Progress in carbon dioxide separation and capture: A review

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Abstract

This article reviews the progress made in CO_2 separation and capture research and engineering. Various technologies, such as absorption, adsorption, and membrane separation, are thoroughly discussed. New concepts such as chemical-looping combustion and hydrate-based separation are also introduced briefly. Future directions are suggested. Sequestration methods, such as forestation, ocean fertilization and mineral carbonation techniques are also covered. Underground injection and direct ocean dump are not covered.

Key words: coal; flue gas; carbon dioxide; sorbent; absorption; adsorption; membrane; separation; sequestration

Introduction

The 20th century has seen the rapid increase of population and explosive growth in energy consumption. As more countries becoming industrialized, it is expected that more energy will be consumed in 21st century. EIA predicts 57 percent increase of energy demand from 2004 to 2030 (EIA, 2007).

Table 1 shows the comparisons of energy use, population and per capita consumption in 1900 and 2001 (Song, 2006). In current stage over 85 percent of world energy demand is supplied by fossil fuels. Fossil-fueled power plants are responsible for roughly 40 percent of total CO_2 emissions, coal-fired plants being the main contributor (Carapellucci and Milazzo, 2003). Environmental issues due to emissions of pollutants from combustion of fossil fuels have become global problems, including air toxics and greenhouse gases (GHG). The CO_2 emission from human activity was on the order of 7 Gt/a in the late 1990's (Yamasaki, 2003). This includes the combustion of fossil fuels in all major industries and other factors such as deforestation and desertification.

Through the studies of the past five decades, particularly the past 15 years, increased GHG levels in atmosphere is believed to cause global warming. Among these GHG, CO_2 is the largest contributor in regard of its amount present in the atmosphere contributing to 60 percent of global warming effects (Yamasaki, 2003), although methane and chlorofluorocarbons have much higher green-

house effect as per mass of gases. There are increasing concerns for global warming caused by the effects of GHG, particularly CO_2. International Panel on Climate Change (IPCC) predicts that, by the year 2100, the atmosphere may contain up to 570 ppmv CO_2, causing a rise of mean global temperature of around 1.9°C and an increase in mean sea level of 38 m (Stewart and Hessami, 2005). Also accompanied is species extinction.

The total amount of carbon on earth is constant and its distribution among lithosphere, atmosphere and biosphere was relatively balanced until the advent of era of industrialized civilization. The CO_2 concentration in the atmosphere is increasing. Fig. 1 shows the change of atmospheric CO_2 level over the years between 1000 and 1997 and actual CO_2 level during 1958–2004 (Song, 2006). CO_2 level increased from 280 ppmv in 1000 to 295 ppmv in 1900 based on Antarctica ice core data. It increased to 315 ppmv in 1958 and further to 377 ppmv in 2004 based on actual data logged in Hawaii.

There are three options to reduce total CO_2 emission into the atmosphere, i.e., to reduce energy intensity, to reduce carbon intensity, and to enhance the sequestration of CO_2. The first option requires efficient use of energy. The second option requires switching to using non-fossil fuels such as hydrogen and renewable energy. The third option involves the development of technologies to capture and sequester more CO_2.

To enhance the sequestration of CO_2, options are sought to accelerate the fixation of carbon in lithosphere and biosphere, either CO_2 fixation by the enhancement of natural sinking process, such as forestation, ocean fertilization and

Table 1 World energy use, population and per capita in 1900 and 2001 (Song, 2006).

