

## CO<sub>2</sub> Separation from Flue Gases Using Different Types of Membranes

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### Abstract

The emission of greenhouse gases such as CO<sub>2</sub> is the main cause of global warming. Its separation from different emission sources such as chemical industries, power stations etc. to reduce greenhouse effect has been a mutual interest of the world. Conventional processes such as absorption, cryogenic distillation and adsorption used for this purpose but there are some drawbacks such as high energy consumption, process complexity and high capital cost are major issues which need some efficient alternative technique to be worked on. The developing technique such as Membrane separation is highly compact, energy efficient, environmental friendly, scale-up flexible and possibly more economical than previously well-established technologies. The purpose of this review is to classify membrane separation process used for CO<sub>2</sub> gas separation from flue gases. This review covers introduction of membrane including polymeric and inorganic membranes, provide recent advancements such as mixed matrix membranes, facilitated transport membranes and carbon membranes which have improved permeability and selectivity. This review also portrays the basic differences between different types of membranes used for CO<sub>2</sub> separation, highlighted operating conditions for different membranes and mention further research possibilities in this field.

**Keywords:** Membrane separation; Polymeric membrane; Inorganic membrane

### Introduction

The separation of CO<sub>2</sub> from flue gases has greatly enhanced greenhouse effect. Presence of gases particularly CO<sub>2</sub> continuously increased earth temperature. Its decrease greatly reduces global warming [1]. CO<sub>2</sub> is mainly found in fuel gas from combustion of fossil fuel, coal gasification and natural gas streams. CO<sub>2</sub> gas due to its acidity reduces the calorific value of gas streams, makes it corrosive, and so causes problems for gas compression and transportation. Natural gas in pipelines contains less than 2% CO<sub>2</sub> to avoid corrosiveness [2]. Keeping in view of this problem there are various methods invented to reduce CO<sub>2</sub> in gas streams before it is compressed. On the other hand CO<sub>2</sub> can be used for enhanced oil recovery where liquid CO<sub>2</sub> is injected into the reservoir to increase the flow of oil, therefore increase the productivity of reservoir. CO<sub>2</sub> level in atmosphere can be reduced by injecting it deep into ocean or depleted well [3] so economically and technically sound methods are needed for CO<sub>2</sub> removal and capture.

Conventional methods for CO<sub>2</sub> separation include chemical absorption with a monoethanolamine (MEA) solvent, cryogenic fractionation, and adsorption using molecular sieves. Although these methods are mature but their equipment complexity, energy consumption and capital cost is high. So, an alternative method membrane separation attracted the scientific community due to its high CO<sub>2</sub> capture efficiency, simple process design, easy scale up, low energy consumption and lower capital cost [4].

This technology is commercially available for gas purification in 1980 [5]. Over the past years several studies are conducted in searching optimum membrane materials, membrane casting techniques and

membrane module configurations for gas separation. Efficiency of membrane decreases with the passage of time which is the biggest challenge for industries.

Nevertheless, this technique is very competitive technology for CO<sub>2</sub> separation from CH<sub>4</sub>. Membrane can never act as a perfect separating device, though from the literature study it has no of advantages compare to conventional process [6-8].

The idea of membrane separation was originated in 1866 by graham [9] with loeb and sourirajan further strengthen this field by proposing anisotropic membrane [10]. The major contribution of gas separation was done in 1980s and 1990s by seporex, generon and cynara [11,12]. These developments make gas separation by membrane a competitive device in industrial sector. Now this technology is widely used in industries for gas sweetening of natural gas to remove CO<sub>2</sub>.

