

# Carbon Dioxide Separation through Polymeric Membrane Systems for Flue Gas Applications

Colin A. Scholes, Sandra E. Kentish\* and Geoff W. Stevens

*Cooperative Research Centre for Greenhouse Gas Technologies, Department of Chemical and Biomolecular Engineering, The University of Melbourne, VIC, 3010, Australia*

Received: October 27, 2007; Accepted: November 6, 2007; Revised: November 15, 2007

**Abstract:** The capture and storage of carbon dioxide has been identified as one potential solution to greenhouse gas driven climate change. Efficient separation technologies are required for removal of carbon dioxide from flue gas streams to allow this solution to be widely implemented. A developing technology is membrane gas separation, which is more compact, energy efficient and possibly more economical than mature technologies, such as solvent absorption. This review examines the recent patented developments in polymeric based membranes designed for carbon dioxide separation from mixed-gas systems. Initially, the background to polymeric membrane separation is provided, with an overview of past polymeric designs. This is followed by a discussion on the current state of the art; in particular developments in mixed matrix polymeric membranes and facilitated transport polymeric membranes for improved carbon dioxide permeation and selectivity. Recent developments in other membrane types, carbon and inorganic, are reviewed for comparison purposes with polymeric developments. Finally, a brief comment on the future directions of polymeric membrane gas separation technologies is provided.

**Keywords:** Polymeric membranes, gas separation, carbon dioxide, mixed matrix membranes, facilitated transport membranes.

## 1. INTRODUCTION

The control of anthropogenic carbon dioxide emissions is one of the most challenging environmental issues facing industrialized countries, because of the implications to atmospheric carbon dioxide levels and climate change [1]. Burning of fossil-fuels is responsible for the majority of these carbon dioxide emissions [1], and therefore there is significant interest in developing technologies that will reduce carbon dioxide emissions. In particular, the capture of carbon dioxide from large point sources allows storage options, such as geo-sequestration, to reduce emission levels. The conventional process for carbon dioxide capture is by reversible solvent absorption [2, 3]. In general, this process has high energy consumption [4], for example, regenerating the solvent requires a high heating utility in the stripper reboiler. The associated cost and environmental impact means that there is need for other more efficient separation processes to be applied to carbon dioxide capture.

The energy efficiency and simplicity of membrane gas separation makes it extremely attractive for carbon dioxide capture [5-7]. The ability to selectively pass one component in a mixture while rejecting others describes the perfect separation device. While no membrane system truly behaves this way, membrane gas separation does have a number of advantages over conventional processes and a number of reviews examining their benefits exist [8-12]. This review covers the recent patented advances in membrane design for carbon dioxide capture, and more broadly for the separation of polar gases from multiple component gas streams. In particular, this review will focus on advances in polymeric membrane design for improved carbon dioxide separation.

Initially, a brief introduction into membranes and performance characterization is provided, followed by an overview of prior patented polymeric membrane designs. The review then focuses on the most recent polymeric membrane designs, mainly mixed matrix membranes and facilitated transport membranes, which provide improved carbon dioxide separation over previous polymeric designs. Both membrane gas absorption and non-polymeric membranes are covered briefly in regards to their performance and recent advances for comparison purposes with polymeric designs.

The concept of membrane separation was originally proposed by Graham in 1866 [13] with Loeb and Sourirajan [14] developing the first anisotropic membrane in 1961. Initially, the majority of membrane separation research was directed towards reverse osmosis, which is extensively covered in the patent literature [15, 16]. Gas separation membranes were first commercialized in 1977 when Monsanto/Perma released their hydrogen recovery system [17]. The success of this and other gas membrane systems by Cynara, Separex and Generon [17-19] led to substantial innovation during the 1980s and 1990s into membrane materials. These innovations have improved the gas separation efficiency and membrane durability, making membrane gas separation commercially competitive with existing separation technologies. Gas separation membranes are now applied to a wide range of industrial processes. In particular, many of the early patents were awarded for the sweetening of natural gas by the removal of carbon dioxide [20, 21] and this is the foundation on which current carbon dioxide capture research is based.

Membranes act as filters to separate one or more gases from a feed mixture and generate a specific gas rich permeate, as shown in Fig. (1). Two characteristics dictate membrane performance, permeability; that is the flux of a specific gas through the membrane, and selectivity; the

\*Address correspondence to this author at the Department of Chemical and Biomolecular Engineering, The University of Melbourne, VIC, 3010, Australia; Tel: +61 3 83446682; Fax: +61 3 83444153; E-mail: sandraek@unimelb.edu.au

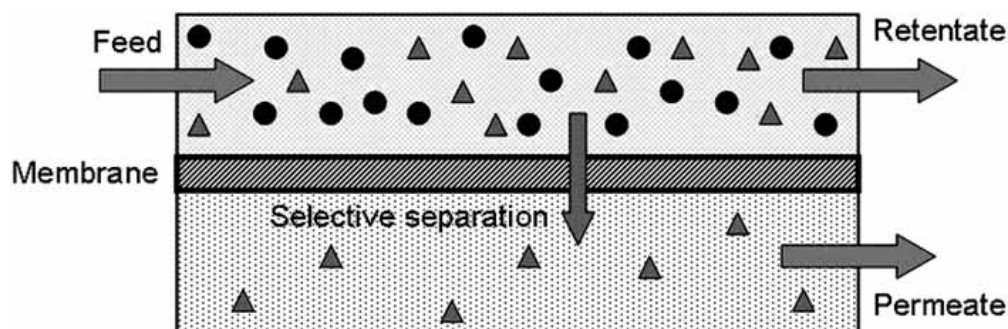


Fig. (1). Schematic of membrane gas separation.

membrane's preference to pass one gas species and not another. There are five possible mechanisms for membrane separation [18, 22]; Knudson diffusion, molecular sieving, solution-diffusion separation, surface diffusion and capillary condensation, of which the first three are schematically represented in Fig. (2). Molecular sieving and solution-diffusion are the main mechanisms for nearly all gas separating membranes. Knudsen separation is based on gas molecules passing through membrane pores small enough to prevent bulk diffusion. Separation is based on the difference in the mean path of the gas molecules due to collisions with the pore walls, which is related to the molecular weight (Table 1). Specifically, the selectivity for any gas pair is determined by the inverse ratio of the square root of their molecular weight. For  $\text{CO}_2/\text{N}_2$  and  $\text{CO}_2/\text{H}_2$  separation, Knudsen diffusion predicts a selectivity of less than unity. Molecular sieving relies on size exclusion to separate gas mixtures. Pores within the membrane are of a carefully controlled size relative to the kinetic (sieving) diameter of the gas molecule. This allows diffusion of smaller gases at a much faster rate than larger gas molecules. In this case, the  $\text{CO}_2/\text{N}_2$  selectivity is greater than unity, as  $\text{CO}_2$  has a smaller kinetic diameter than  $\text{N}_2$ . Surface diffusion is the migration of adsorbed gases along the pore walls of porous membranes [23, 24]. The rate of surface diffusion is determined by the level of interaction between the adsorbed gases and pore surface. Thus, molecules diffuse along the pore walls relative to the strength of this interaction, and separation is mainly achieved by the difference in the degree of this interaction for the individual gases. An extension of surface diffusion is when the vapour pressure becomes low, adsorbed gas can undergo partial condensation within the pores. This condensed component diffuses more rapidly through the pore than gases, causing separation of the condensable gas. This is known as capillary condensation [25, 26].

Polymeric membranes are generally non-porous, and therefore gas permeation through them is described by the solution-diffusion mechanism [18]. This is based on the solubility of specific gases within the membrane and their diffusion through the dense membrane matrix. Hence, separation is not just diffusion dependent but also reliant on the physical-chemical interaction between the various gas species and the polymer, which determines the amount of gas that can accumulate in the membrane polymeric matrix. The relationship between permeability, diffusivity and solubility can be described by:

$$P = DS \quad (1)$$

where  $P$  is the permeability coefficient, a measure of the flux of the membrane ( $\text{cm}^3(\text{STP}) \text{cm}^{-2} \text{s}^{-1} \text{cmHg}^{-1}$ ). The common unit of permeability is the barrer ( $10^{-10} \text{cm}^3(\text{STP}) \text{cm}^{-2} \text{s}^{-1} \text{cmHg}^{-1}$ ).  $D$  is the diffusivity coefficient ( $\text{cm}^2 \text{s}^{-1}$ ), the mobility of molecules within the membrane and  $S$  the solubility coefficient ( $\text{cm}^3(\text{STP}) \text{cmHg}^{-1}$ ), which measures the solubility of gas molecules within the membrane.

For ideal gases, the permeability is related to the gas permeation rate through the membrane ( $Q$ ), the surface area of the membrane ( $A$ ), the thickness of the membrane ( $l$ ) and the driving force for separation, the pressure difference across the membrane ( $\Delta p$ ):

$$\frac{P}{l} = \frac{Q}{A\Delta p} \quad (2)$$

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

$$\alpha = \frac{P_A}{P_B} \quad (3)$$

Polymeric membranes are further classified as rubbery or glassy, dependent on operating temperature relative to the glass transition temperature of the polymer [27]. 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 polymer matrix follows Henry's Law and is linearly proportional to the partial pressure, or fugacity,  $f$ :

$$C_D = K_D f \quad (4)$$

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

Conversely, 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 in the polymeric matrix. Within these voids Langmuir adsorption of gases occurs that increases the solubility. Therefore, the total concentration of absorbed gas within glassy membranes ( $C$ ) can be described by [18]:

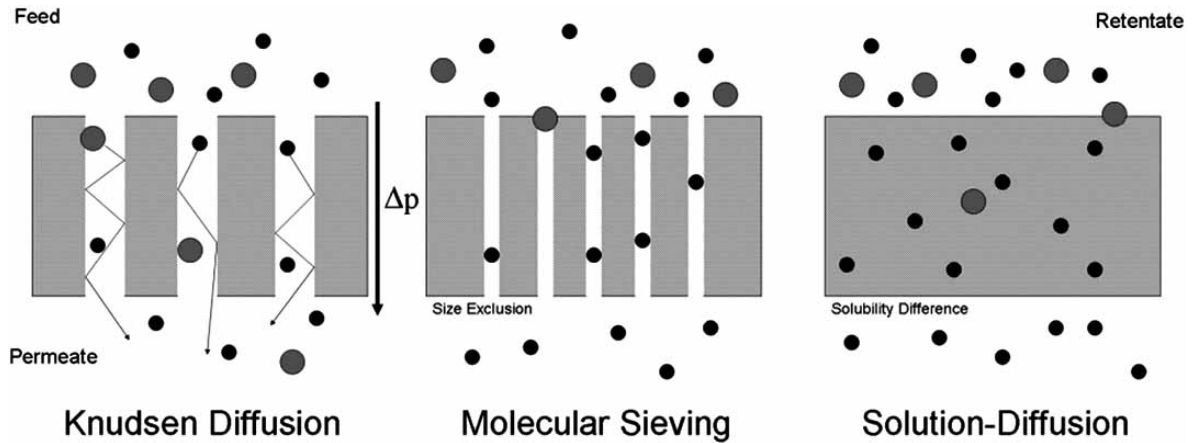


Fig. (2). Schematic representation of three of the different possible mechanisms for membrane gas separation, Knudsen diffusion, molecular sieving and solution-diffusion.

