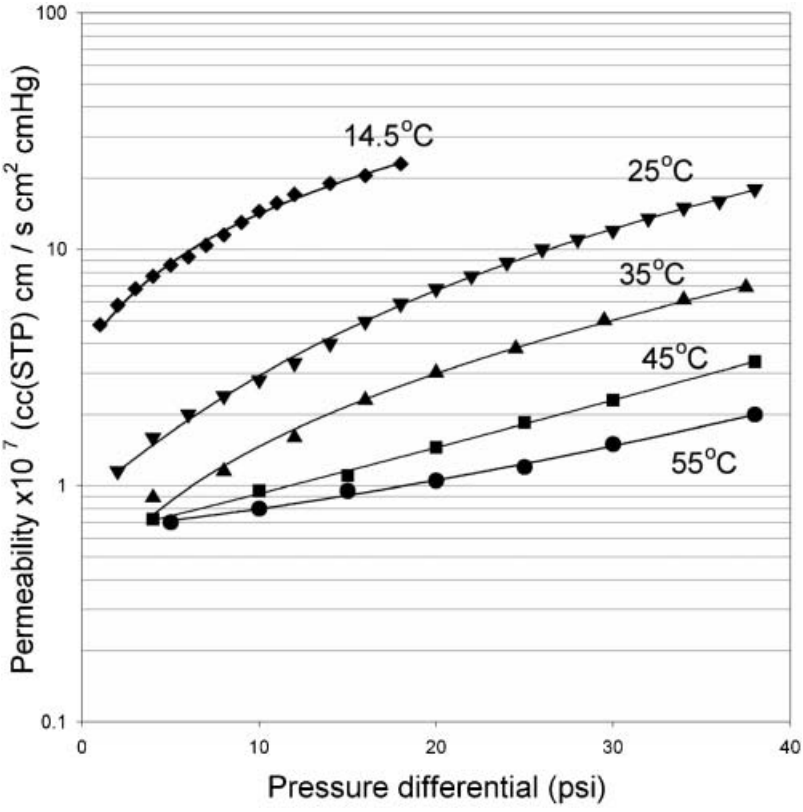

Figure 5. SO_2 plasticization of polyvinylidene. Data is taken from Zavaleta and Candless (58).

polysaccharide-based polymer, with water present, the SO_2 permeability experiences a 30-fold increase, which is undoubtedly due to sulfuric acid attack increasing the size of the free volume through acidic degradation of the polymer matrix. In comparison, polyvinyl chloride has a decrease

Table 5. Effect of humidity and SO_2 concentration on membrane performance at room temperature (48).

Membrane	Relative Humidity (%)	SO_2 Permeability (Barrer)
Cellafan	0	0.256
Cellafan	84	7.14
Polyvinyl chloride	0	412
Polyvinyl chloride	84	45

in SO_2 permeability with water present, indicating the more resistant nature of the polymer. The observed permeability reduction in the presence of water is attributed to competitive sorption of water in the membrane reducing SO_2 flux (see later). Hence, in post-combustion the presence of both water and SO_2 could lead to degradation of polymeric membranes over time. However, this is dependent on the polymer's resistance to acidic attack; therefore, separation performance will vary.

Sulfur Trioxide

The other component of SOx is SO_3, of which the performance in gas separation membranes has not been reported in the literature to the best of the authors' knowledge. This is probably because pure SO_3 is liquid at room temperature, and therefore information on possible permeation through membranes is experimentally difficult to achieve. However, given the condensable nature of SO_3 compared to SO_2 and CO_2 (critical temperature, Table 1), it can be reasonably assumed that it will experience a greater permeation through glassy polymeric membranes than either of those gases due to higher sorption. The lack of experimental data associated with SO_3 needs to be addressed through future research and should be included in studies of the effects of SOx in general on polymeric membrane gas separation.

Nitric Oxides (NOx)

Combustion at high temperature in air results in the generation of nitrogen oxides, NOx; of which the dominant component is NO and to a lesser extent NO_2 (36). These exist in flue gas on the order of 500 ppm (Table 2). To the best of the authors' knowledge there appears to be no information available that provides insight into the effect of NO on polymeric membranes. Based on kinetic diameter (Table 1), NO should diffuse faster through membranes than CO_2. However, the larger difference in critical temperature suggests that CO_2 will sorb more strongly in the membrane than NO, and so will dominate in solubility-selective membranes.

For NO_2, only poly tetrafluoroethylene has been documented, with a permeability of 15.9 barrer and a NO_2 / CO_2 selectivity of 1.6 (68). This is expected in view of the higher critical temperature of NO_2 leading to stronger sorption in a glassy membrane compared to CO_2. The plasticization and aging effects of NOx are unknown. However, in the presence of water NOx forms nitric acid that will degrade polymeric

membranes over time, similar to that reported above for SOx. Therefore, future research should focus on determining NO and NO_2 permeability and selectivity against CO_2 in polymeric membranes, as well as aging studies on the performance influence of NOx with water present.

Carbon Monoxide (CO)

Carbon monoxide is present in both pre- and postcombustion processes. It is found in flue gas as the product of partial combustion, notably when there is a reduced availability of oxygen. More importantly, it is a major component of syngas, and significant quantities can be present in fuel gasification due to the equilibrium nature of the water-shift reaction (4). Given its importance in syngas, a number of inorganic and carbon based membranes exist that ensure separation from hydrogen (69–72). The performance of CO in polymeric membranes is less documented, due to their limitations in processing syngas at high temperatures. The permeability of CO through a range of polymeric membranes are provided in Table 6 and displayed in Figure 6. The quoted selectivity of CO / CO_2 is based on permeabilities of CO_2 for the same membrane material stated elsewhere (8, 53) and the H_2/CO selectivity is provided for an indication of syngas separation application. Polymeric membrane results reported in Table 6 show reduced CO permeability compared to CO_2. As mentioned above, the larger kinetic diameter of CO compared to CO_2 means diffusion through a glassy membrane will be slower. Furthermore, the solubility of CO is expected to be lower because of the critical temperature difference (Table 1) (73).

When diffusive selectivity dominates as with this gas pair, the limit of separation performance is bound by a line known as Robeson's bound (74). The gradient of the bound is dependent on the ratio of kinetic diameters of the two species (75):

$$\lambda_{A/B} = \left(\frac{d_B}{d_A}\right)^2 - 1 \tag{14}$$

where $\lambda_{A/B}$ is the gradient of the bound and d_A and d_B the kinetic diameters of gas A and B respectively. Given that CO has a larger kinetic diameter than CO_2 (Table 1), the Robeson's bound has the opposite gradient to that commonly observed (Figure 6). This means that as CO permeability decreases the selectivity of the membrane towards CO against CO_2 also decreases, because CO_2 diffuses at a faster rate than CO through the membrane.

Table 6. CO permeability and selectivities for polymeric membranes relative to H_2 and CO_2 (* indicates thin composite membrane).