Two properties of membrane dictate its performance: 1) Flux 2) selectivity. Membrane separation process depends upon of five mechanisms of separation including molecular sieving, Knudsen diffusion, solution diffusion, surface diffusion and capillary condensation (Figure 1). Among which solution diffusion and molecular sieving are the leading ones. Knudsen diffusion occurs when radius of pore is less than mean free path of gas molecules; molecules strike with pore walls more than with each other, then absorb and reflected in random direction. The separation is achieved on the basis of different mean free path of gas molecules which depend upon its molecular weight. Surface diffusion depends on the interaction manner of gas molecules which are adsorbed with the pore surface. The separation is achieved on the interaction level. At low vapor pressure partial condensation of gas molecules begin which have high diffusing capability than non- adsorbed gas components known as capillary condensation [13-15]. CO<sub>2</sub>/N<sub>2</sub> selectivity is greater than unity, as selectivity is related to the inverse of square root of molecular

weight. Polymer membranes are usually dense and a phenomenon is explained by solution diffusion model.

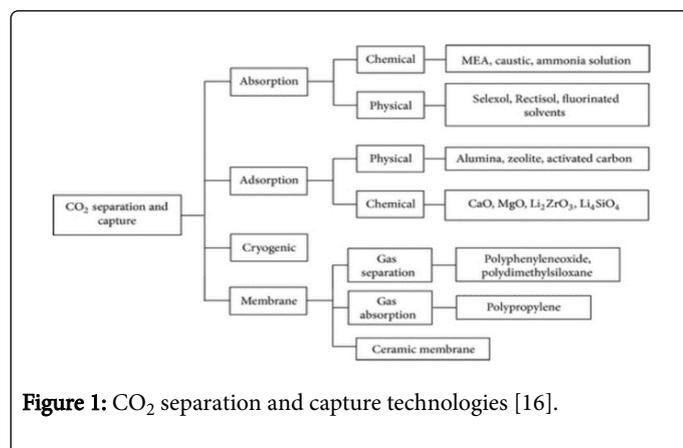


Figure 1: CO<sub>2</sub> separation and capture technologies [16].

The permeability is the product of diffusion coefficient and sorption coefficient. Diffusion coefficient represents kinetic description that reflects the environmental conditions on the permeating molecules. Sorption coefficient is relating component concentration in fluid phase with the polymeric phase. Thermodynamics can be used to find solubility of gases in membrane polymeric phase. Generally changes in membrane material effects diffusion coefficient more than the sorption coefficient.

Permeability is also related to permeation rate in case of ideal gases which is given as

$$P/I = Q/(\Delta P) \quad (1)$$

Where P is permeability, I refer to membrane thickness;  $\Delta P$  is pressure difference which is the driving force.

Although non-porous inorganic membranes can be in practice, but mostly porous inorganic membranes are used which are explained by pore flow model in which transportation of permeants take place through pressure driven convective flow. Characterization of polymeric membrane is based on glass transition temperature. Polymeric membrane refers to rubbery when it is operated at temperature above glass transition temperature and refers to glassy when it is operated at temperature below glass transition temperature. Rubbery state makes the polymer soft and elastic, and glassy state makes it tough and rigid.

This review starts with the brief introduction of membrane process, then covers the recent development in membrane process and advances in membrane design to capture CO<sub>2</sub> from flue gases. In particular this review focuses on latest membrane designs such as facilitated transport membrane and mixed matrix membranes which perform improved separations over simple polymeric membrane. Other membranes designs also discussed in this review.

## Membrane Technology used for CO<sub>2</sub> Separation

### Polymeric membranes

Earlier Cellulose acetate and its derivatives are used for CO<sub>2</sub> separation. These membranes consist of thin dense selective skin layer on less dense non-selective porous support. Porous support provides mechanical strength against high pressure. This type of membrane is called asymmetric membrane.

Flux of CO<sub>2</sub> decrease with time due to plasticization effects. High performance of CO<sub>2</sub> separation polymeric membranes can be achieved by increasing the solubility of CO<sub>2</sub> in membrane and increasing the CO<sub>2</sub> diffusion through membrane. Solubility can be increased by through changes in polymer composition and CO<sub>2</sub> diffusion can be increased by increasing free space volume. Free volume can be increased by the insertion of bulk substitution groups, improve membrane casting methods and annealing conditions [17].

Some Patented polymeric membranes follow these approaches are polyaniline [18-20], polypyrrolones [21] and polyarylates [22,23] Polysulfone is very chemically and thermally stable polymeric for gas separation with high selectivity and high permeability [24,25].