Table 1. Molecular Weight (Da) and Kinetic Diameter (Å) of Gases Encountered in Membrane Gas Separation

Molecule	Molecular Weight	Kinetic Diameter (Å)
CO <sub>2</sub>	44	3.3
O <sub>2</sub>	32	3.46
N <sub>2</sub>	28	3.64
H <sub>2</sub> O	18	2.65
CH <sub>4</sub>	16	3.8
H <sub>2</sub>	2	2.89

$$C = C_D + C_H \quad (5)$$

Where  $C_H$  is the standard Langmuir relationship

$$C_H = \frac{C'_H b f}{(1 + b f)} \quad (6)$$

$C'_H$  is the maximum adsorption capacity,  $b$  is the ratio of rate coefficients of adsorption and desorption, defined as:

$$b = \frac{C_H}{(C'_H - C_H) f} \quad (7)$$

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

$$C = K_D f + \frac{C'_H b f}{(1 + b f)} \quad (8)$$

The relationship between the specific volumes and temperature of a polymer from the glassy to rubbery state is shown in Fig. (3).

Currently, for a flue gas of 10% CO<sub>2</sub> content, the cost of membrane separation post-combustion is greater than solvent

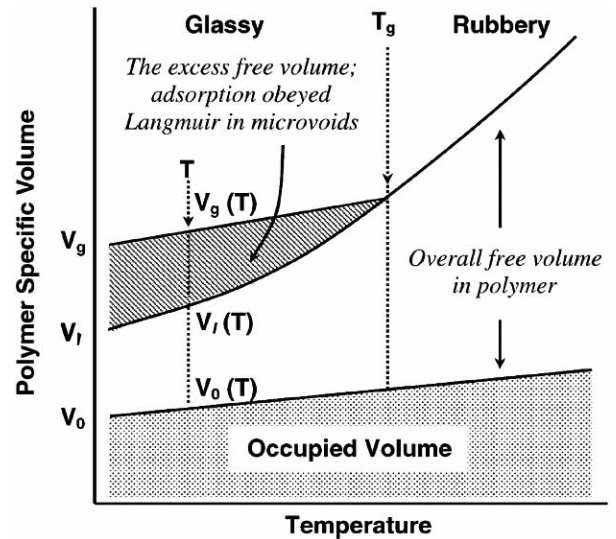


Fig. (3). Schematic representation of the relationship between the polymer specific volume and temperature in an amorphous polymer (reprinted with permission from [28]).

absorption separation [29]. The majority of this cost is associated with creating the pressure difference across the membrane to drive separation, usually achieved through feed gas compression [30]. To make gas membrane separation cost competitive for this CO<sub>2</sub> content, it has been suggested that CO<sub>2</sub>/N<sub>2</sub> selectivity needs to exceed 120 [29]. When the CO<sub>2</sub> content of the gas exceeds 20%, experienced in a range of industrial processes such as cement production, the selectivity needed reduces to >60. While these degrees of separation appear not to be achievable with current commercial membrane material [31], many of the recently patented polymeric materials discussed here overcome these benchmarks. Similarly, membrane permeability is inversely proportional to the membrane area required for separation. Thus high permeability leads to lower capital cost. However, for most membranes, there is a trade-off between selectivity and permeability. A highly permeable membrane tends to have low selectivity, and visa versa. Robeson [32] has suggested that this trade-off may be represented as an upper

bound to membrane performance. This upper bound can clearly be seen in Fig. (4), for a range of membranes involved in CO<sub>2</sub>/N<sub>2</sub> separations. Overcoming this upper bound is the focus of many recently awarded patents in polymeric membranes, because achieving both high carbon dioxide permeability and selectivity is desirable.

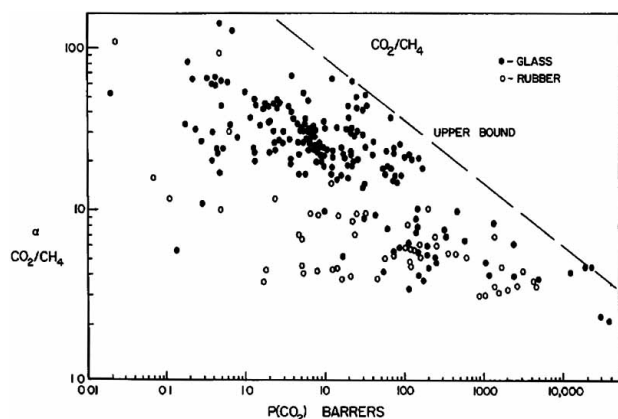


Fig. (4). Comparison of Robeson's curve for CO<sub>2</sub>/N<sub>2</sub> separation by carbon membranes (o) and polymeric membranes (•) [9, 33].

Improving permeability and selectivity are not the only membrane properties that are important. For membrane materials to be viable, they need to be thermally and chemically robust, resistant to plasticisation and aging affects to ensure continual performance over long time periods, and be cost effective to manufacture as standard membrane modules.

Patents have been awarded for a wide range of polymeric based membranes that claim to meet these aims. Here, original polymeric and inorganic membrane patents are reviewed briefly to inform the reader of past developments in the art, since the majority of these patents were awarded in the 1980s and early 1990s. This review will then focus on recent novel approaches in polymeric membranes that achieve separation performance above Robeson's upper bound and therefore are possibly more commercially competitive than present membrane gas separation technologies.

## 2. MEMBRANE TECHNOLOGY - STATE OF THE ART

### 2.1. Polymeric Membranes

The first carbon dioxide separating membranes were based on cellulose acetate and derivatives thereof, originally designed for reverse osmosis [14, 34]. These polymeric membranes are characterized by a thin, dense selective surface 'skin' on a less dense porous support that is non-selective. This is the basis of all asymmetric membrane materials that are readily used in industry. However, the

carbon dioxide flux of cellulose acetate based membranes decreases substantially with time, due to the material being susceptible to plasticisation and compaction under feed stream conditions. Therefore, later polymeric membrane patents focus on more robust polymers that achieve greater selectivity and/or permeability. Improving the performance of the CO<sub>2</sub>-selective polymeric membrane is achieved by two approaches; increasing the solubility of carbon dioxide in the membrane through changes in polymeric composition, and increasing the diffusion of carbon dioxide by altering the polymer packing within the membrane. Diffusion is generally enhanced by increasing the volume of free space within the membrane and this can sometimes be achieved through the addition of bulk substituent groups [9]. The polymer packing in glassy membranes and thus the free volume is also influenced by the casting method and annealing conditions. Therefore, along with the polymeric materials, casting methods have also been patented [35].

The combination of these approaches has produced a wide range of polymeric membranes with reasonable permeability and selectivity to provide good carbon dioxide separation. Some patented polymeric membranes are based on polyamides [36-44], polysemicarbazides [45], polycarbonates [46-50], polyarylates [51, 52], poly(phenylene oxide) [53-57], polyaniline [58-60] and polypyrrolones [61]. These all have reasonable permeability and selectivity, with some achieving performance around Robeson's upper bound. The difference between individual patents for each polymeric system is through the addition of bulky substituent and functional groups to the polymer, as well as cast history.

One of the most widely patented polymeric materials are polysulfones [62-72]. They are regarded as among the most chemically and thermally durable thermoplastic polymers available; and polysulfones have been extensively applied to gas separation. More recently, polyimides based membranes have out performed polysulfones, displaying some of the best permeability and selectivity properties for purely polymeric membranes [73-95]. This coupled with their thermal, chemical and plasticisation resilience, as well as considerable mechanical strength makes them an attractive material for gas separation membranes. The performance of these two polymers has resulted in a large number of patents. Differences between patents deal with substituent groups to change the carbon dioxide solubility, membrane packing density and free volume, as well as improving the membrane resistance to harsh environments.

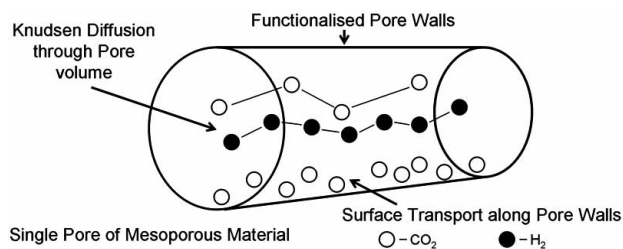
More recent patents on purely polymeric membranes have focused on combining different polymers to produce composite polymeric membranes. The copolymers used generally have a glassy (hard) polymer segment and a rubbery (soft) polymer segment [9]. The hard segment forms the structural frame and provides 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, hence greater permeability. The idea is to combine the selectivity of one polymer with the permeability of the other to provide a better performance membrane. Again, a considerable number of patents have been awarded for copolymer membranes, with the best performance based on blends of polyimide [77, 96-

100]. These copolymer blends have improved separation performance over polyimides, while retaining high mechanical, thermal and chemical stability.

## 2.2. Inorganic Membranes

Inorganic membranes represent an alternative gas separation technology; however it is not the purpose of this review to cover these membranes in detail. There are two major categories of inorganic membranes, porous and non-porous. Non-porous membranes are generally used in highly selective separation of hydrogen, where transportation is through alloys of palladium [101] or oxygen through perovskite systems [102-104]. Porous inorganic membranes are generally cheaper but less selective. The attraction of inorganic systems is their ability to operate at high temperatures. A particular high temperature operation of interest is the separation of carbon dioxide from hydrogen in syngas processes.

The large size of carbon dioxide relative to hydrogen means that achieving a carbon dioxide rich permeate stream by simple molecular sieving is not possible Table 1. Inorganic membranes overcome this by functionalizing the pores of the membrane to increase the carbon dioxide loading. Permeability then becomes a function of surface diffusion. Recent patents describe inorganic membranes that consist of a ceramic support, such as  $\text{Al}_2\text{O}_3$ , onto which a porous separating layer is added, often silica, alumina or zirconia. To this a functional layer is added,  $\text{BaTiO}_3$  by Ku *et al.* [105] or  $\text{MgO}$  by Gobina [106]. These functional groups have a high chemical affinity for carbon dioxide and therefore the pore walls become saturated, which increases the permeability, as shown in Fig. (5). For  $\text{BaTiO}_3$  on alumina, for 5 nm pores a  $\text{CO}_2/\text{H}_2$  selectivity of 3.1 is achieved at  $500^\circ\text{C}$  and for 1 nm pores a selectivity of 18.4 is achieved. Similarly for  $\text{MgO}$ , a  $\text{CO}_2/\text{N}_2$  selectivity of 120 is obtained with a carbon dioxide permeability of  $> 0.02$  barrer at  $350^\circ\text{C}$ . These membrane performances approach Robeson's upper bound for carbon dioxide separation and are therefore compatible with polymeric membranes.