Membrane	CO Permeability (Barrer)	H_2 / CO Selectivity	CO / CO_2 Selectivity	Ref.
Caprolactam *	0.013	115		(76)
Cellulose acetate	0.35	37.2	~0.19	(76)
Dacron *	0.012	110		(76)
Mylar Type S	0.019	74		(76)
Parylene C	0.013	110		(76)
Parylene N	0.11	25.4		(76)
PDMS	500	1.8	0.16	(77)
Polyethylene	3.78	5.3	~0.25	(76)
Low Density Polyethylene	1.46	6.7	0.12	(78)
High Density Polyethylene	0.2		0.56	(78)
Polyimide	0.027	74	~0.01	(76)
Polyimide	0.0351	17	~0.02	(79)
Poly(4-methyl-1-pentene)	7	12.4	0.1	(66)
Polyox *	0.419	4.3	~0.03	(76)
Polysulfone	0.37	37.8	~0.07	(76)
Polystyrene	0.917	12		(76)
PTMSP	5000	2	0.3	(77)
Polyvinyl chloride	0.62	12.9	~0.03	(76)
Poly (vinyl chloride) plasticized	0.37	9.6		(80)
Polyvinyl fluoride	0.009	74		(76)

For pre-combustion gas separation through polymeric membranes, the low permeability implies that CO will be retained in the retentate stream. No information exists in the literature on CO plasticization effects in polymeric membranes, but these would be expected to be minimal.

Hydrogen Sulfide (H_2S)

Polymeric Membranes

H_2S removal from 'sour' gas to produce 'sweet' gas is a significant process in both the natural gas and biogas industries (81, 82). H_2S is also a trace product of gasification and is often found in sufficient quantities in syngas to warrant removal because of its highly toxic and corrosive nature. This is currently achieved through chemical scrubbing (83) and chemical conversion with lime (81). Information on H_2S in gas separation

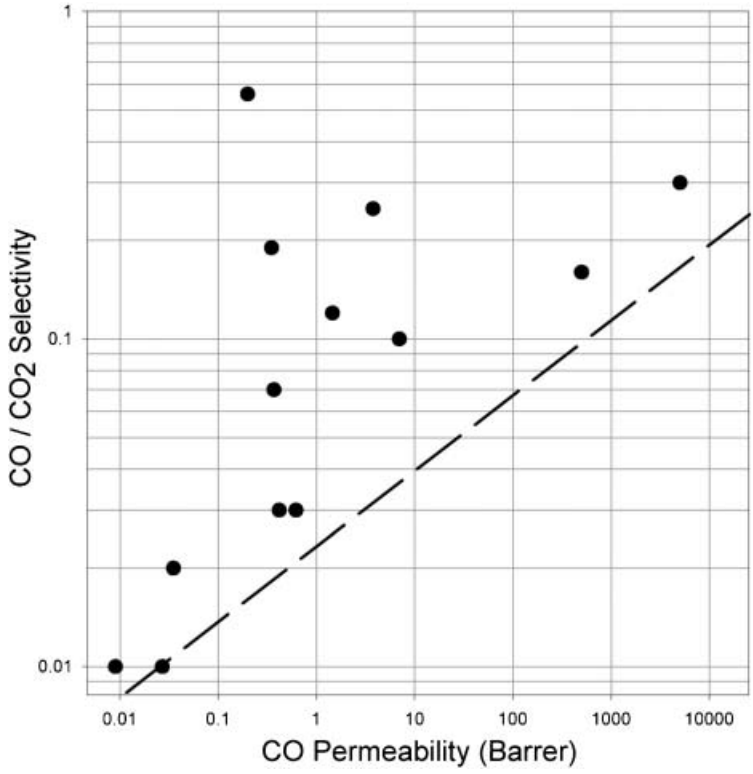

Figure 6. CO permeability within polymeric membranes and selectivity relative to CO_2, the reverse permeability-selectivity trend arising from plotting for the less selective component.

membranes is mainly restricted to treatment of natural gas, with a number of materials exhibiting high permeability for H_2S and CO_2 with a large selectivity relative to methane (83). Because of this, the permeability and selectivity of H_2S for a wide range of polymeric membranes is relatively well known and a range of these data are provided in Table 7 and Figure 7. Generally, these demonstrate an increased selectivity of H_2S over CO_2, arising from the high condensability of hydrogen sulfide (Table 1). Similar to pre-combustion, separation of H_2S from H_2 is also of interest, with selectivities provided in Table 8.

Other Effects of H_2S

As for CO_2 and SO_2, prolonged exposure to H_2S can lead to plasticization of polymeric membranes (87). A clear example of nonideal

Table 7. H_2S permeability and selectivities for polymeric membranes relative to CO_2 and H_2O (* indicates thin composite membrane).

Membrane	H_2S Permeability (Barrer)	H_2S / CO_2 Selectivity	H_2S / H_2 Selectivity	Ref.
Cellulose acetate *		15–20		(84)
Cellulose acetate	2.13	0.86		(85)
Cellulose acetate	20			(86)
Cellulose acetate	6.09	0.26	1.74	(86)
Cellulose acetate (plasticized 15% dibutyl phthalate)	61			(86)
Cellulose acetate asymmetric *		7.4	0.73	(87)
Cellophane	0.57	2.2	1.82	(37)
Ethyl cellulose	320	3.8	4.9	(86)
MDK composite	0.1	3.7	13.8	(66)
Mylar A	0.7			(86)
Nylon	3.3		2.5	(86)
Nylon 6	0.34	3.86		(86)
Pliofilm	1			(86)
Poly (bis-(phenoxy) phosphazene PPOP 45% crystallinity	12	2.5	1.6	(83)
Poly(bis-(3,5-di-ter-butylphenoxy) 1,2-chloro)0.8 phosphazene) [PDTBP]	20	0.74	0.27	(83)
PDMS (20 Psia)	5100	1.6	5.37	(77)
PDMS (65 Psia)		4.8	10	(88)
Low Density Polyethylene	36	2.84	3.6	(89)
High Density Polyethylene	8.6	24		(89)
Poly ethylene	433			(86)
Poly ethyl methacrylate	3.83	0.76		(90)
Poly (ether urethane urea)	150	4.69		(81)
Poly (ether urethanes) poly(propylene oxide) 1	211	3.2		(85)
Poly (ether urethanes) poly(propylene oxide) 2	615	1.6		(85)
Poly (ether urethanes) poly(propylene oxide) 3	276	4.5		(85)
Poly (ether urethanes) poly(propylene oxide) 4	102	4.64		(85)
Poly (amide-co-ether) MX1074	624	4.5		(85)
Poly (amide-co-ether) 4033SA00	312	3.7		(85)
Polyimide A2		2.52		(82)
Polyimide 6FDA-HAB	1.5	0.25		(82)
PTBP	16	0.94		(83)
Poly phosphazene 6% MEE	38	4	9	(91)
Poly phosphazene 48% MEE	1003	8.7	42.3	(91)

Table 7. Continued.