Recent patent have more focused on composite polymeric membranes. These membranes consist of glassy segment which is hard and rubbery segment which is soft. Hard polymeric segment makes the structural backbone and soft or rubbery segment makes a thin film on hard support. The resultant membranes have high selectivity due to dense skin layer and high permeability due to porous support. Blends of polyimide shows very high performance [26-29].

### Inorganic membranes

Inorganic membranes due to its stability at high temperature present an attractive way of gas separation. It can be classified into porous and non-porous. Non-porous inorganic membrane such as palladium is mostly used for separation of hydrogen. Non-porous membrane is costly compare to porous but its selectivity is high relative to porous.

Knudsen diffusion, surface diffusion and surface adsorption dominate when pore diameter decreases as seen in Figure 2. Adsorption becomes viewable when pore diameter decreases below 100Å°. Significant adsorption of gas takes place particular the effect is more enhance if gas is condensable.

Simple molecular sieving is not possible in case of CO<sub>2</sub> due to smaller gas molecules of H<sub>2</sub>. In this case a functional layer is added onto the casting thin layer having high affinity for the CO<sub>2</sub> is a possible solution, so saturation occur and surface diffusion occurs which increases the permeability of CO<sub>2</sub>. Recent studies shows high CO<sub>2</sub> permeability, when functional layer ratio 3 is added onto porous separating layer such as silica or zirconia [30].

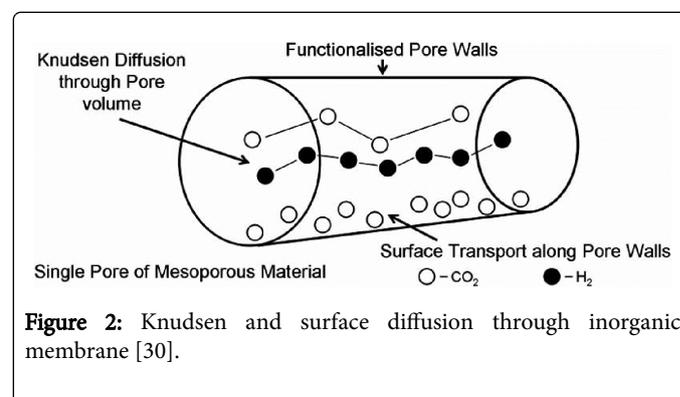


Figure 2: Knudsen and surface diffusion through inorganic membrane [30].

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## Recent Development in Membrane for CO<sub>2</sub> Separation

### Carbon membranes

The use of carbon membranes for gas separation emerges in 1970. Carbon membranes are very famous among inorganic membranes due to its molecular sieving characteristics which play a vital role in gas separation [31]. Carbon membranes have high selectivity, high permeability and high stability in corrosive and harsh environments, so it is becoming more attractive for gas separation [32]. Carbon membranes have high cost compare to polymeric membranes so, the performance of carbon membranes must be high to compensate their high cost [32,33]. Carbon membranes prepared from 6FDA-mPDA/DABA have shown high permeability and performance compared to other polymers [34,35].

Optimization of fabricated parameters is done to achieve high performance for carbon membranes. Carbon membranes have high permeability and selectivity compare to polymeric membranes for CO<sub>2</sub> separation from fuel gas systems [32]. Carbon membranes have very high permeability and selectivity compare to polymeric membrane for CO<sub>2</sub> separation from fuel gas systems [36].

These membranes show high brittleness as compared to polymeric membranes. Brittle behavior decreases its separation performance [36]. Pyrolysis is the main step for carbon membrane preparation and this determine its separation ability for gases like CO<sub>2</sub> [37]. Pyrolysis of thermosetting polymers like, cellulose, cellulose triacetate, saran copolymer, polyacrylonitrile (PAN) and phenol formaldehyde produce carbon membranes [38].