**Fig. (5).** Schematic of inorganic membrane operation through Knudsen and surface diffusion (adapted from [107]).

Molecular sieves exist in both natural and synthetic forms, and can be classed as zeolites (aluminosilicate compositions), or non-zeolites, such as aluminophosphates, silico-aluminophosphates and silica [108]. The molecular sieve framework forms a well-defined repeating structure of regular channels and cages. Gas separation is dependent on the size of these channels and cages relative to the kinetic diameter of the gas. The difference in kinetic diameter of gas

molecules (Table 1) dictates which molecular sieves are useful and provides an indication of selectivity [17]. For example, Zeolite 3A separates hydrogen effectively from hydrocarbon feeds because the pore diameters are  $\sim 3 \text{ \AA}$  [109]. Zeolite 4A has pore sizes of  $\sim 4 \text{ \AA}$ , which will separate carbon dioxide from nitrogen and methane.

Molecular sieving based inorganic membranes incorporate such materials into the pores of a porous support. This integrates the size exclusion properties of the molecular sieve within the pores, providing selective gas separation [110]. A major difficulty with this approach is to achieve an efficient trap of the sieve particles within the pores. Both the pore and sieve sizes must be well-known and sufficiently similar to ensure strong packing of the pores. Otherwise, the gaps between the sieves and the pore walls will allow bulk diffusion of gas molecules, diminishing selectivity performance [111].

## 3. RECENT DEVELOPMENTS IN POLYMERIC MEMBRANE SYSTEMS

The current research into polymeric membranes is focused on increasing the polymeric performance above Robeson's upper bound to become cost competitive with solvent absorption, as well as improving the resilience of the membrane material. McKeown *et al.* [112] disclose the formation of microporous polymeric structures with very high free volumes. These polymers of intrinsic microporosity (PIMs) are rod-like randomly contorted structures which generate intrinsic cavities within the membrane. They exhibit behaviour analogous to conventional molecular sieves, but have greater solubility.

Young *et al.* [113] detail the cross-linking of polybenzimidazole for improved mechanical properties. Unmodified polybenzimidazole has been covered in past patents and provides reasonable permeability and selectivity for carbon dioxide separation from methane [114, 115]. Cross-linking of the polymer improves the mechanical properties, by increasing the yield stress of the membrane, which also results in increased separation performance. The patented example has a carbon dioxide permeation of 7.9 barrer with a selectivity over nitrogen of 27, when the polymer is cross-linked, compared to a carbon dioxide permeability of 0.3 barrer with a selectivity of 18 for unmodified linear polybenzimidazole, at  $23^\circ\text{C}$  tested by single gases. The effect of cross-linking on performance is dependent on the linking agent.

Wang and Yeager [116] present solvent resistant polymeric membranes that can reduce the plasticisation effects of hydrocarbons in the feed stream. The patent covers polyketone, polyether ketone, polyarylene ether ketone, polyimide, polyetherimide and polyphenylene sulphide, which have intrinsic solvent inertness and can therefore withstand organic rich operation conditions. Ekiner and Simmons [117] describe the controlled annealing of hollow fiber polyimide membranes. The annealing conditions patented are for the polyimide based membrane to exist under a vacuum less than 15 inches of mercury at between  $100\text{-}250^\circ\text{C}$  for 6-30 hours. This controlled annealing improves chemical resistance and ensures that the resulting hollow fibers have the necessary mechanical strength for

high pressure and temperature applications. However, annealing conditions for polymeric membranes are relatively well known and therefore the novelty of some of the patent's claims is questionable. Weinberg [83] deals with aromatic-polyimide based membranes that have improved performance at low temperature. This allows the membrane to be utilized in cold temperature applications without the need for heating of the feed gas. The improved performance relies on the increased solubility of carbon dioxide at these temperatures being greater than the loss in diffusivity. The patented example of asymmetric hollow fibers of this aromatic polyimide can be seen in Table 2. However, none of these recent patents are able to achieve a selectivity and permeability combination that exists above Robeson's upper bound.

**Table 2. The Temperature Dependent Permeability (Barrer) and Selectivity of an Aromatic-Polyimide Based Membrane, for a CO<sub>2</sub>/N<sub>2</sub> Gas Mixture of 72:28 Mole Ratio at 448 kPa [81].**

Temperature performance of novel aromatic-polyimide membranes			
	-22°C	10°C	50°C
CO <sub>2</sub> Permeability (barrer)	0.232	0.147	0.091
N <sub>2</sub> Permeability (barrer)	0.0035	0.0045	0.0053
CO <sub>2</sub> /N <sub>2</sub>	66.3	32.7	17.1

Two recent patents have been awarded for polymeric blends. The patent awarded to Ekiner and Simmons [100] covers polyamide, polyimide and polyamide-imide blends, which have increased mechanical strength and chemical resistance over the pure polymeric membranes, with only slight changes in permeability and selectivity. Seo [118] describes semi-crystalline amorphous polymeric blends with a compatibilizer agent within the membrane matrix to ensure miscibility of the two polymers. The patent examples of poly(phenylene oxide) with Nylon 6 are provided in Table 3. Poly(phenylene oxide) has been patented previously as a gas separation membrane material, with reasonable selectivity and permeability. The addition of the semi-crystalline Nylon 6, results in a decrease in permeability for only a slight increase in selectivity. However, addition of the compatibilizer poly(styrene-co-maleic anhydride) (PSMA)

results in a doubling of selectivity, with a loss in permeability. This arises because the compatibilizer prevents phase separation within the membrane and hence reduces the free volume. Too much PSMA in the membrane leads to itself phase separating, which affects both selectivity and permeability to the detriment of performance Table 3.

### 3.1. Carbon Membranes

Carbon membranes are a variant of polymeric membranes that operate as molecular sieves [119]. These membranes generally have higher permeability and selectivity for carbon dioxide than polymeric, Fig. (4). However, the carbon structures are not easily formed into thin layers and so while the permeability may be high, the actual flux through the thick membranes may not. The membranes are fabricated by pyrolyzing organic materials, typically polymers, in a non-oxidizing atmosphere upon a structural support that can withstand the high temperatures. The resulting membrane is comprised almost entirely of carbon and manifests as an active surface with controlled pore structure. These pore structures allow for effective separation of composite gas mixtures through both a molecular sieve mechanism, as well as by surface diffusion. The choice of the organic precursor material is important, because this will influence pore size and structure, and hence determine the performance of the membrane. Suitable precursors include resins, surfactants, graphite and polymers [120]. Their advantage over polymeric membranes is that they can withstand high temperatures and are more durable. Therefore, carbon membranes are often employed in chemical reactors and catalytic systems. Different production processes for carbon membranes have been covered [121-124]. These patents generally involve heating of the organic material above its decomposition temperature in an argon or nitrogen rich environment.

Carbon membranes can be relatively brittle and this can lead to cracking, greatly diminishing their performance [119], as well as making fabrication of carbon based membrane modules difficult. Furthermore, differences in the thermal expansion coefficient with the support can exasperate cracking at high temperature or if the membrane experiences thermal cycling. This increases the associated cost of the membrane modules compared with polymeric membranes. The recent patent of Foley, Rajagopalan and Merritt [125] strengthens carbon membranes by incor-

**Table 3. Permeability (Barrer) and Selectivity of Poly (Phenylene Oxide) (PPO) Membranes with Nylon 6, with the Addition of a Compatibilizer, Poly(Styrene-co-Maleic Anhydride) (PSMA), for Single Gases at 35°C and 1 atm [118].**

Separation performance of poly (phenyl oxide) nylon 6 blends				
	Compatibilizer	Permeability CO <sub>2</sub>	Permeability N <sub>2</sub>	Selectivity CO <sub>2</sub> /N <sub>2</sub>
PPO		61	4.1	14.4
PPO - Nylon(20%)		24.8	1.53	16.15
PPO - Nylon (20%)	PSMA (2wt%)	12.0	0.309	38.7
PPO - Nylon(20%)	PSMA (4wt%)	17.0	0.474	35.87
PPO - Nylon (20%)	PSMA (6wt%)	12.9	0.469	27.43

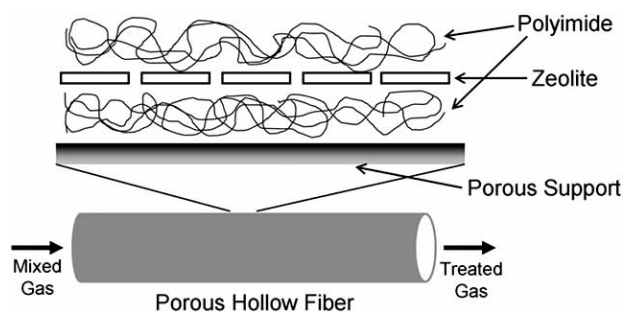
porating particulate matter into the membrane. Having particulate matter inside relieves stress on the carbon structure, hence improving the mechanical strength and reducing the possibility of cracking. Furthermore, there is evidence that if the particulate matter is selected with care, enhanced permeability can also be achieved. The patent covers a wide range of suggested materials, ranging from oxides, nitrides, carbides, oxynitrides, oxycarbides, as well as nanoparticles of Si, Al, Ti, Zr, Fe and the different forms of carbon. These are doped in the membrane at the polymeric precursor preparation stage. High selectivity for  $H_2/CO$  (21) and for  $H_2/CO_2$  (5) makes the membrane applicable for syngas separation and hydrogen production through the water-shift reaction of syngas [126].

Carbon membranes are also known to suffer from aging effects, with a corresponding loss in permeability and selectivity. These aging effects differ from polymeric membranes, and involve pore filling, cracking, and chemical degradation of the carbon matrix [118]. In particular, exposure to oxygen causes the surface to become hydrophilic, and after this any exposure to water results in a loss of performance. Similar to polymeric membranes, various techniques have been proposed to regenerate the membrane, including thermal, chemical, electrothermal, ultrasonic or microwave processes. Hagg and Lie [127] deal with methods of increasing the performance of the membrane at the same time as improving the regenerative properties. The patent focuses on membranes formed from mixtures of cellulose and hemicellulose, with an acid used to degrade the cellulosic structure before pyrolysis to oligo- and monosaccharides. Acid pre-treatment for 6 days is ineffective, but after 2 weeks of acid pre-treatment a critical threshold in the hydrolysis process is overcome, and separation performance improves. The examples quoted for permeability and selectivity are above Robeson's bound. Furthermore, this patented membrane design has improved regeneration properties, taking advantage of the conductive nature of carbon membranes for electrothermal regeneration.