Membrane	H_2S Permeability (Barrer)	H_2S / CO_2 Selectivity	H_2S / H_2 Selectivity	Ref.
Poly phosphazene 74% MEE	1140	5	39.6	(91)
Poly propylene	3.2	0.35	0.08	(89)
PTMSP	21400	1.2	1.8	(77)
Fluorinated TFE/PMVE49		0.61		(88)
Poly (vinyl butyral)	105			(86)
Poly vinyl alcohol	0.007	0.56	0.77	(37)
Poly vinyl chloride	0.19	1.2	0.11	(89)
Poly (vinyl trifluoroacetate)	3			(86)
Poly [vinylidene chloride] Saran	0.036	1.24		(86)
Saran	0.3			(86)

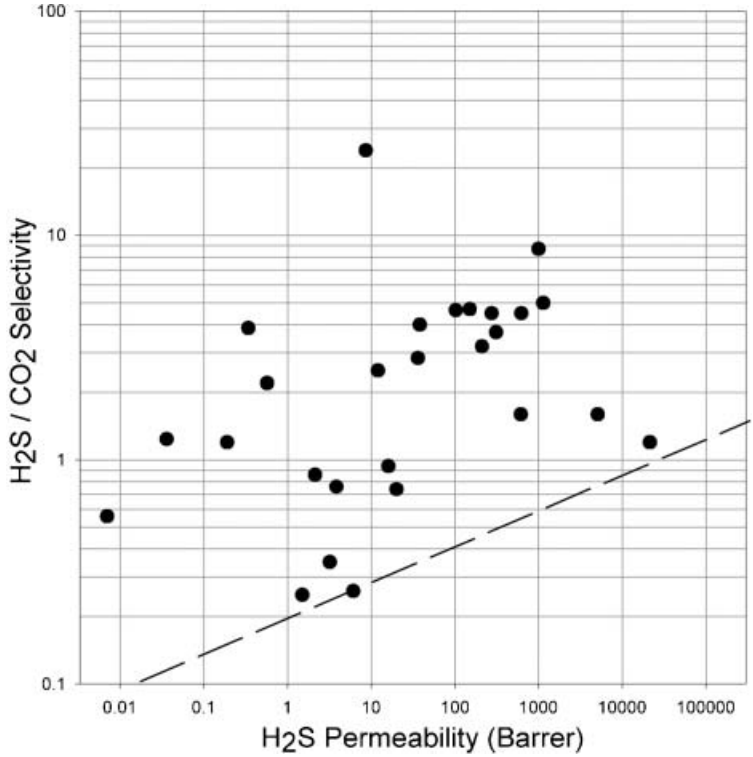

Figure 7. H_2S permeability within polymeric membranes and selectivity relative to CO_2.

Table 8. NH_3 permeability and selectivities for polymeric membranes relative to N_2 and CO_2 (* indicates thin composite membrane).

Membrane	NH_3 Permeability (Barrer)	NH_3 / N_2 Selectivity	NH_3 / CO_2 Selectivity	Ref.
Cellulose acetate	3.2	111		(96)
Cellulose Nitrate	56.9		26.9	(38)
Cellophane	176.9		692.7	(37)
Dimethyl silicone rubber	5000	20	1.57	(97)
Ethyl cellulose	703.6		6.24	(38)
Nylon 6	1.2		13.3	(89)
Poly-4,4′-diphenylene sulfoneterephthalamide	1185			(97)
Poly etherimide *	48.4	134	~21	(97)
Low Density Polyethylene	27.9		2.21	(89)
High Density Polyethylene	10.6		29.6	(89)
Polypropylene	9.2		1	(89)
Polysulfone *	53		~7.7	(97)
Polyvinyl chloride	4.9		30.8	(89)

behaviour occurs for poly dimethylsiloxane (PDMS), a rubbery polymeric membrane, where the permeability increases with increasing pressure (Figure 8) (88). Given that this is a rubbery membrane, this behaviour indicates that Henry's Law is not applicable for H_2S at low pressures, even when it is for N_2, H_2 and CO_2. No information relating to plasticization of glassy polymers by H_2S has been found by the authors, and this should be an area of future research.

The effect of H_2S on cellulose acetate over a fortnight period is shown in Figure 9 (92). There is little evidence of deterioration over this time, with a decrease of ~5% in permeance within the range of experimental uncertainty. With the addition of water, cellulose acetate experiences a 35% loss in permeability. This loss is probably related to water sorption effects (see below). However, it is also possible that the presence of water allows for weak acidic degradation induced by H_2S, which may alter the membrane structure, hindering gas diffusion.

Ammonia (NH_3)

Ammonia is present in pre-combustion as a product of gasification (Table 2). Its removal is generally required and there exist a number of highly selective commercial membranes for NH_3 separation, mainly designed for the Haber process (93–95). These are not reviewed here.

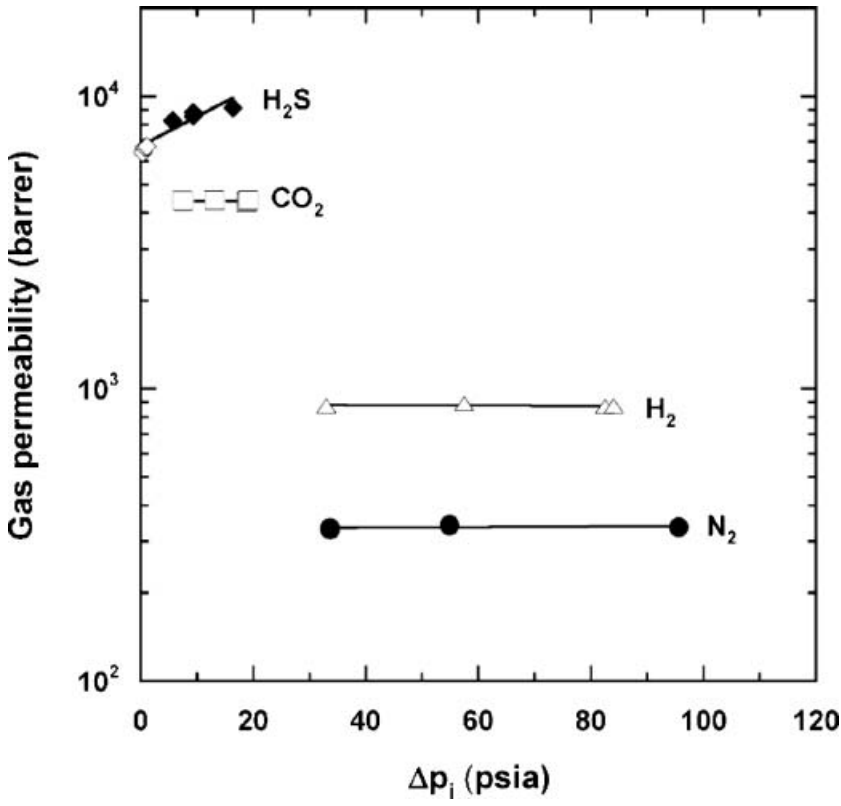

Figure 8. Permeability of gases through poly dimethyl siloxane as a function of differential pressure at 21°C, for 15% H_2S in N_2 mixture. Reprinted with permission from (88). Copyright 2006 American Chemical Society.

Provided are the permeability of NH_3 and selectivity over N_2 and CO_2 for a number of polymeric membranes that have potential application for CO_2 capture, Table 8, graphed in Figure 10. The polymeric membrane performance indicates that NH_3 has a greater permeability through polymeric membranes than CO_2, and therefore in membrane capture, the permeate stream would become NH_3 rich.

NH_3 is known to plasticize polymeric membranes, a good example are membranes based on polyvinylammonium thiocyanate (98). In the presence of NH_3 the polymers change from a glassy to rubbery state, which is advantageous for the Haber process because it improves both the permeability and selectivity of NH_3. However, in CO_2 capture, the plasticization effects of NH_3 are less likely to be relevant, due to the low partial pressure in precombustion compared with CO_2.