Carbon membranes can be produced from pyrolysis process by using elements having carbon such as graphite, plants etc. under controlled inert atmosphere. Different precursors play a significant role in this process including polyimide and their derivatives, phenolic resin, polyfurfuryl alcohol (PFA), polyvinylidene chloride-acrylate terpolymer (PVDC-AC), phenol formaldehyde, polyacrylonitrile (PAN), cellulose etc. [32].

Separation through porous membranes consists of four phenomena naming capillary condensation, Knudsen diffusion, surface diffusion and molecular sieving. Carbon membranes predominantly follows molecular sieving phenomena (Figure 3) [39,40].

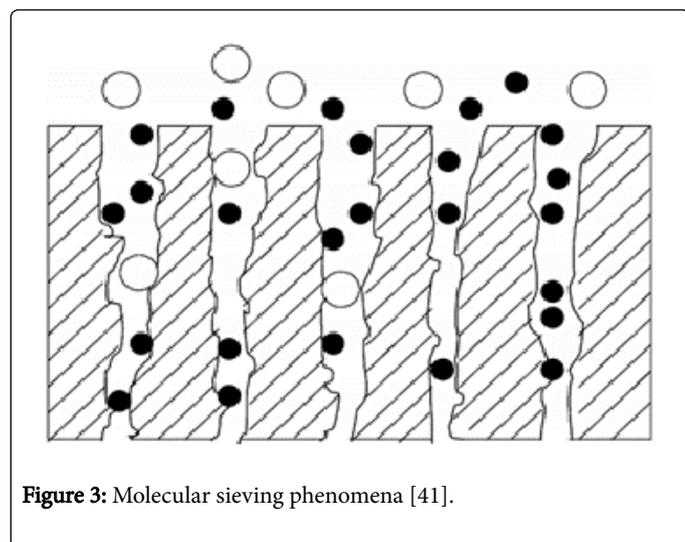


Figure 3: Molecular sieving phenomena [41].

Carbon matrix contains constrictions in molecular transport that obstruct the larger gas molecule and permit the smaller one [41]. In case of molecular sieving the pore diameter decreases below 5-10 Å but it is very difficult to make pores of this dimension. In the constriction in carbon matrix there are repulsive and dispersive forces present. As the pore size becomes smaller repulsive forces dominate and molecules close to pore size are passes, and rest of them is blocked [42]. Carbon molecular sieves depend on the surface properties, internal surface area and pore dimensions, while in case of polymers bulk properties are more important [43].

Carbon membrane can be used in different types of modules i.e. flat sheet, capillary, hollow fiber depending on the application (Figure 4).

Ogawa, et al. has demonstrated the effect of gelation conditions on the carbonized membrane properties. They found the specific gelation conditions: temperature 275K, pH 9.4 and time 6h which shows high permeance of CO<sub>2</sub> and high CO<sub>2</sub>/CH<sub>4</sub> permselectivity. They summarized that Adsorption effects described transport of CO<sub>2</sub> and molecular sieving effect described transport of CH<sub>4</sub> [44].

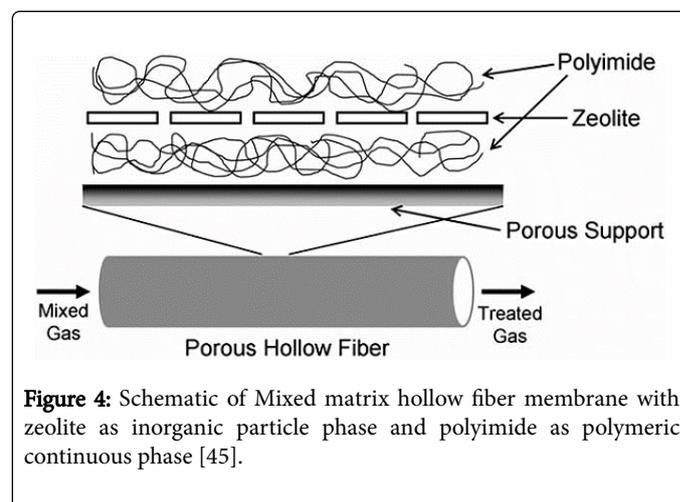


Figure 4: Schematic of Mixed matrix hollow fiber membrane with zeolite as inorganic particle phase and polyimide as polymeric continuous phase [45].