### 3.2. Mixed Matrix Membranes

A relatively recent advance that takes advantage of inorganic and polymeric membrane approaches is mixed matrix membranes. These are characterized by a heterogeneous gas separation layer comprising a dispersed phase of discrete inorganic particles in a continuous polymeric phase [128, 129]. The inclusion of dispersed particles can have three possible effects on the permeability of gases; the discrete particles can act as molecular sieves, altering permeability in relation to molecular size, the particles can disrupt the polymeric matrix resulting in increased micro-cavities and hence increase permeability, or they can act as a barrier to the gas transport and reduce permeability. A possible arrangement within a hollow fiber is shown in Fig. (6). The mixed matrix membranes provide the opportunity to overcome the individual deficiencies of molecular sieves and polymers, and achieve carbon dioxide separation performances above Robeson's upper bound.

The continuous phase of the mixed matrix membrane can be almost any polymeric material; examples are polysulf-



**Fig. (6).** Schematic of mixed matrix membranes hollow fiber, with the zeolite particulate matter within the polymeric phase (adapted from [141]).

ones, polyetherimides and polyimides. The particle size of the molecular sieve within the membrane influences performance, with average dimensions of 200-900 Angstroms suggested [130] to prevent the membrane thickness becoming too great to operate effectively. This is in view of some of the early mixed matrix patents quoting thickness of the order of 100-1000 micrometers [131], which are too thick for effective membrane modules.

An example of molecular sieves in mixed matrix membranes is covered by Hasse *et al.* [132] (Table 4). The inclusion of Zeolite 4A into the membrane results in a loss of permeability and selectivity compared to the polymer-only membrane. The cause of this is poor association between the zeolite and the polymer leading to an increased free volume within the membrane. For mixed matrix membranes to perform effectively, there needs to be a high affinity between the sieve and the polymeric phase. Otherwise, during casting the polymer will dissociate from the sieve's surface leaving micro-cavities throughout the membrane. This will enhance the permeability of gas and limit the sieving mechanism. Therefore, many of the patents in this field deal with functionalizing molecular sieves to have high affinity with the polymeric phase.

KFI is an aluminosilicate molecular sieve (pore size 3.9 Å) that has a greater affinity for poly vinyl acetate. This reduces the micro-cavities in the mixed membrane and enhances the selectivity of the membrane through size exclusion. Chabazite molecular sieves of differing forms (H-ZK-5, Na-SSZ-13, SAPO-34 and SAPO-44) also associate well with the poly vinyl acetate, controlling micro-cavity formation within the membrane and therefore the permeability of nitrogen.

To improve the affinity of the particles for the continuous phase, other chemically grafted zeolites have been patented [133]. Common binding agents are the monofunctional organosilicon compounds [130, 134]. These bond to the zeolite surface with the silicon segment miscible with the continuous polymer phase. This is covered by Kulkarni *et al.* [135], with carbon dioxide selectivities provided in Table 5. The treated Na-SSZ-13 in polyvinylacetate has a 22% increase in selectivity over the non-treated Na-SSZ-13 zeolite because the aminopropyltrimethylethoxysilane (APD-MS) binding agent increases association with the polymeric matrix and hence reduces micro-cavity formation.

**Table 4. Carbon Dioxide Permeability (Barrer) and Selectivity in Mixed Matrix Membranes Based on Polyvinylacetate Within the Inclusion of Various Zeolites, Measured for Single Gases at 35°C and 410 kPa [132].**

Separation performance of mixed matrix membranes based on poly vinyl acetate				
Continuous Phase	Zeolite	Conc. (pph)	CO <sub>2</sub> Permeability	Selectivity (CO <sub>2</sub> /N <sub>2</sub> )
Polyvinyl acetate			3.1	34.7
Polyvinyl acetate	4A	15	2.4	30.7
Polyvinyl acetate	KFI	20	4.9	53.6
Polyvinyl acetate	H-ZK-5	15	4.9	41.0
Polyvinyl acetate	Na-SSZ-13	15	4.5	41.7
Polyvinyl acetate	SAPO-34	15	4.4	44.4
Polyvinyl acetate	SAPO-44	15	4.9	51.8

Silicalite, is a common non-zeolite hydrophobic crystalline silica. Grose and Flanigen [136] show that treating such a non-zeolite with organosilicon compounds also improves the selectivity of a polyvinyl acetate based mixed matrix membrane through the reduction of micro-cavities, in this case by 33% (Table 5).

**Table 5. Gas Selectivity of Mixed Matrix Membranes Based on Polyvinylacetate with Various Molecular Sieves Included, Measured for Single Gases at 35°C and 410 kPa [135].**

Continuous Phase	Molecular Sieve	Selectivity (CO <sub>2</sub> /N <sub>2</sub> )
Poly vinyl acetate	Na-SSZ-13	34.7
Poly vinyl acetate	APDMS treated Na-SSZ-13	51.2
Poly vinyl acetate	Silicalite	32.3
Poly vinyl acetate	APDIPS-treated Silicalite	36.9
Poly vinyl acetate	APDMS-treated silicalite	43.1

Additional treatments of molecular sieves can be undertaken to improve performance, with washed zeolites covered in the patent awarded to Kulkarni *et al.* [137]. Washing zeolites in aqueous ionic solutions alters their operating pH and surface functionality, in this case making a more basic structure that will therefore increase the solubility of carbon dioxide within the mixed matrix.

Mixed matrix membranes based on polymers with intrinsic porosity (PIMs) as well as rubbery continuous phases have also been patented [138, 139]. Kulprathipanja and Charoenphol [138] add activated carbon to increase the selectivity of silicone rubber by surface diffusion. The activated carbon has a particle size between 0.1 and 5 microns. Improvements in both the selectivity and permeability are shown in Table 6. The inclusion of polyethylene glycol acts as a plasticizer on the silicone rubber and therefore assists the emulsion with activated carbon. An

**Table 6. The Carbon Dioxide Permeability (Barrer) and Selectivity of Liquid-Phased Based Mixed Matrix Membranes Made of Silicone Rubber on a Porous Polysulfone Support, with the Inclusion of Poly Ethylene Glycol (PEG), Activated Carbon or Carbonate to Improve Separation Performance, Measured for Single Gases at Ambient Temperature**

Phase	Particle	CO <sub>2</sub> Permeability	Selectivity (CO <sub>2</sub> /N <sub>2</sub> )
Silicone Rubber		14.3	11
Silicone Rubber	Polyethylene Glycol	4.89	42
Silicone Rubber	Activated Carbon	29.4	15
Silicone Rubber	Polyethylene Glycol + Activated Carbon	24.2	47
Silicone Rubber	Activated Carbon + carbonate	16.2	20.1
Silicone Rubber	PEG + Activated Carbon + carbonate	14.3	40.5

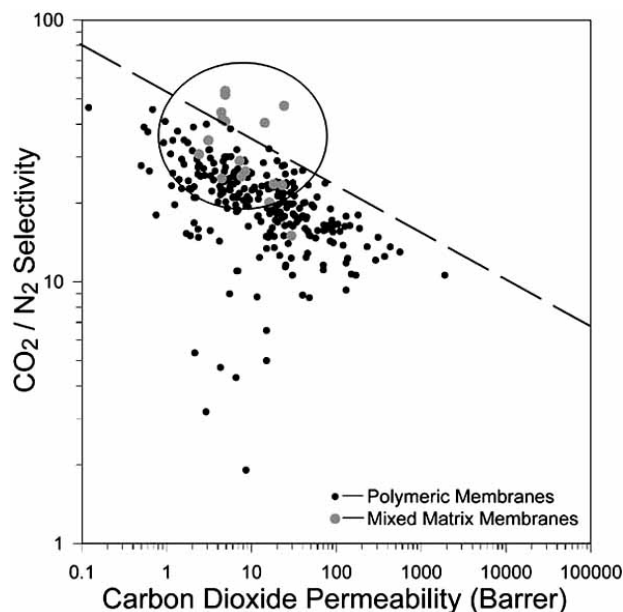
increase in permeability of 70% and selectivity by a factor of 4 is achieved, compared to previous silicone rubber membranes on porous and non-porous supports [140].

Marand and Kim [141] cover the inclusion of mesoporous silica into mixed matrix membranes. The patent example is based on polysulfone for the polymeric phase, with obtained permeabilities and selectivities provided in Table 7. The inclusion of mesoporous silica MCM41 and MCM48 into polysulfone increases the permeability of carbon dioxide with slight changes to the selectivity. Increasing the weight of the silica substantially increases the permeability of carbon dioxide because of the increase in micro-cavities within the membrane, resulting in a small loss in selectivity. Functionalizing the silica with amine groups increases the association with the polysulfone phase and

**Table 7. Permeabilities (Barrer) and Selectivity of Polysulfone Based Mixed Matrix Membranes with Mesoporous Silica [141]**

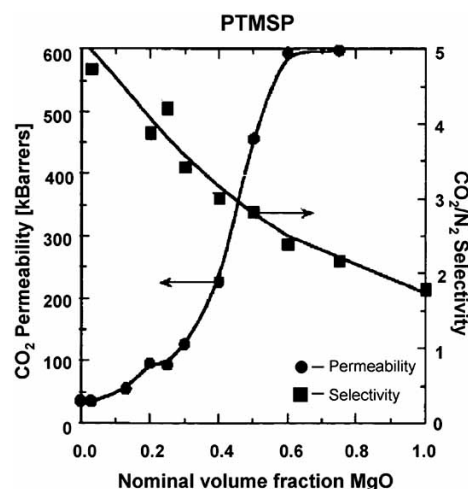
Membrane	Mesoporous silica wt%	CO <sub>2</sub> Permeability	N <sub>2</sub> Permeability	Selectivity CO <sub>2</sub> /N <sub>2</sub>
Poly sulfone	0	4.46	0.18	24.8
MCM41/ poly sulfone	20	7.59	0.30	25.3
MCM41/ poly sulfone	30	22.93	0.98	23.4
Amine-MCM41/ poly sulfone	20	7.25	0.25	29
MCM48/ PSF	10	8.45	0.32	26.4
MCM48/PSF	20	18.21	0.77	23.6

therefore reduces the number of micro-cavities present, this produces an increase in selectivity as nitrogen permeability is reduced because of size exclusion. The relative performance of some of these mixed matrix membranes can be seen in Fig. (7). In addition, Freeman *et al.* [142] incorporates various nanoparticles into a range of polymeric membrane to increase the performance, an example is shown in Fig. (8). Increasing the weight percentage of nanoparticle corresponds with an increase in permeability, at the expense of selectivity, again due to increased micro-cavity formation. However, the patent examples show this is not true for all mixed matrix membranes.