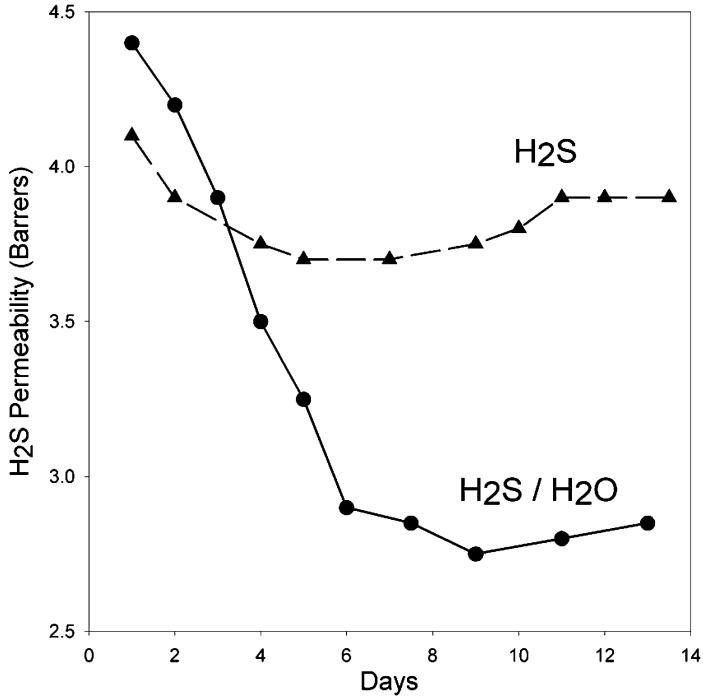

Figure 9. Permeation of H_2S and H_2S / H_2O through cellulose acetate membranes at 10 psi H_2S and 26°C. Reprinted with permission from (92). Copyright 1986 AIChE.

Argon (Ar)

Air-based gasification and combustion, especially oxyfuel combustion, introduces Ar to the flue gas in concentrations ~ 1 mol% (3). The permeability and selectivity of Ar through a number of polymeric membranes are provided in Table 9. In all reviewed membranes, selectivity favours CO_2 separation. This is because the inert nature of Ar limits the solubility of the gas within the polymeric matrix, and therefore diffusion is the driving mechanism. The kinetic diameter of this species is also small. Hence, Ar will remain in the retentate during polymeric membrane gas separation.

CONDENSABLE COMPONENTS

Condensable components, e.g., water and hydrocarbons, differ from gas minor components because they exist in the feed gas in the subcritical state, and in the case of water in significant quantity. Hence,

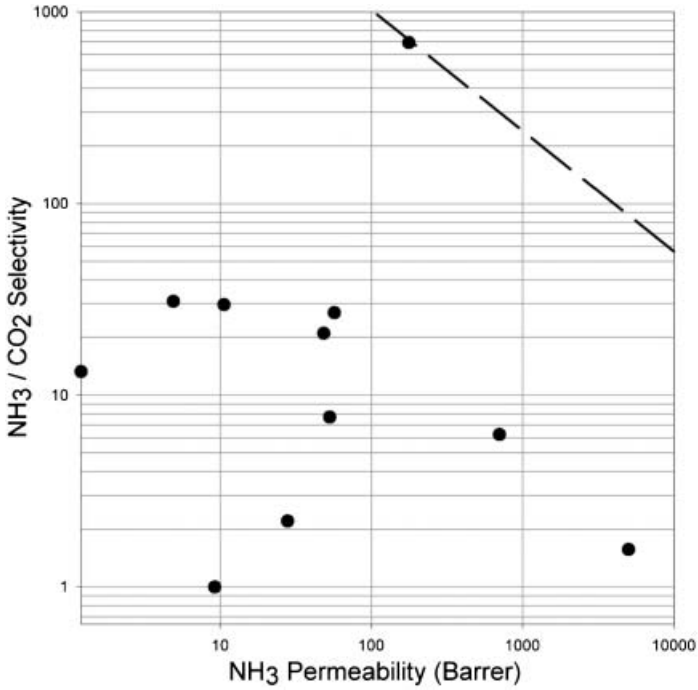

Figure 10. NH_3 permeability within polymeric membranes and selectivity relative to CO_2.

condensation within the membrane is a possibility, which can significantly alter separation performance. Here, the effects of water and hydrocarbons in general are reviewed. However, because only limited research into these condensable components has been undertaken, it is difficult to draw generalised conclusions on their behaviour. This is because of the underlying relationship between the membrane's affinity for the various condensable components, as well as structure of the polymer matrix, which varies widely between membranes depending on the polymer and annealing history.

Water (H_2O)

Generally, pre- and postcombustion process streams for CO_2 capture are saturated with water vapour (4). Therefore, competitive water sorption in the membrane, as well as plasticization and aging affects, will have a much stronger influence on membrane performance compared to the minor gas components discussed above.

Table 9. Ar permeability and selectivities for polymeric membranes relative to CO_2.

Membrane	Ar Permeability (Barrer)	Ar / CO_2 Selectivity	Ref.
Cellulose acetate	0.34		(99)
Cellulose nitrate	0.1	0.052	(38)
Ethyl cellulose	10	0.09	(38)
Nafion 117	0.49		(100)
Nylon 11	0.19	0.19	(101)
Poly acrylonitrile	0.00018		(38)
Poly (bis(trifluoro ethoxy) phosphazene	27.4		(102)
Poly (butadiene)	40.9	0.29	(103)
Poly carbonate bisphenol chloral	0.65		(104)
Poly carbonate bisphenol-A	0.8		(105)
Poly carbonate tetramethyl bisphenol-A	2.4		(106)
Poly chloroprene	3.8		(107)
Liquid-crystalline polyester	0.0001		(108)
Poly ethersulfone	0.229		(109)
Poly ethylene	3.96		(109)
Poly (ethyl methacrylate)	0.58	0.11	(90)
Poly imide	0.06		(110)
Poly (isoprene)	23		(78)
Poly L-leucine	7.6		(111)
Poly (γ-methionine)	0.58		(111)
Poly (methyl methacrylate)	0.027		(112)
Poly (oxydimethylsilylene)	550	0.17	(113)
Poly (2,6-dimethyl-1,4-phenylene oxide)	5.01		(109)
Poly sulfone	0.421		(109)
Poly styrene	5.4		(114)
Poly (tetrafluoroethylene)	2	0.15	(115)
Poly urethane	0.36		(116)
Poly (vinyl acetate)	0.15		(117)
Poly (vinyl alcohol)	0.001		(118)
Poly (vinyl benzoate)	0.47	0.086	(119)
Poly (vinyl chloride)	0.01	0.07	(120)
Silicone rubber	673		(121)

The water permeability through polymeric membranes is generally higher than carbon dioxide, in many cases substantially, as can be seen in Table 10 and Figure 11. This is because water has both a smaller kinetic diameter than CO_2 and therefore diffuses faster and also has a higher critical temperature, which results in greater sorption in the membrane. Hence, for membrane CO_2 capture the permeate stream will have a

Table 10. H_2O permeability and selectivities for polymeric membranes relative to CO_2.