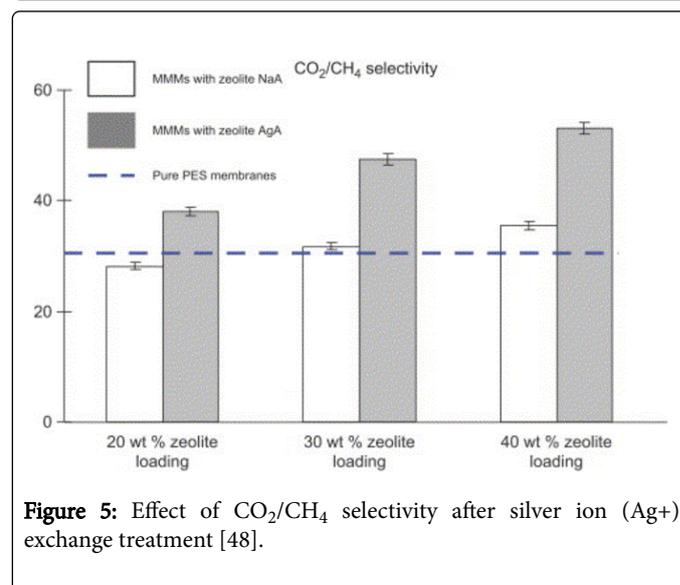


Figure 5: Effect of CO<sub>2</sub>/CH<sub>4</sub> selectivity after silver ion (Ag<sup>+</sup>) exchange treatment [48].

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### Mixed matrix membrane

Mixed matrix membrane consists of inorganic and polymeric particle phases. Polymeric phase is usually the bulk phase while inorganic particle phase comprises the disperse phase such as nano-sized particles, zeolite etc. Due to inherent superior separation characteristics of inorganic particle phase, mixed matrix membrane give high permeability and selectivity compare to only polymeric phase membrane. Enhancement of polymeric membrane by insertion of disperse inorganic particle phase was first observed in 1970. Paul and Kemp observed that addition of 5A zeolite to polymeric membrane (polydimethyl siloxane) increases the diffusion time lag for CO<sub>2</sub> and increases separation performance [46,47].

Li et al. increase the CO<sub>2</sub> selectivity by using noble metal ions such as Ag<sup>+</sup> and Cu<sup>+</sup>. These noble metal ions change the chemical and physical properties of penetrants. CO<sub>2</sub> react with these noble metal ions and CO<sub>2</sub>/CH<sub>4</sub> selectivity increases of about 70% at 40wt% zeolite (Figure 5) [48].

Hasse et al. measured the selectivity of CO<sub>2</sub>/N<sub>2</sub> at different zeolites and using polyvinyl acetate as a continuous phase (Table 1).

Separation performance of mixed matrix membranes based on poly vinyl acetate				
Continuous Phase	Zeolite	Conc.(pph)	CO2 Permeability	Selectivity (CO2/N2)
Poly vinyl acetate			3.1	34.7
Poly vinyl acetate	4A	15	2.4	30.7
Poly vinyl acetate	KFI	20	4.9	53.6
Poly vinyl acetate	H-ZK-5	15	4.9	41
Poly vinyl acetate	Na-SSZ-13	15	4.5	41.7
Poly vinyl acetate	SAPO-34	15	4.4	44.4
Poly vinyl acetate	SAPO-44	15	4.9	51.8

**Table 1:** Selectivity of CO<sub>2</sub>/N<sub>2</sub> by using different zeolites at fixed temperature of 350°C and 410 kpa and permeability is measured in barrier [49].

Maxwell in 1973 presents a model used to find effective gas permeability in mixed matrix membrane with aspect to near unity ratio. The two-phase Maxwell model equation to effective gas permeability is as below [46].