**Fig. (7).** Carbon Dioxide permeability against selectivity relative to nitrogen of mixed matrix membrane examples presented here, grey, and polymeric membranes, black [9], with Robeson's upper bound on performance.

The conversion of mixed matrix membrane designs to asymmetric membrane systems, the preferred form for industrial use, is covered by Kulkarni and Hasse [143], based on the asymmetric method proposed by Ekiner and Fleming



**Fig. (8).** Variation in mixed matrix membrane performance with change in the amount of MgO nanoparticles present within a poly (1-trimethylsilyl-1-proyne) (PTMSP) based membrane (reproduced from [142]).

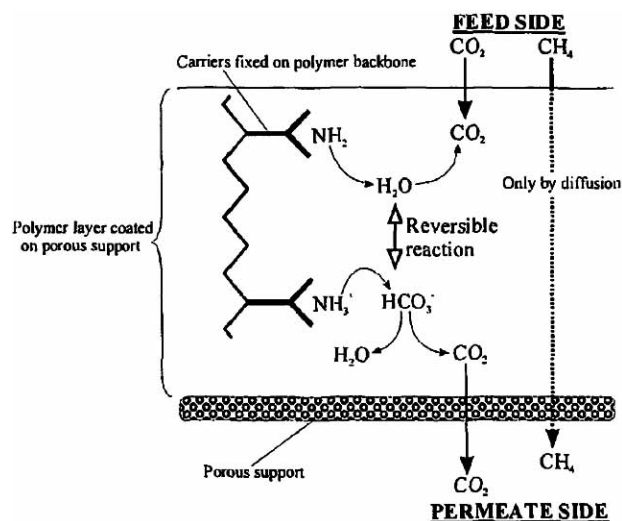
[144]. The resulting membranes showed mixed performance, Matrimid based mixed matrix hollow fibers have no enhancement in selectivity over just Matrimid hollow fibers [145]. In contrast, P84 polyimide has improved CO<sub>2</sub>/N<sub>2</sub> selectivity with SAPO-34 and carbon molecular sieves, 20.2 and 25.5 respectively, in hollow fiber modules.

Mixed matrix membranes containing molecular sieves can foul rapidly due to the accumulation of condensable impurities, most importantly water [138, 146, 147]. This hinders the molecular sieve mechanism and greatly reduces the selectivity of the membrane. Much more research in mixed matrix membranes will continue in the future, with the type of the dispersed particles of most interest. Recent publications in the literature are focused on the inclusion of nanoparticles and it would be expected that future patents will be awarded in this area.

### 3.3. Facilitated Transport Membranes

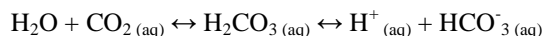
Facilitated transport membranes rely on a chemical reaction occurring between the gas of interest and a component of the membrane (carrier). The reacted species is

readily carried across the membrane, whereas diffusion of non-reactive gases is inhibited, see Fig. (9). The active carrier is generally basic in nature, given that carbon dioxide is acidic. The driving force for gas transportation remains the partial pressure difference across the membrane; however the facilitator carrier increases both the permeability and selectivity of the membrane through the increased loading. The facilitator carrier can be either fixed-sited within the polymeric matrix or mobile. An illustrated schematic of a fixed-sited carrier, polyvinylamine, in operation is provided in Fig. (9).

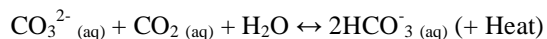


**Fig. (9).** Schematic of fixed carrier facilitator transport membrane for transport of carbon dioxide (reprinted from [148]).

The first facilitated transport membranes patent was awarded to General Electric in 1967 [149, 150]. This related to cellulose acetate films swollen by the inclusion of an aqueous carbonate solution. Carbon dioxide readily dissolves and reacts with water to form the bicarbonate anion.



Carbonate acts as a carrier by increasing the amount of carbon dioxide absorbed:



Hence, this reaction occurs on the feed side of the membrane and the bicarbonate anion transports through to the permeate side, where the reverse reaction occurs and carbon dioxide is released. This patent also allows for the inclusion of catalysts into the facilitator membrane to increase the rate of reaction between the carbonate and

carbon dioxide, of which arsenite salts are suggested to be the most practical. With the inclusion of carbonate in these membrane systems, as well as the catalysts, the permeability and selectivity are dramatically increased. The difference in carbon dioxide permeability and selectivity can be compared in Table 8.

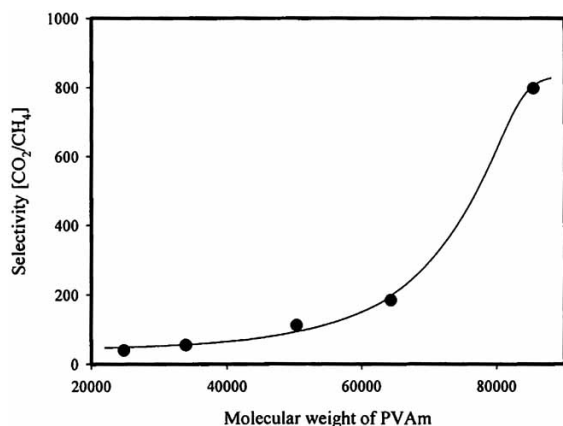
The immobilized liquid nature of the facilitator membrane poses practical problems, such as leakage and evaporation of water, as well as loss of the facilitator through degradation. Hence, their performance over long periods of time presents problems for large scale applications. Much of the recently patented facilitated transport membranes have focused on reducing these aging effects. In this regard, Sirkar *et al.* [151] disclose the use of dendrimers as carriers. The use of an amine-rich dendritic structure such as the Starburst polyamidoamine (PAMAM) [152] leads to high  $\text{CO}_2$  solubility. These structures can be immobilised in a polymeric matrix or alternatively, dissolved in a  $\text{CO}_2$ -philic liquid solvent which is placed within a mesoporous substrate.

Recent patents have been awarded for the incorporation of fixed carriers into existing porous polymeric supports, generating a composite structure [153, 148]. This is then swollen by the addition of water vapour, facilitating the transfer of carbon dioxide along the polymer chain through the membrane. Methods differ for the casting and cross-linking of the fixed carrier layer, as well as attachment to the porous polymeric support, with the desired result improving mechanical and thermal properties of the composite layer to increase stability of the membrane [153, 148]. Use of a polyvinylamine selective layer on a porous poly sulfone support, when polymer cross linking occurs by glutaraldehyde, results in a carbon dioxide permeability of 4100 barrer and a  $\text{CO}_2/\text{CH}_4$  selectivity of 70, at room temperature for a  $\text{CO}_2/\text{CH}_4$  gas mixture. In contrast, fluorine based cross-linkers, such as  $\text{NH}_4\text{F}$ , provide fixed facilitator layers with greater permeability (3095 Barrer) and  $\text{CO}_2/\text{CH}_4$  selectivity (1143) [148]. A possible reason for this is the fluorine anion, being considerably basic, allows increased carbon dioxide loading within the membrane. The molecular weight of the fixed facilitator polymer influences the selectivity but not the permeability of carbon dioxide in the membrane, as shown in Fig. (10).

More recent patents have focused on hydrogel films from cross-linked hydrophilic polymers, such as polyvinyl alcohol, polyvinylacetate, polyvinyl pyrrolidone, polyethylene oxide, polyacrylamide, bends and copolymers, cast on permeable supports [154, 155]. These hydrogels have a high water absorbing power and therefore can accommodate

**Table 8.** Wet Cellulose Acetate Facilitated Membranes for Carbon Dioxide Separation, at Ambient Temperature and 4 kPa [149]

	Facilitator	$\text{CO}_2$ Permeability (barrer)	Selectivity ( $\text{CO}_2/\text{O}_2$ )
Cellulose Acetate	Pure water	400	22
Cellulose Acetate	2 N $\text{KHCO}_3$	500	78
Cellulose Acetate	2 N $\text{KHCO}_3$ + 0.5 N $\text{NaAsO}_2$ (catalyst)	2000	600-800



**Fig. (10).** Influence of the molecular weight of the fixed carrier on carbon dioxide selectivity over methane (reproduced from [148]).

considerable loading of the carrier species. Copolymer composite membranes take advantage of the different swelling potential of each polymer component, whereas cross-linking agents are used to generate a strong polymer matrix. As a consequence, even though the membranes are thin, the high water content hydrogel film can retain its shape upon being subjected to pressure. Hence, they can function as a separation membrane with a long service life by exhibiting good water- retention and weatherability [156].

Fixed carriers are generally polyamines, examples are polyallylamine, polyethylenimine and polyvinylamine. Mobile carriers are basic compounds, and are often a combination of hydroxide salts, organic ammonium salts, amino-acids, carbonates, alkanolamines and polydentate ligands, such as EDTA [154].

Carbon dioxide selectivity and permeability through various mobile carrier facilitator membranes are provided in [157,158] Table 9, based on patented examples. Correlation between mobile carriers is difficult because of the different chemistry and kinetics involved. However, carbonate appears to provide very high carbon dioxide permeabilities through the membranes. Interestingly, with the addition of other mobile carriers the permeability is reduced. However, as a trade off, having mixed mobile carriers with carbonate improved the selectivity against nitrogen. The EDTA -

carbonate combination provides permeability and selectivity well above Robeson's upper bound, Fig. (11), making this membrane an attractive option.

Patented examples of fixed and mobile carrier combinations in polyvinylalcohol (PVA) are provided in Table 10. The selectivity and permeability of the membrane is unaffected by cross-linking with formaldehyde, and therefore the mechanical strength can be increased using this approach without penalty. The hydroxide anion present ensures the immobilized liquid is basic and therefore increases the carbon dioxide loading. This is most obvious for the dimethylglycine - polyethylene system, where the selectivity for carbon dioxide against hydrogen is tripled when hydroxide is present. The higher the weight percentage of fixed carrier within the membrane, the greater selectivity is achieved with the permeation of carbon dioxide remaining the same [154], similar to that observed for simple fixed carrier membranes. The type of mobile carrier present influences the permeability of carbon dioxide, with amino-isobutyric acid better than dimethylglycine and glycine. However, the relationship between mobile carrier concentration and carbon dioxide permeability is not clear in these mixed systems.