Membrane	H_2O Permeability (barrer)	H_2O / CO_2 Selectivity	Ref.
Cellulose acetate	5493	238.7	(122)
Cellulose nitrate	6278	2968.6	(38)
Cellophane	25137	98438	(37)
Ethyl cellulose	8911	79	(38)
Nylon 6	0.185	2.1	(123)
Poly acrylonitrile	305.9	22272	(124)
Poly acrylonitrile-co-styrene	851	58181	(124)
Poly acrylonitrile-co-methylacrylate-co-butadiene	1290	80833	(124)
High density polyethylene	11.97	33.33	(122)
Poly ethyl methacrylate	3165	627.9	(90)
Poly methacrylonitrile	412.3	129167	(124)
Poly methacrylonitrile-co-styrene	492	62712	(124)
	931	18421	(124)
	1729	6190	(124)
	1862	3684	(124)
	2128	1818	(124)
	1995	625	(124)
Poly methacrylonitrile-co-styrene-co butadiene	598.5	40909	(124)
	665	33333	(124)
	771	24167	(124)
Poly propylene 50% crystal	67.8	7.4	(125)
Poly propylene 43% crystal	21	2.9	(53)
Poly styrene	953.6	90	(124)
Poly tetrafluoroethylene	17.8	1.34	(53)
Teflon FEP	49.6	3.9	(126)
Poly tetrafluoroethylene-co-ethylene	98.4	16.9	(127)
Poly trifluorochloroethylene	0.29	1.38	(128)
Poly trifluorochloroethylene-co-ethylene	3.7	6.1	(53)
Poly vinyl chloride	274	1717	(120)
Poly vinylidene chloride (Saran)	9.3	321.1	(122)
Poly vinyl fluoride	13.4	146.4	(127)

higher water percentage than the feed, and if the permeate temperature is below the dew point, i.e., supersaturated, there is the possibility of condensation formation. This will create an additional transfer layer for the gases to cross, reducing performance, and generating problems in the further processing of the permeate. Evaporation of condensed water from porous membrane substructures can also cause mechanical damage due to capillary pressure effects.

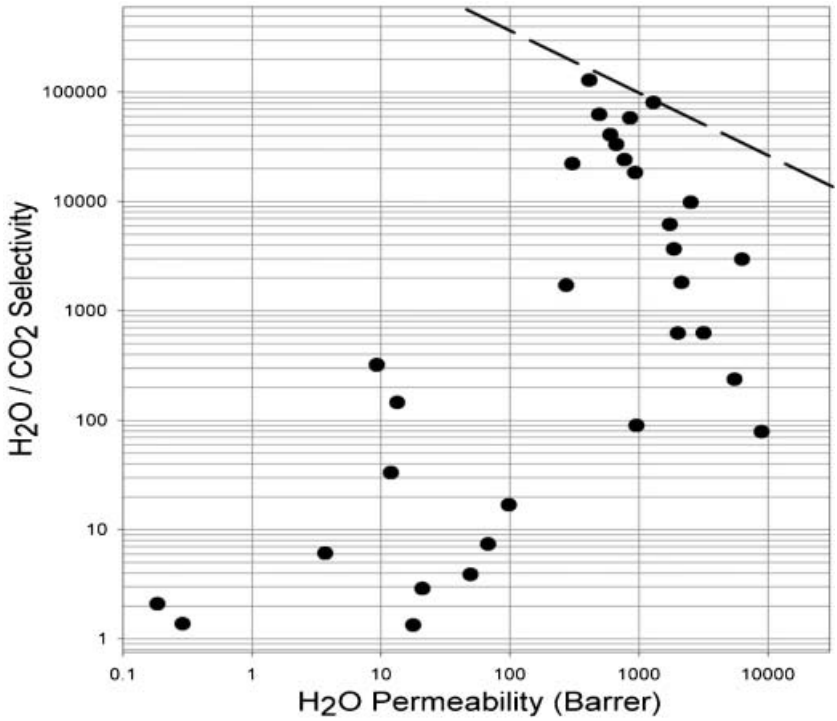

Figure 11. H_2O permeability within polymeric membranes and selectivity relative to CO_2.

The effect of competitive sorption of water on CO_2 permeability can be seen in Figure 12, for Kapton (a polyimide) (21). The trend of decreasing permeability with increased CO_2 pressure, irrespective of humidity, is due to decreasing CO_2 solubility at these pressures, which is a feature of the dual mode sorption model corresponding to saturation of the Langmuir voids. The decrease in CO_2 permeability with increasing relative humidity (RH) signifies water progressively excluding CO_2 from these Langmuir voids. A total exclusion from all Langmuir sites is indicated by the permeability falling to a level consistent with Henry's Law sorption alone ($P = k_D D_D$). The permeability depressing effect of the water tends to be most serious at low CO_2 pressures, where Langmuir sorption is most significant.

The competitive effects of water have also been observed for sulfolene modified polyvinylidene fluoride, Table 11 (129). Increased humidity levels decreases the flux ~20%, while the selectivity compared to CH_4 is constant or slightly higher, dependent on temperature (129). Plasticization due to water sorption is clearly observed for polyethersulfone and polysulfone (Table 11) (129). Upon

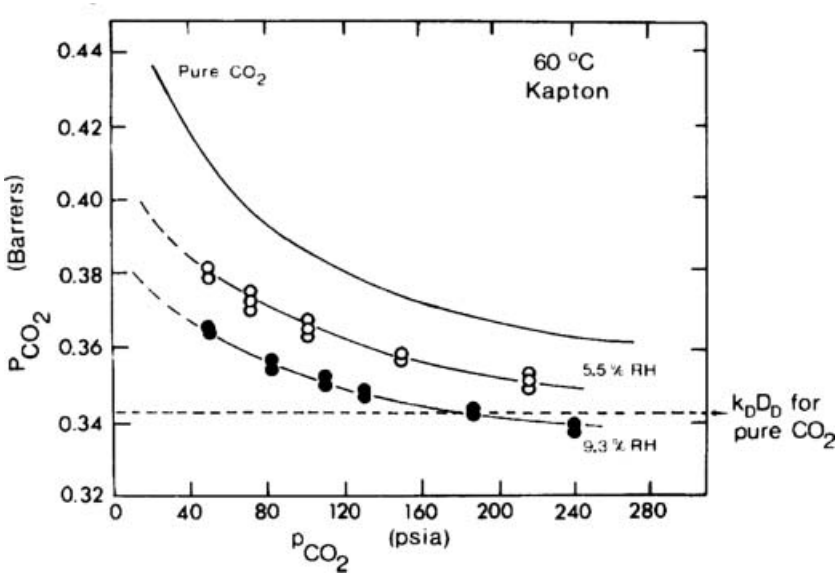

Figure 12. Depression of CO_2 permeability in Kapton caused by water vapour at 60°C. Reprinted from (21) with permission from Elsevier.

exposure to water, the flux through the polyethersulfone membrane dramatically increases by ~250%, and remains high irrespective of humidity concentration. Correspondingly a decrease in selectivity is

Table 11. Water flux through various polymeric membranes, at 90°C with ~2000 kPa difference (129).

Membrane	% H_2O Feed	Dry flux (cm^3 / cm^2 s)	CO_2 / CH_4 Selectivity	% H_2O Permeate	Water only flux (cm^3 / cm^2 s)
Cellulose acetate	0	7.3×10^{-4}	9	–	–
	0.25	9.0×10^{-4}	7	24.4	2.9×10^{-4}
	0.85	7.7×10^{-4}	7	35.5	4.3×10^{-4}
Poly ethersulfone	0	4.0×10^{-5}	32	–	–
	0.85	8.7×10^{-5}	24.5	13.9	1.4×10^{-5}
	0.96	8.3×10^{-5}	24	25.2	2.8×10^{-5}
Poly sulfone	0	3.1×10^{-5}	11	–	–
	0.36	5.3×10^{-5}	10	32.9	2.6×10^{-5}
	0.6	7.6×10^{-5}	10.5	33.9	3.9×10^{-5}
Sulfolene modified poly vinylidene fluoride)	0	3.8×10^{-4}	9	–	–
	0.36	3.2×10^{-4}	10	24.9	1.1×10^{-4}
	0.5	3.1×10^{-4}	10	35.7	1.7×10^{-4}

observed, a 25% loss. Water-induced plasticization swells the polymeric matrix, increasing the diffusion of gases through the membrane at the expense of solubility.