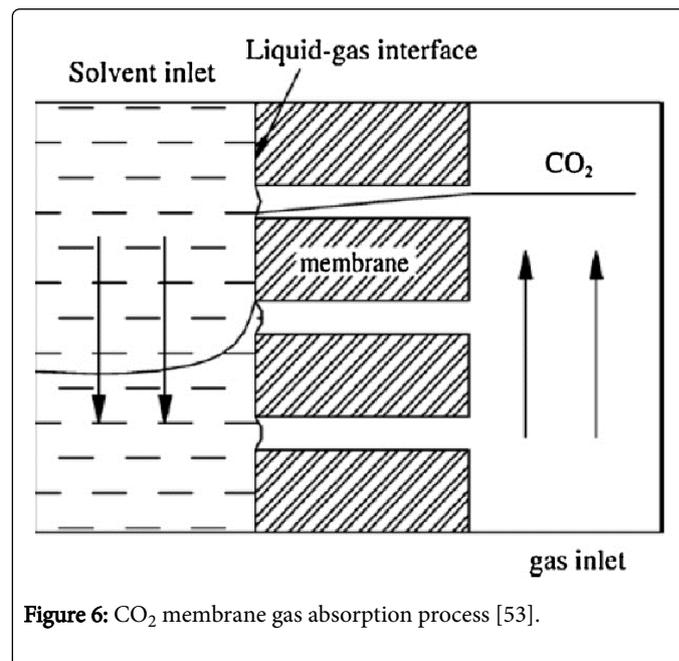
$$P_{eff} = P_c \left[ \frac{P_D + 2P_c - 2\phi_D(P_c - P_D)}{P_D + 2P_c + 2\phi_D(P_c - P_D)} \right] \quad (2)$$

Where  $\phi$  volume fraction and  $P_{eff}$  is effective gas permeability in gas membrane, D and C represents disperse and continuous phase. Other models are also used to calculate gas permeability in mixed matrix membrane like Higuchi model in 1958. Mostly Maxwell model is used to calculate gas permeability in which the disperse phase is spherical inorganic particles and polymeric material is embedded as a continuous phase [50].

The gas permeability in mixed matrix membrane depends on the intrinsic molecular sieves of inorganic material and polymeric material [51]. Inorganic particles in mixed membrane matrix can be

categorized into porous and non-porous. Some metal oxides shows good affinity to CO<sub>2</sub> like magnesium oxide etc. [52].

One of the major problems encountered in preparation of mixed matrix membrane is to disperse the inorganic particle phase into continuous polymeric phase. Sometimes this nano-sized particles formed aggregates which will weaken the membrane and cracking can occur by the application of external force. This also decreases the membrane separation performance. For example this deterioration can be observed by using zeolite as inorganic particles and glassy polymer is used as a polymeric material [52].



**Figure 6:** CO<sub>2</sub> membrane gas absorption process [53].

Chemical treatment is often very effective in eliminating this inorganic particle and polymeric interface defect. Primary is another very important method of eliminating segregation. In this method addition of small amount of polymeric material into inorganic particle solution prior to the insertion of bulk polymeric material forms a coating on the inorganic particles which prevents segregation due to insertion of bulk polymeric material into the suspension. The addition of saline coupling agent established a chemical link between polymeric and inorganic particle phases eliminating interfacial void which leads to weaken the membrane. The selection of inorganic particle chosen depends upon the compatibility with the polymeric material, which is determined by particle shape, average particle size, physical properties, particle composition, and particle dispersibility in polymeric phase [50]. There are also some other very effective techniques developed used for removal to interfacial voids [53-56].