As previously mentioned, dehydration of facilitated membranes is a major concern, and the cross linking of the polymer is believed to minimise water loss. For the fixed carrier polyvinylamine facilitated membrane, exposure to dry feed gas for 5 days decreased the carbon dioxide permeability by 20% whereas exposure for 35 days resulted in a 90% permeability decline, as shown in Fig. (12) [153]. The flux was restored when the membrane was re-wetted implying that permeability loss is due to evaporation, rather than carrier degradation. Similarly, with a simple mobile carbonate carrier, the permeability decreased by 35% after 30 days with a similar loss in selectivity [153]. In industrial applications, the performance loss would be lower, since real flue gases are saturated with water and this would keep the facilitated membranes hydrated to some degree.

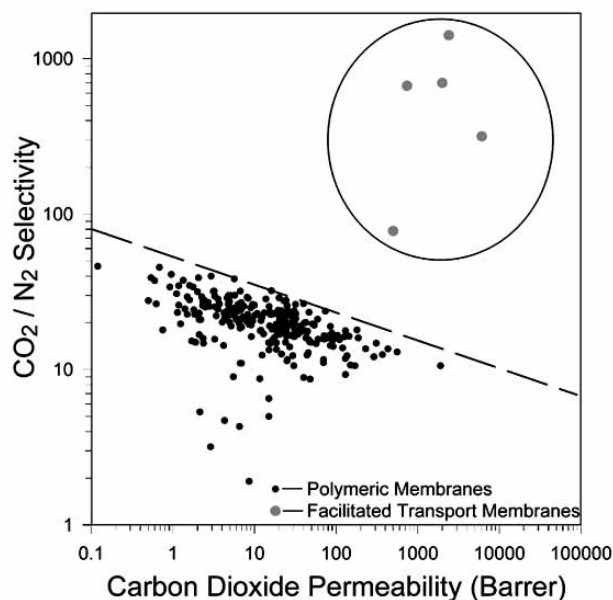
The highly selective nature of both facilitated and mixed matrix membranes means that a combination of the two may be advantageous. Kulprathipanja and Charoenphol [156] describe such a combination, with a mixed matrix membrane of polyethylene glycol in silicone rubber, within which

**Table 9. Carbon Dioxide Permeability (Barrer) and Selectivity in a Range of Mobile Carrier Facilitated Transport Membranes. Test Gases are Mixtures of 90% N<sub>2</sub> 10% CO<sub>2</sub> at 98 kPa or 75% H<sub>2</sub> 25% CO<sub>2</sub> at 300 kPa, at Ambient Temperature**

	Facilitator	CO <sub>2</sub> Permeability	Selectivity (CO <sub>2</sub> /N <sub>2</sub> )	Selectivity (CO <sub>2</sub> /H <sub>2</sub> )
Polyvinylalcohol [157]	Ethylene diamine (50 %wt)	161		26.1
Polyvinylalcohol [157]	Aminoisobutyric acid – ethylene diamine (50 %wt)	67		14.3
Vinyl alcohol - acrylate copolymer [158]	2 M K <sub>2</sub> CO <sub>3</sub>	6100	317	
Vinyl alcohol / acrylate copolymer [158]	2 M K <sub>2</sub> CO <sub>3</sub> and 0.05 M 18-crown-6	740	670	
Vinyl alcohol / acrylate copolymer [158]	2 M K <sub>2</sub> CO <sub>3</sub> and 0.05 M EDTA	2400	1417	

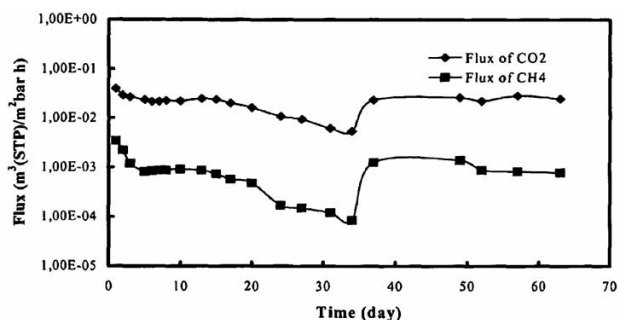
**Table 10. Carbon Dioxide Permeability (Barrer) and Selectivity in a Range of Mobile, Fixed and Combined Carrier Facilitated Transport Membranes, for Gas Mixtures of 40/20/40 or 75/25/0 of H<sub>2</sub>, CO<sub>2</sub> with N<sub>2</sub>, at 200-300 kPa and Ambient Temperature**

	Facilitator	CO <sub>2</sub> Permeability	Selectivity (CO <sub>2</sub> /H <sub>2</sub> )
Polyvinyl alcohol [155]	Glycine (50 %wt) - polyethylenimine (25 %wt)	194	28
Polyvinyl alcohol (cross linked formaldehyde) [155]	Glycine (50 %wt) - polyethylenimine (25 %wt)	186	31
Polyvinylalcohol (cross linked) [155]	Dimethylglycine (23.6 %wt) - polyethylenimie (23.6 %wt)		602
Polyvinylalcohol (cross linked formaldehyde) [155]	(23.6 % wt) Dimethylglycine - polyethylenimine (23.6 %wt) - KOH (6.4 %wt)	338	1782
Polyvinylalcohol (cross link) [155]	Aminoisobutyric acid (27.2 %wt) - polyallylamine (10.1 %wt) - KOH (16.8 %)	6196	262
Polyvinylalcohol (cross link) [155]	Aminoisobutyric acid (19.6 %wt) - polyallylamine (9.8 %wt) - KOH (18.1 %wt)	8278	170

**Fig. (11).** Carbon Dioxide permeability against selectivity relative to nitrogen of facilitated transport membrane examples presented here, grey, and polymeric membranes, black [9], with Robeson's upper bound on performance.

inorganic particles (0.1 - 200  $\mu\text{m}$ ) are dispersed. Examples are activated carbon, zeolites, alumina and silica. The mobile facilitator is carbonate and improves the selectivity of the membrane.

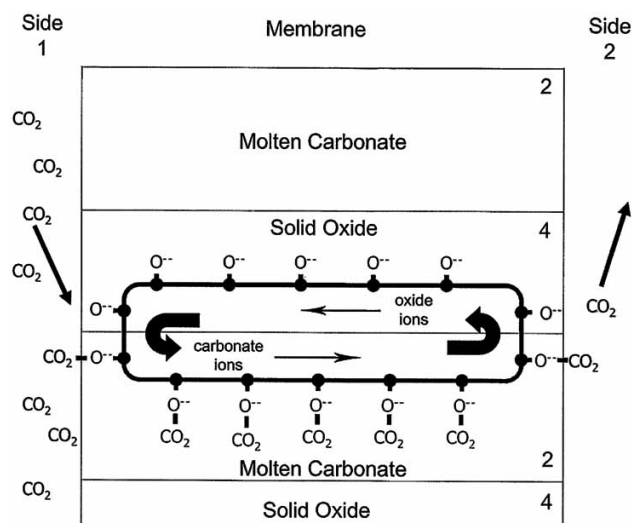
One of the restrictions of facilitated transport membranes is their inability to operate at high feed temperatures due to evaporation problems. Indeed in the mixed carrier membranes performance drops off substantially above 100°C due to evaporation losses which shuts down the transport process within the membrane. Lackner *et al.* [159] overcomes this by using a molten carrier phase within a porous solid oxide structure. In this non-polymeric system carbon dioxide reacts

**Fig. (12).** Changes in facilitated transport membrane flux over time, at the 35 day mark the feed is altered to be wet, which rehydrates the membrane (reproduced from [148]).

on the feed side with a molten carrier, such as potassium carbonate, diffuses through the molten carbonate channels within the solid oxide structure, and is released on the permeate side. The corresponding oxide anion is transferred back through the oxide support, schematically shown in Fig. (13). This novel design allows the facilitator mechanism to operate at high temperatures, above the melting point of the carrier, for carbonates 600-900°C. Thus, facilitator membrane separation can be applied to processes such as partial combustion recycle, or syngas production, which are not available to polymeric membranes. While, the quoted selectivity of 5, with values up to 500 possible, are small compared to previously mentioned facilitated membrane patents, the advantage of operating at high temperature is attractive and more patents in this area will be seen over the coming years.

### 3.4. Membrane Gas Absorption

Membrane gas absorption (MGA) is a hybrid of membrane and solvent separation that seeks to exploit the advantages of both processes [160-162]. MGA involves the transfer of carbon dioxide through a non-selective membrane before chemically absorption into a solvent, Fig. (14). The polymeric membrane facilitates a controlled flow of gas into

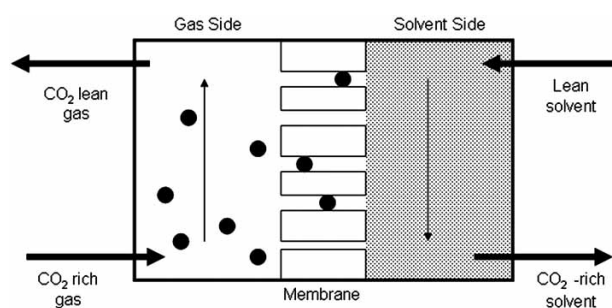


**Fig. (13).** Schematic of molten carbonate facilitated transport membrane for high temperature [159].

the solvent and provides high gas-liquid contact surface area. This physical separation of the liquid and gas flows eliminates foaming and channelling problems that can occur in classical solvent absorption processes.

Early patents in MGA studied the removal of acid gases [163, 164], and this has been developed in recent years for specific carbon dioxide separation. The focus of the majority of research has been on solvent development. For a solvent to be acceptable, it must be able to absorb carbon dioxide at relatively low partial pressures, achieve high carbon dioxide loading, as well as have low volatility and viscosity. Importantly in membrane absorption applications, it must not wet through the membrane pores, as this leads to inefficient mass transfer. Further, it must be inert towards the membrane material. Amine based solvents [165], such as monoethanolamine (MEA), diethanolamine and methyldiethanolamine, are the industry standard for column-based solvent absorption but are known to cause pore wetting and membrane degradation in MGA applications. Other examples are potassium carbonates and hydroxide solutions [166]. Potassium carbonate is more resilient to degradation and less toxic compared to MEA. The major drawback of this solvent is the slow reaction time. This can be overcome with the addition of promoters such as piperazine which improve the performance. Aqueous ammonia has also been suggested as an alternative solvent because the byproduct, ammonium bicarbonate, can potentially be used as a fertilizer [167]. The patent literature also covers the possibility of solvent mixtures, which alter the physical characteristics of the liquid phase to enhance absorption. Some examples are solvent compatible alcohols, esters and glycols [168, 169].