Cellulose acetate (Table 11) in the presence of water displays a combination of plasticization and competitive sorption behaviour (129). Initially, with small amounts of H_2O present the flux increases, indicative of plasticization. At higher humidity (0.85%) the flux decreases compared to the lower humidity result. Cellulose acetate is a dry membrane, however it is highly hydrophilic (92) and it is therefore not surprising that water rapidly hydrates the polymer leading to swelling (plasticization). At higher humidity levels the polymer matrix is fully hydrated, and therefore rather than further plasticization, water undergoes competitive sorption with CO_2 in the free volumes, resulting in the observed reduction in flux.

The effect of water on cellulose acetate flux over a number of days can be seen in Figure 13 for a N_2/CO_2 gas mixture (92). Moisture levels up to 20% RH appear tolerable in terms of only a 20% reduction in flux over a month. However, higher humidity levels cause a rapid irreversible loss in flux. This is postulated to be due to moisture condensation in the

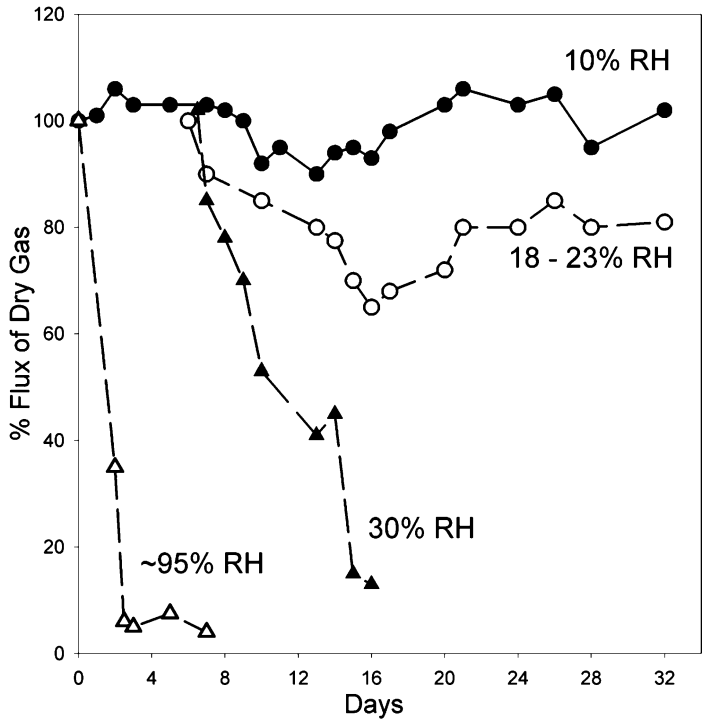

Figure 13. Cellulose acetate flux for moist N_2 / CO_2 mixed gas at 0.7 MPa (100 psi) (92).

Table 12. Permeability of 50% H_2 in CH_4 gas mixture in polyimide based membranes dry, wet (15 mm H_2O vapour pressure) and after re-drying, at 14.7 psia, 30°C (130).

Membrane	Permeability (barrer)					
	Gas	Dry	Wet	% loss	Re-dry	% loss
Polyimide – 1,3 diaminobenzne	H_2	35.57	28.17	21	28.58	20
Polyimide – 1,3 diaminobenzne	CH_4	0.132	0.111	16	0.121	8
Polyimide – 2,5 diaminobenzoic acid	H_2	31.68	12.73	60	30.1	5
Polyimide – 2,5 diaminobenzoic acid	CH_4	0.075	0.033	56	0.073	3
Polyimide – 1,5 diaminonaphthalene	H_2	76.37	61.6	19	77.59	−2
Polyimide – 1,5 diaminonaphthalene	CH_4	0.682	0.57	16	0.692	−1

porous substructure on the permeate side of the membrane leading to an additional barrier to gas transport. Most commercial membrane operations aim to operate at least 10°C above the dew point of the gas mixture to avoid such condensation effects.

Water-induced plasticization effects can permanently alter the membrane structure, and initial performance does not always return once the membrane is dried. This is clearly seen in Table 12 for a range of polyimide based membranes (130), and while they do not consider CO_2 specifically, the effect on performance would be similar. In all cases the permeability of the gas decreases as a result of competitive sorption of water. In the 2,5-diaminobenzoic acid polyimide membrane, a 60% decrease is observed for H_2. Upon drying the membranes through the use of a dry feed gas, initial performance conditions are not always achieved with permanent permeability losses of up to 20% (130).

Interestingly, the presence of water within the feed gas may dictate the flow regime across the membrane surface. Generally, membrane separation is under counter-current conditions. However, Matsmiya et al. (131) has postulated that when water is present, higher separation is achieved by a co-current flow pattern. The reasoning is that the permeate stream is diluted by the water vapour over the whole active area in a co-current flow pattern, whereas water vapour exists only in a narrow region in the counter-current flow pattern. Consequently, the co-current flow mode generates a wider membrane area with a large CO_2 driving force than the counter-current regime.

It should be noted that the presence of water is not always detrimental to the performance of membranes. Specifically, for most

facilitated transport systems, the presence of water is essential to the transport mechanism (60, 61, 132). In these cases, a loss of moisture within the membrane structure leads to a rapid decline in CO_2 permeability and selectivity.

HYDROCARBONS

Typical natural gas processing streams can contain trace components of numerous paraffinic and aromatic hydrocarbons. This can also be true for pre-combustion, due to incomplete reformation of the fuel (4). The presence of even trace quantities of these condensable hydrocarbons (C6 and higher) can seriously alter the performance of polymeric membranes.

The permeability against selectivity of various hydrocarbons through polymeric membranes compared with carbon dioxide is shown in Figure 14. This covers a wide range of hydrocarbons and in general shows that permeabilities are less than CO_2 for most polymeric membranes. This is due to the kinetic diameter of hydrocarbons (Table 1), which favours CO_2. PDMS-based membranes display selectivities greater than 1 because

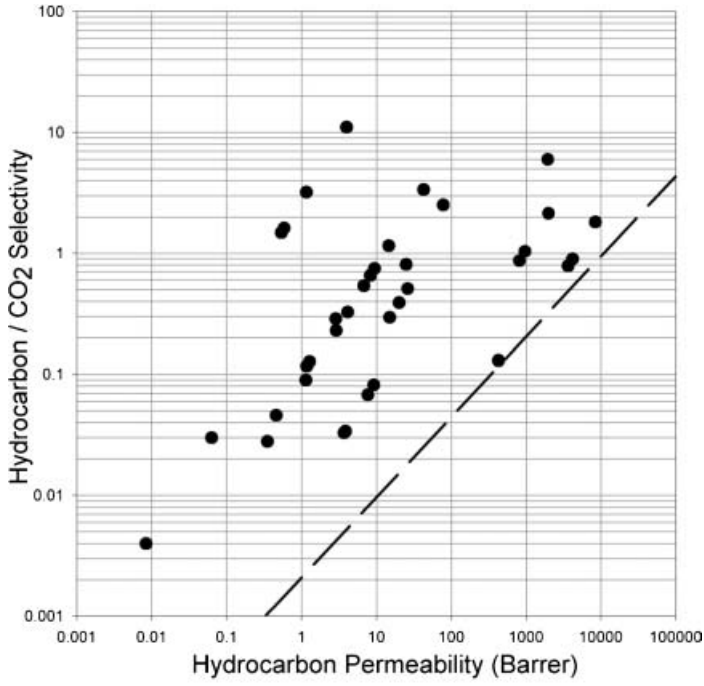

Figure 14. Hydrocarbon (aromatic and paraffins) permeability within polymeric membranes and selectivity relative to CO_2 (53).