### Facilitated transport membranes

Facilitated transport membranes are very important for improvement of selectivity without compromising on permeability. In this type of membrane reaction occurs between reactive carriers and CO<sub>2</sub> reversibly in membrane. Reactive carriers incorporated into the membrane facilitate the transport of CO<sub>2</sub> by diffusion process (Figure 6). The carrier react with CO<sub>2</sub> to form complexes, moved across the membrane towards the permeate side and release CO<sub>2</sub> by hopping phenomena described by Cussler et al., [57]. Components of gas which do not react due to insufficient contact with the carrier follow solution

diffusion model to pass towards permeate side or these will retained on retentate side. So, high permeability and selectivity can result using facilitated transport membranes. Facilitated transport membranes available in different forms such as fixed carrier membranes, liquid support membranes and fixed carrier membranes. Mobile carrier membrane shows high permeability and less stability compared to fixed carrier membranes [57,58]. Electrostatic force can be used as a tool to retained ion exchange carriers in ion exchange membrane inside membrane. The disadvantage in this type of membrane is carrier leakage. So, it is more preferred to use fixed carrier membranes which is very stable and covalently bonded with the polymer matrix [59,60]. Polyvinylamine is very good carrier for CO<sub>2</sub> is sometimes blended with PVA and cast it on porous support such as polysulfone. This shows high permeability and high selectivity. To achieve high separation performance for CO<sub>2</sub> along with high stability, simple and cheap process a blend is making with polyallylamine and polyvinyl alcohol. The chlorine present in commercial polyallylamine restricts the permeance of non-polar gases [61]. Sulfonated polybenzimidazole is also used as a material for making membrane substrate [62]. It is observed that water swollen membrane compare to dry membrane gives high permeability and selectivity [62-64].

Various studies are conducted on mobile carrier membranes to increase the stability of carrier, decrease the evaporating loss, vapor pressure and viscosity [65]. Studies on bulk flow liquid membrane is also seen in which facilitation of CO<sub>2</sub> is conducted through the permeation of carrier solution which is continuously recycle with the feed gas [66-68]. Ion exchange membrane is better than immobilized liquid membranes because carriers in ion exchange membrane are contained in membrane under the influence of electrostatic forces, IEM carriers have high stability compare to ILM. Similarly evaporation solvent can be reduced by the use of non-volatile solvent [69-72]. Long term solvent was also demonstrated from studies by the use of ionic liquids [73-76]. There is no issue about carrier instability in case of fixed carrier membrane because carriers are covalently bounded to the membrane matrix, but its permeability and selectivity are much lower than mobile carrier membranes. In fixed carrier, membrane carrier only around the equilibrium position [57]. In most cases of facilitated transport membranes feed preconditioning by moisture is very necessary in order to make it selective and increase the reaction rate between CO<sub>2</sub> and carrier, since water increase the mobility of the carriers.

A major problem with fixed carrier membrane is the decrease of CO<sub>2</sub> permeance with the passage of time due to saturation of carrier. When feed gas pressure is low and CO<sub>2</sub> permeance is high, so permeance of CO<sub>2</sub> depends mainly on transportation through carrier complexes and less on solution diffusion mechanism. While with the increase of feed gas pressure CO<sub>2</sub> permeance sharply decreases due to prominent solution diffusion mechanism compare to CO<sub>2</sub> carrier transport [77,78]. So, FTM is not recommended at low gas pressure.

### Hollow fiber membrane

With the help of hollow fiber membrane high surface area can be achieved but it costs fluxes, so hollow fiber membrane give high surface area and low fluxes. For separating CO<sub>2</sub> from flue gases mostly hollow fine fibers are used with shell side feed at high pressure of 30 to 100 bars. Polyvinylidene difluoride (PVDF), asymmetric hollow fiber membrane is very appropriate for CO<sub>2</sub> separation. In general inorganic membranes have high permeability and low selectivity but some of inorganic membranes such as Y (FAU) with alumina as support are

highly selective for CO<sub>2</sub>/N<sub>2</sub> separation. Adsorption efficiency in this process is very high compare to conventional gas adsorption process due to larger surface area for gas-liquid interface [79-81].

### Research Possibilities

In flue gases there are condensable vapors such as water and hexane present which can cause accumulation in membrane matrix changing permeability and selectivity. With this membrane mechanical strength also decreases. Also, some condensable vapors deteriorate membrane layer. These areas need active research.

Apart from this industrial life of membrane is around 4 to 5 years which needed to be reduced. The membrane module cost can be reduced by searching different cheap polymer blends.

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