The importance of the polymeric membrane material is different for MGA compared to gas separation processes, because it has a non-selective role. Generally, the major criteria are the hydrophobicity of the membrane, pore size and chemical resistance to the solvent. The hydrophobicity of the membrane ensures wetting of the pores is minimal and therefore that mass transfer rates remain high. The dimen-



**Fig. (14).** Schematic of Membrane Gas Absorption for carbon dioxide separation.

sions of the pore are dependent on the operating characteristics, such as pressure difference across the membrane, and typically range from 0.01 to 0.1 micron [168, 169]. Some examples of patented polymeric membranes for MGA are porous polysulfone, polypropylene, Teflon, polyethylene, polyethersulfone, polyethene and polypropene [170, 171].

#### 4. CURRENT & FUTURE DEVELOPMENTS

As has been shown, the current trend in polymeric membranes is to incorporate an additional agent into the polymeric phase to improve separation performance. This can be another polymer (polymeric blends), particulate matter (mixed matrix membranes) or a carrier molecule (facilitated transport). Alternatively, a solvent can be used in conjunction with a polymeric membrane for the same effect (membrane gas absorption). This research will continue into the future, shifting Robeson's bound further to the upper right corner of a Permeability/Selectivity plot. However, membranes that succeed commercially need to be cheap and readily processed into hollow fibre format. Therefore, there will also be future patents awarded into manufacturing techniques, not covered in this review, that make possible the transformation of many of these novel polymeric membrane materials into acceptable industrial module designs. Future polymeric membrane research will also be focused on improving the membrane durability under adverse conditions. Future patents will be awarded for methods that improve the mechanical strength, chemical and thermal resistance, as well as reducing aging effects, without compromising performance. This can already be seen with patents awarded for a range of polymer cross-linking agents and methodologies.

Importantly, in all gas separation membrane applications minor components exist that will influence performance. Condensable vapour, such as hexane in natural gas and water in flue gas, can accumulate within the membrane matrix altering both the permeability and selectivity. Their existence within the polymer can also lead to plasticization, altering the mechanical properties of the membrane and increase the chance of membrane failure [172, 173]. Minor gas components, such as CO, NH<sub>3</sub>, H<sub>2</sub>S, SO<sub>x</sub> and NO<sub>x</sub>, found in both natural and flue gases, can also degrade the polymeric material, reducing performance and causing premature aging. However, very little research on the effect of these components has been reported in the patent literature. Therefore, given the interest in maintaining membrane performance and

the efforts to prevent membrane degradation, the study of minor component effects will be an area of interest in the near future.

To conclude, with the rapidly increasing interest in carbon dioxide capture to mitigate global warming, gas separation polymeric membranes will remain an active research area and the patented literature will continue to grow as new discoveries are made in the art.

## REFERENCES

- [1] Carapellucci R, Milazzo A. Membrane systems for CO<sub>2</sub> capture and their integration with gas turbine plants. *Proc Inst Mech Eng Part A. J Power Energy* 2003; 217: 505-517.
- [2] Thambimuthu K, Davidson J, Gupta M. CO<sub>2</sub> capture and reuse. In: *Proc. Canda; IPCC Workshop on carbon capture and storage*; 2002.
- [3] Aaron D, Tsouris C. Separation of CO<sub>2</sub> from flue gas: a review. *Separ Sci. Technol* 2005; 40: 321-348.
- [4] Rao A, Rubin E. A technical, economic and environmental assessment of amine-based CO<sub>2</sub> capture technology for power plant greenhouse gas control. *Environ Sci Technol* 2002; 36: 4467-4475.
- [5] Feron P. CO<sub>2</sub> capture: The characterisation of gas separation/removal membrane systems applied to the treatment of flue gases arising from power generation using fossil fuel. Cheltenham: IEA Greenhouse Gas R & D Programme; 1992.
- [6] Abertz V, Brinkmann T, Dijkstra M, *et al.* Developments in membrane research: from material via process design to industrial application. *Adv Eng Mater* 2006; 8: 328-358.
- [7] Basu A, Akhtar J, Rahman M, Islam M. A Review of separation of gases using membrane systems. *Petrol Sci Technol* 2004; 22: 1343-1368.
- [8] Stern S. Polymers for gas separation: the next decade. *J Membrane Sci* 1994; 94: 1.
- [9] Powell C, Qiao G. Polymeric CO<sub>2</sub>/N<sub>2</sub> gas separation membranes for the capture of carbon dioxide from power plant flue gases. *J Membrane Sci* 2006; 279: 1-49.
- [10] Mäyser G. Gas separation with polymer membranes. *Angew Chem Int Ed.* 1998; 37: 2960.
- [11] Koros W. Gas separation membranes: needs for combined materials science and processing approaches. *Macromol Symp* 2002; 188:13.
- [12] Baker R. Future directions of membrane gas separation technology. *Ind Eng. Chem Res* 2002; 41: 1393.
- [13] Graham TP. *Mag* 1866; 32: 402.
- [14] Loeb, S., Sourirajan, S.: US3133132 (1964).
- [15] Jawad M. Future for desalination by reverse osmosis. *Desalination* 1989; 72: 23-28.
- [16] Podall H. Recent advances in reverse osmosis membranes for desalination. *Chem Eng Prog* 1971; 67: 260-266.
- [17] Koros W. Gas Separation, in: *Membrane Separation Systems - Recent Developments and Future Directions* Baker RW. William Andrew Publishing; 1991.
- [18] Paul D, Yampol'skii Y. *Polymeric gas separation membranes*. baton rouge: CRC Press 1994.
- [19] Spillman R. Economics of gas separation by membranes. *Chem Eng Prog* 1989; 85: 41.
- [20] Mazur W, Chan M. Membranes for natural gas sweetening and CO<sub>2</sub> enrichment. *Chem Eng Prog* 1982; 78: 38-43.
- [21] Coady A, Davis J. CO<sub>2</sub> recovery by gas permeation. *Chem Eng Prog* 1982; 78: 43-49.
- [22] Fritzsche A, Kurz J. The separation of gases by membranes, in: *Handbook of industrial membrane technology* porter MC, editor. William Andrew Publishing 1990; 559-593.
- [23] Hill T. Surface diffusion and thermal transpiration in fine tubes and pores. *J Chem. Phys.* 1956; 25: 730-745.
- [24] Hwang S-T, Kammermeyer K. *Membrane Separations*. New York: Wiley-Interscience 1975.
- [25] Rhim H, Hwang S-T. Transport of capillary condensate. *J Colloid Interf. Sci.* 1975; 52: 174-181.
- [26] Lee K-H, Hwang S-T. The transport of condensable vapors through a microporous Vycor glass membrane. *J Colloid Interf. Sci.* 1986; 110: 544-555.
- [27] Plate N, Yampol'skii YP. Relationship between structure and transport properties for high free volume polymeric materials, in: *Polymeric Gas Separation Membranes*. Baton Rouge: CRC Press 1994; 115-208.
- [28] Kanehashi S, Nagai K. Analysis of dual-mode model parameters for gas sorption in glassy polymers. *J Membrane Sci* 2005; 253: 117-138.
- [29] Favre E. Carbon dioxide recovery from post-combustion processes: Can gas permeation membranes compete with absorption? *J Membrane Sci* 2007; 294: 50-59.
- [30] Hendriks C. *Carbon dioxide removal from coal-fired power plants*. Dordrecht: Kluwer Academic Publishers; 1994.
- [31] Roberts C., Gibbins J.R., Panesar R., Kelsall G. Improvement in power generation with post-combustion capture of CO<sub>2</sub>. Cheltenham: IEA Greenhouse Gas R & D Programme; 2004.
- [32] Robeson L. Correlatoin of separation factor versus permeability for polymeric membranes. *J Membr Sci* 1991; 62: 165-185.
- [33] Saufi S, Ismail A. Fabrication of carbon membranes for gas separation - a review. *Carbon* 2004; 42: 241-259.
- [34] Watson, E.R., Rowley, G.V., Wunderlich, C.R.: US3432585 (1969).
- [35] Lee, M.-S., Choi, S.-H., Shin, Y.-C.: US20030134550 (2003).
- [36] Hoehn, H.H., Richter, W.J.K.: US3899309 (1975).
- [37] Hoehn, H.H.: US3822202 (1974).
- [38] Bentz, F., Elfert, K., Kunzel, H.E., Wolf, G.D.: US4217227 (1980).
- [39] Richter, W.J.K., Hoehn, H.H.: DE1941022 (1970).
- [40] Richter, W.J.K., Hoehn, H.H.: DE1941932 (1970).
- [41] Steadly, H., Laccetti, A.J.: US4770777 (1988).
- [42] Hayes, R.A.: US5076817 (1991).
- [43] Harris, J.E., Berger, A., Chopdekar, V.M., Matzner, M., Spanswick J.: US4713438 (1987).
- [44] Manos, P.: EP0219878 (1987).
- [45] Richter, W.J.K., Hoehn, H.H.: US3567632 (1971).
- [46] Sanders, E.S.J., Wan, H.S., Beck, H.N.: US4975228 (1990).
- [47] Sanders, E.S.J., Overman, D.C.: EP0500974 (1992).
- [48] Beck, H.N., Sanders, E.S.J., Lipscomb, G.G.: US4962131 (1990).
- [49] Anada, J.N., Feay, D.C., Bales, S.E., Jeanes, T.O.: EP0242147 (1987).
- [50] Jeanes, T.O.: EP0316960 (1989).
- [51] Chen, N., Tien, C.-F., Patton, S.M.: US5232471 (1993).
- [52] Tien, C.-F., Surnamer, A.D.: EP0455216 (1991).
- [53] Pedretti, U., Gandini, A., Roggero, A., Sisto, R., Valentini, C., Assogna, A., Stopponi, A.: US5169416 (1992).
- [54] Laverty, B.W., Vujosevic, R., Dang S., Yao B., Matsuura T., Chowdhury G.: GB2334526 (1999).
- [55] Percec, E.S., Li, G.S.: US4596860 (1986).
- [56] Li, G.S.: US4586939 (1986).
- [57] Farias, O., Gandini, A., Monga, R., Roggero, A., Sisto, R., Valentini, C.: EP0360318 (1990).
- [58] Hachisuga, H.: JP11342322 (1999).
- [59] Hachisuga, H., Matsumoto, K., Obara T.: JP6238138 (1994).
- [60] Illing, G.: DE19936044 (2001).
- [61] Koros, W.J., Walker, D.R.B.: US5262056 (1993).
- [62] Chiao, C.C.: US4717395 (1988).
- [63] Bikson, B., Coplan, M.J., Goetz, G.: US4508852 (1985).
- [64] Coplan, M.J., Park, C.H., Williams, S.C.: US4414368 (1983).
- [65] Rose, J.B.: US4268650 (1981).
- [66] Rose, J.B.: US4273903 (1981).
- [67] Quentin, J.: US4054707 (1977).
- [68] Quentin, J.: US3709841 (1973).
- [69] Chiao, C.C.: US4828585 (1989).
- [70] Bourganel, J.: US4026977 (1977).
- [71] Graefe, A.F., Saltonstall, C.W.J., Schell, W.J.: US3875096 (1975).
- [72] Kawakami, J.H., Bikson B., Gotz, G., Ozcaayir, Y.: EP0426118 (1991).
- [73] Hayes, R.A.: US4880442 (1989).
- [74] Hayes, R.A.: US4717393 (1988).
- [75] Hayes, R.A.: US4705540 (1987).
- [76] Kohn, R.S., Coleman, M.R., Chung, T.-S.: US5055116 (1991).
- [77] Macheras, J.T.: US5635067 (1997).
- [78] Black, L.E., Boucher, H.A.: US4571444 (1986).
- [79] Wan, W.-K.: US4836927 (1989).
- [80] White, L.S.: US20016180008 (2001).
- [81] Carlsen, D.B., Andrus, R.G., Hall, R.T.: US5605627 (1997).
- [82] Ekiner, O.M., Simmons, J.W.: WO9405404 (1994).
- [83] Weinberg, M.G.: EP0554862 (1993).