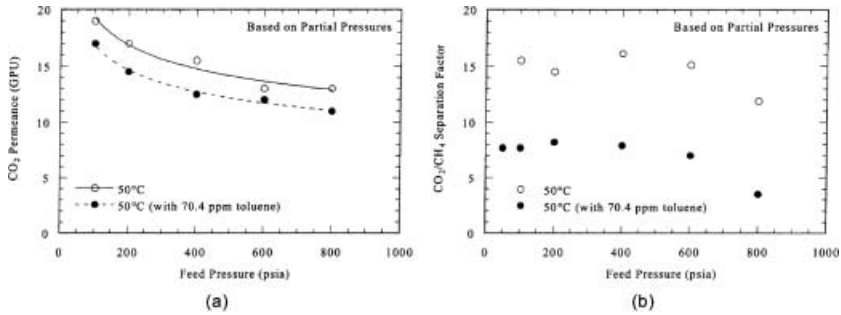

Figure 15. Polyimide hollow-fiber membrane performance in the presence of 70.4 ppm toluene, 10% CO_2 / 90% CH_4. Reprinted from (134) with permission from Elsevier.

being a non-polar rubbery membrane they have a much greater hydrocarbon solubility compared with CO_2 and therefore higher permeability is observed. This graph however, is a general overview of a range of hydrocarbons, and differences in structure, i.e., aromatics or paraffins, will cause both solubility and diffusivity to differ for the same polymeric membrane. However, in most membrane CO_2 capture systems the hydrocarbon will not be separated as efficiently as CO_2 and will leave in the retentate stream.

The change in permeability and selectivity of polyimide membranes in the presence of hydrocarbon impurities can be seen in Table 14 (133) and Figure 15 (134). The addition of 0.055 vol% toluene to a 6FDA-DMB polyimide results in an increase in the permeability of methane, while no change occurs for CO_2 (Table 13). Conversely, the addition of 0.007% toluene to a 6FDA/BPDA-DAM polyimide (Figure 15) causes a

Table 13. Polyimide performance of 10% CO_2 in CH_4 separation in the presence of toluene (0.055% $^{v}/_{v}$) and hexane (0.23% $^{v}/_{v}$), at 1000 psi and 48°C (133).

Membrane test conditions	Permeance CO_2 (GPU)	Permeance CH_4 (GPU)	CO_2 / CH_4 selectivity
Mixed Gas no additive	56	3.8	14.6
Mixed Gas with Toluene	56	5.7	9.7
Nitrogen 2 day flush	59	3.6	16.2
Mixed Gas with Hexane	87	10.2	8.4
Nitrogen 1 day flush	69	4.1	16.6

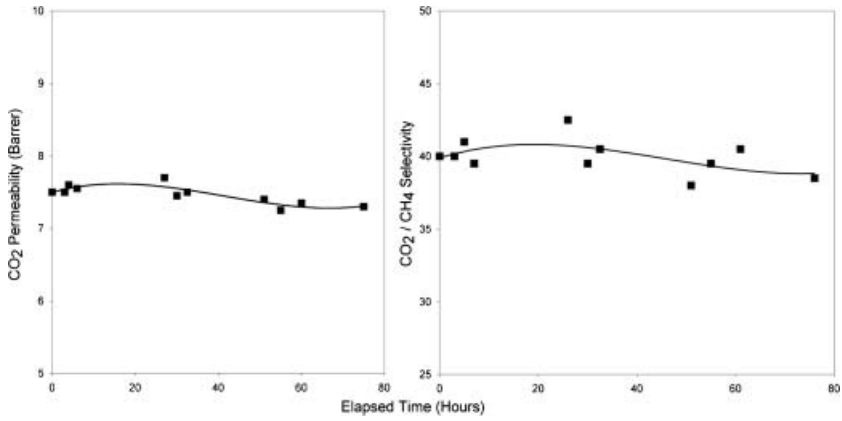

Figure 16. Elapsed time studies of Matrimid separating 10% CO_2 in CH_4, exposed to toluene (70.4 ppm) at 500 psia and 35°C. Data is taken from Vu et al. (135).

slight decline in CO_2 permeability. In both cases, the CO_2/CH_4 selectivity falls significantly. These effects can be related to a combination of plasticization that will generally increase the permeability of both components and competitive sorption, which will tend to decrease permeability more strongly for the more condensable CO_2.

Similarly, sorption of 0.23 vol% hexane into the 6FDA-DMB polyimide causes dramatic increases in permeability of both components through plasticization but still with a net loss of selectivity. Membrane performance is only partly recovered after one day of flushing due to the long time constants associated with the plasticization phenomenon.

Time-elapsed exposure of the polymeric membrane Matrimid (polyimide) to toluene, Figure 16, indicates stable performance, within experimental uncertainty. Hence, no age-induced degradation is observed in either CO_2 permeability or selectivity for this polymeric membrane (135).

In view of industrial application, Pereira et al. (24, 27, 136) examined the performance of a range of membranes in the presence of pump oil vapour, similar to that which would be experienced in a real industrial process. The dual-sorption parameters of Henry's law solubility constant (K_D), maximum adsorption capacity (C'_H) and Langmuir affinity constant (b) for various polymers experiencing different vapour pressures of SH-46 oil are shown in Figure 17. First, the K_D of both CO_2 and N_2 increases in each polymeric membrane with increased amount of oil vapour. This implies plasticization of the membrane by the oil, which allows increased gas within the polymer structure.

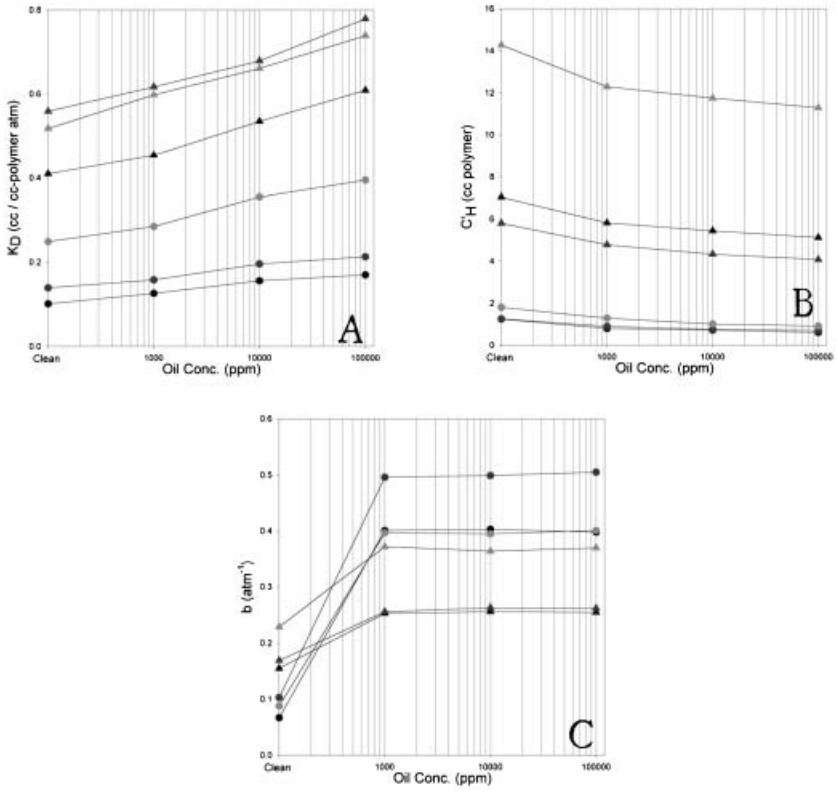

Figure 17. Dual-sorption model parameters of CO_2 (triangle) and N_2 (circle) separation in poly carbonate (black), poly sulfone (dark grey) and poly carbonate 2 (light grey) exposed to SH-46 machine oil at 35°C. Henry's Law constant, k_D (a), Maximum adsorption capacity, C'_H (b) and Langmuir affinity constant, b (c). Data is taken from Pereira et al. (24, 27).