- [84] Iwama, A., Iwahori, H., Kazuse, Y.: US4358378 (1982).
- [85] Makino, H., Nakatani, M.: US4690873 (1987).
- [86] Alegranti, C.W.: US4113628 (1978).
- [87] Pfeifer, J., Ciba, G.A.: EP0141781 (1985).
- [88] Makino, H., Yoshihiro, H.T., Shimazaki, H.: US4370290 (1983).
- [89] Makino, H., Kusuki, Y., Harada, T., Shimazaki, H., Isida, T.: US4528004 (1985).
- [90] Makino, H., Kusuki, Y., Harada, T., Shimazaki, H., Isida, T.: US4474858 (1984).
- [91] Shimatani, S., Yamamoto, M., Shimazu, A., Iwama, A.: US4964887 (1990).
- [92] Blinka, T.A., Itatani, H., Wang, I.-F.: US5042992 (1991).
- [93] Jeunes, T.O., Summers, J.D., Sanders, E.S.J.: US4988371 (1991).
- [94] Chung, T.-S., Chng, M.L., Shao, L.: US2004017753 (2004).
- [95] Lee, Y.-M., Park, H.B., Lee, C.-H.: US20040236038 (2004).
- [96] Maeda, M.: US5969087 (1999).
- [97] Simmons, J.W.: WO0249747 (2002).
- [98] Langsam, M.: US5939520 (1999).
- [99] Sakellaropoulos, G.P., Kaldis, S.P., Kapantaidakis, G.C., Dabou, X.S.: EP0778077 (1997).
- [100] Ekiner, O.M., Simmons, J.W.: US20060156920 (2006).
- [101] Hsieh H. Inorganic membranes. *Membr Mater Proc* 1990; 84: 91.
- [102] Iwahara, H., Yamaji, T., Azuma, S.: JP56041804 (1981).
- [103] Oshima, H., Seki, Y.: JP8071385 (1996).
- [104] Shreiber, E.H., Eardley, E.P., Srinivasan, V., van Hassel, B.A., Shah, M.M.: US20026623714 (2002).
- [105] Ku, A.Y.-C., Ruud, J.A., Molaison, J.L., Schick, L.A., Ramaswamy, V.: WO07037933 (2007).
- [106] Gobina, E.: US2006112822 (2006).
- [107] Ku, A.Y.-C., Ruud, J.A., Molaison, J.L., Schick, L.A., Ramaswamy, V.: WO07037933 (2007).
- [108] Dyer A. *An Introduction to Zeolite Molecular Sieves*. New York: J Wiley & Sons 1988.
- [109] Guiver, M.D., Robertson, G.P., Thi, H.N.L.: CA2421875 (2004).
- [110] Suzuki, H.: EP0180200 (1986).
- [111] Berger, C.: US3567666 (1971).
- [112] McKeown, N.B., Budd, P.M., Msayib, K., Ghanem, B.: WO05012397 (2005).
- [113] Young, J.S., Long, G.S., Espinoza, B.F.: WO06028594 (2006).
- [114] Davis, H.J., Thomas, N.W.: US4020142 (1977).
- [115] Dye, R.C., Jorgensen, B., Pesiri, D.R.: US20046681648 (2004).
- [116] Wang, H., Yeager, G.W.: US2007056901 (2007).
- [117] Ekiner, O.M., Simmons, J.W.: US2006196355 (2006).
- [118] Seo, Y.: US2007185264 (2007).
- [119] Ismail A., David L. A review on the latest development of carbon membranes for gas separation. *J Membrane Sci* 2001; 193: 1-18.
- [120] Soffer, A., Koresh, J.E., Saggy, S.: US4685940 (1987).
- [121] Rao, M.B., Sircar, S., Golden, T.C.: US5104425 (1992).
- [122] Rao, M.B., Sircar, S., Abrado, J.M., Baade, W.F.: US5354547 (1994).
- [123] Rao, M.B., Sircar, S., Golden, T.C.: US5431864 (1995).
- [124] Lee, Y.M., Park, H.B., Seo, I.Y.: KR008782 (2002).
- [125] Foley, H.C., Rajagopalan, R., Merritt, A.R.: US2007017861 (2007).
- [126] Lee S. *Handbook of alternative fuel technologies*. New York: Taylor & Francis 2007.
- [127] Hagg, M.-B., Lie, J.A.: WO07017650 (2007).
- [128] Zimmerman C, Singh A, Koros W. Tailoring mixed matrix composite membranes for gas separation. *J Membrane Sci* 1997; 137: 145.
- [129] Mahajan R, Zimmerman C, Koros W. Fundamental, practical aspects of mixed matrix gas separation membranes. *ACS Symp Series* 1999; 733: 277.
- [130] Rojey, A., Deschamps, A., Grehier, A., Robert, E.: US4925459 (1990).
- [131] Rhone, P.: FR2079460 (1971).
- [132] Hasse, D.J., Kulkarni, S.S., Corbin, D.R.: US2003089227 (2003).
- [133] Sterzel, H.-J., Sanner, A.: EP0154248 (1985).
- [134] Kulprathipanja, S., Neuzil, R.W., Li, N.N.: US5127925 (1992).
- [135] Kulkarni, S., Hasse, D.J., Corbin, D.R., Patel, A.N.: US20036508860 (2003).
- [136] Grose, R.W., Flanigen, E.M.: US4061724 (1977).
- [137] Kulkarni, S., Ekiner, O.M., Hasse, D.J.: US2005230305 (2005).
- [138] Kulprathipanja, S., Charoenphol, J.: US2003089228 (2003).
- [139] Te, H.H.J.C., Mulder, M.H.V., Smolders, C.A., Bargeman, D., Schroder, G.A., Setec, B.V.: EP0254759 (1988).
- [140] Henis, J.M.S., Tripodi, M.K.: US4230463 (1980).
- [141] Marand, E., Kim, S.: US2007022877 (2007).
- [142] Freeman, B.D., Matteucci, S., Lin, H.: US2007137477 (2007).
- [143] Kulkarni, S., Hasse, D.J.: US2007199445 (2007).
- [144] Ekiner, O.M., Fleming, G.K.: US5468430 (1995).
- [145] Vu D, Koros W, Miller S. Mixed matrix membranes using carbon molecular sieves. *J Membrane Sci* 2003; 211: 335.
- [146] Miller, S.J., Yuen, L.-T.: US2005043167 (2005).
- [147] Miller, S.J., Kuperman, A., Vu, D.Q.: US2006107830 (2006).
- [148] Hagg, M.-B., Kim, T.-J., Li, B.: WO05089907 (2005).
- [149] Gen, E.: GB1076438 (1967).
- [150] Gen, E.: GB1167797 (1967).
- [151] Sirkar, K.K., Kovvali, S., Chen, H.: WO03008070 (2003).
- [152] Kovvali A, Chen H, Sirkar KK. Dendrimer Membranes: A CO<sub>2</sub>-Selective Molecular Gate. *J Am Chem Soc* 2000; 122: 7594-7595.
- [153] Wang, Z., Wang, S., Lu, Q.: CN1363414 (2002).
- [154] Ho, W.S.W.: US20006099621 (2000).
- [155] Ho, W.S.W.: WO06050531 (2006).
- [156] Kulprathipanja, S., Charoenphol, J.: WO03039728 (2003).
- [157] Ho, W.S.W.: US5611843 (1997).
- [158] Nakabayashi, M., Okabe, K., Mishima, T., Mano, H., Haraya, K.: EP0638353 (1995).
- [159] Lackner, K., West, A.C., Wade, J.L.: WO06113674 (2006).
- [160] Qi Z, Cussler EL. Microporous hollow fibres for gas absorption II: Mass transfer across the membrane. *J Membrane Sci* 1985; 23: 333-345.
- [161] Feron P, Jansen A, Klaassen R. Membrane technology in Carbon Dioxide removal. *Energy Conv Man* 1992; 33: 421-428.
- [162] Yeon S-H, Lee K-S, Sea B, ParkY-I, Lee K-H. Application of pilot-scale membrane contractor hybrid system for removal of carbon dioxide from flue gas. *J Membrane Sci* 2005; 257: 156-160.
- [163] Thakore, Y.B., Stoy, V.: US4954145 (1990).
- [164] Ward, W.J.: US4147754 (1979).
- [165] Lee, G.S., Lee, G.H., Park, Y.I., Seo, B.G., Yoen, S.H.: KR0042656 (2004).
- [166] Baba, T., Fukazama, T., Nishino, Y.: JP3218912 (1991).
- [167] Yuan H.: US2007163432 (2007).
- [168] Birbara, P.J., Nalette, T.A.: US5281254 (1994).
- [169] Jansen, A.E., Feron, P.H.M.: US5749941 (1998).
- [170] Feron, P.H.M., Jansen, A.E.: NL9400483 (1995).
- [171] Hesse, H.J.F.A., Smit, M.J., du Toit, F.J.: US20016312655 (2001).
- [172] Al-Juaied M, Koros W.J. Performance of natural gas membranes in the presence of heavy hydrocarbons. *J Membrane Sci* 2006; 274: 227-243.
- [173] Vu DQ, Koros WJ, Miller SJ. Effect of condensable impurities in CO<sub>2</sub>/CH<sub>4</sub> gas feeds on carbon molecular sieve hollow-fiber membranes. *Ind Eng Chem Res* 2003; 42: 1064-1075.