The Langmuir maximum (Figure 17b) decreases for CO_2 and N_2 in each membrane with increasing oil present, attributed to competitive sorption of the oil in the microvoids. The change in the Langmuir affinity constant (Figure 17c) is of most interest; since there is a substantial increase in the N_2 affinity when oil vapour is present, in the case of polysulfone, it is a six-fold increase. Correspondingly, while the CO_2 affinity constant also increases, the N_2 value is higher when oil is present and thus, N_2 has a greater affinity for the free volume of the membrane. This arises from sorption of N_2 into the non-polar oil that has accumulated in the free volume, which substantially improves its loading within the membranes. Hence, upon exposure to the oil vapour the loading of N_2 increases substantially more than CO_2, resulting in a loss of selectivity.

OTHER IMPURITIES

Heavy Metals

Depending on the fuel source, heavy metals exist within the fly ash of both pre- and post-combustion exhaust gases (35). While filters may remove the ash, heavy metals will remain present at the ppb level. Mercury is a particular issue as it is highly toxic and also increases corrosion rates in aluminium and other construction materials. There is no information in the literature about the permeability of these metals through gas separation membranes, probably because most natural gas installations use guard beds upstream of these membrane units to capture these contaminants. However based on their size and small partial pressure a number of conclusions can be made. Membranes based on a molecular sieving or Knudsen mechanism for separation will ensure the metals leave in the retentate stream and not pass through the membrane due to their large kinetic diameter. Similarly for polymeric membranes, the diffusion through the free volume will be small compared to the gases present and therefore the heavy metals will leave in the retentate. However, there is the possibility of metal accumulation within the membrane free volume over time, due to the very high critical temperature of this species.

Halogens

The presence of halogens in ppm quantities within pre- and postcombustion gases may hasten membrane degradation, due to their ability to form strong acids in the presence of water. The only information found on HCl is for polytetrafluoroethylene and poly tetrafluoroethylene-co-ethylene, which have permeabilities of 2.7 and 22 barrer, with 0.2 and 0.5 HCl/CO_2 selectivities, respectively (53). If this separation performance can be generalized to all polymeric membranes, it would imply the halogens present within the feed gas leave in the retentate, given the partial pressure driving force is very small. However, the important issue of acid-induced aging by these components has not been considered and represents another area for future academic research.

MEMBRANE CHOICE

This review has shown that in many cases there is insufficient information in the public domain to make a considered membrane choice. However, for post-combustion, the choice in polymeric membrane will depend

primarily on achieving both a high CO_2 permeability and CO_2/N_2 selectivity. If a glassy polymer is used in this application, competitive sorption of water, NO_2, SOx and hydrocarbons is likely to reduce both the CO_2 permeability and selectivity relative to the pure gas value. Indeed, it is possible that water molecules may completely fill the Langmuir sites, thus negating the use of such a high free volume polymer. The combination of SOx, NOx and water may also lead to acidic degradation and both water and trace hydrocarbons may cause plasticisation of the polymer. These are all important factors to consider in membrane choice. Depending on the flue gas conditions, it may be necessary to sacrifice a high CO_2 separation performance in favour of increased mechanical strength and resistance to acidic and plasticisation effects for long-time performance.

Most studies suggest that the CO_2 concentration in a post-combustion permeate stream should be >90 mol% for effective geological storage (137), although a detailed economic comparison of the relative costs of capture and storage may indicate the use of lower concentrations(138). However, for the majority of the selected polymeric materials, transportation of SOx, NO_2 and water across the membrane will reduce the maximum CO_2 concentration that can be achieved. While much of the water in the permeate can be removed by simple condensation during subsequent compression, residual water levels can lead to pipeline corrosion. It will be important to understand the water concentrations that can be tolerated in the transportation pipeline, as these are higher in supercritical carbon dioxide than in comparable natural gas streams (139). Further, it will be necessary to understand whether the regulatory and political environment will allow co-storage of SOx and NOx with carbon dioxide underground.

For precombustion, a polymeric membrane that achieves a high CO_2 selectivity against H_2 is of primary importance, given the difficulty of this separation due to the small kinetic diameter of H_2. This is likely to necessitate the use of a rubbery polymer, as these tend to be solubility selective. In terms of minor components, the general permeabilities observed for H_2S, NH_3 and water imply they will enrich the permeate stream along with CO_2; this is most likely an advantageous situation since it removes the corrosive components from the downstream combustion process. However, further separation of minor components from the permeate will be required, especially of water, to increase the CO_2 fraction to desired levels and reduce pipeline corrosion. Again, it will be necessary to understand the regulatory framework for geological storage with respect to co-storage of H_2S and NH_3. Given the reducing environment of gasification, polymeric membranes in pre-combustion situations will experience less acidic conditions compared to postcombustion, though the presence of water and hydrocarbons have the potential for plasticization. Therefore,

polymeric membrane choice will again need to focus on those polymers that show resistance to performance deterioration as a result of plasticisation.

CONCLUSIONS AND FUTURE DIRECTIONS

This review has covered the performance and effect of minor components on membrane gas separation for application in pre- and postcombustion CO_2 capture. In particular, polymeric membrane performance has been examined for SOx, NOx, CO, H_2S, NH_3, Ar, water and hydrocarbons. Generally, SOx, NOx, H_2S, NH_3 and water have greater permeability through glassy polymeric membranes than CO_2 and therefore will enrich the permeate stream. This permeability increase can be related to the higher critical point of these species. CO, Ar and hydrocarbons have lower permeability compared with CO_2 and therefore remain in the retentate stream.

The review has highlighted the need for more research on key minor components, specifically SO_3, NO and NO_2, given the lack of data and their presence in flue gas. Further, SO_2, H_2S and water all demonstrate plasticization effects on polymeric membrane performance. However, only a few membranes have been tested for these effects and a general understanding cannot be drawn from reported results. Importantly, future research should focus on gas mixtures of CO_2 with minor components present at similar concentrations to real flue gas to determine the competitive sorption effects on CO_2 permeability and selectivity, as well as long time plasticisation induced performance changes. This will provide a critical understanding on polymer types that can retain a high CO_2 permeability with competition from minor components. Another important area for future research is membrane performance in the presence of water, SOx and NOx, and the potential for acidic degradation, as well as plasticization. As reported above, this is an area lacking in the literature on membrane gas separation. Investigations of the change in separation performance as well as mechanical and chemical resilience of polymeric membranes under humid conditions are important studies required before any polymeric material can be used for commercial CO_2 capture.

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