Energy source	1900 Use		2001 Use	
	MTOE[a]	% or Unit	MTOE[a]	% or Unit
Coal	501	55	2,395	24
Petroleum	18	2	3,913	39
Natural gas	9	1	2,328	23
Nuclear	0	0	662	6
Renewables[b]	383	42	750	8
Total	911	100%	1,004.8	100%
Population	1,762	Million	6,153	Million
Per capita E use	0.517	TOE[a]	1.633	TOE
Global CO_2 emission	534	MMTCE[a]	6,607	MMTCE
Per capita CO_2 emission	0.30	MTCE	1.07	MTCE
Atmospheric CO_2	295	ppmv[a]	371	ppmv
Life expectancy	47.3	Years	77.2	Years

[a] TOE: Ton oil equivalent; MTOE: million ton of oil equivalent; MMTCE: million metric ton of carbon equivalent; MTCE: metric ton of carbon equivalent; ppmv: part per million by volume. [b] including hydroelectric power, biomass, geothermal, solar and wind energy.
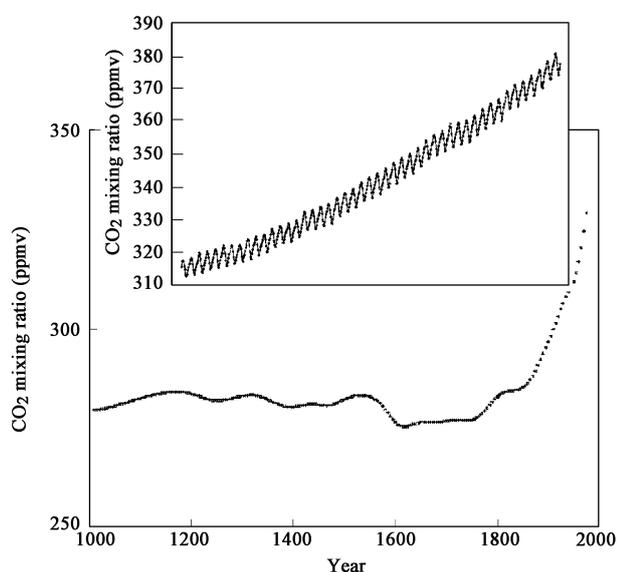
Fig. 1 Atmospheric CO_2 concentrations during 1000–2004 based on the analysis of ice cores and logged atmospheric CO_2 concentrations during 1958–2004 (Song, 2006).

mineral carbonation, or direct artificial CO_2 sequestration, such as injection into geological formations and ocean.

Carbon dioxide sequestration provides a mid-term solution to mitigate environment impacts and allows human continue to use fossil energy until renewable energy technologies mature. Since CO_2 capture and sequestration is a relatively expensive mitigation option, it can be regarded as an insurance policy (Herzog and Drake, 1996). Riahi *et al*. had a modeling study of CO_2 capture and sequestration incorporating factors of economic, demographic, energy demand and alternative policy (Riahi *et al*., 2004). They concluded that carbon capture and sequestration (CCS) is one of the obvious priority candidates for long-term technology policies and enhanced R&D efforts to protect human against the risks associated with high environmental impacts of climate changes even widespread deployment of CCS requires decades to come.

Since the CO_2 separation is the first and most energy

intensive step of CCS, many research have targeted at improving the current technologies or developing new approaches of CO_2 separation and capture. This paper reviews recent progress of CO_2 separation and capture. Various technologies are introduced although geological carbon injection and ocean dump are not covered.

1 CO_2 capture schemes for fossil-fueled power plants

In a global context, among all the industries emitting CO_2, fossil-fueled power plants generate the largest amount of CO_2 emission and that accounts for about 33–40 percent of the total (Carapellucci and Milazzo, 2003; Stewart and Hessami, 2005). CO_2 needs to be separated and captured from the flue gases of such point sources before direct sequestration. For these power plants, CO_2 separation and capture processes can be divided into several scenarios: post-combustion processes for a tradition coal-fired power plant, pre-combustion processes for gasification or reforming and oxy-fuel processes. Oxy-fuel combustion is sometimes referred to as oxy-firing or oxy-combustion. Newly emerged technologies, such as chemical-looping combustion (CLC), significantly reduce the complexity of separating CO_2 from a gas stream.

1.1 Pulverized coal combustion CO_2 separation and capture process

In this post-combustion process, CO_2 is separated from a flue gas environment containing NO_x and SO_2. Fig.2 shows this process flow (Feron and Hendriks, 2005).

One way to do post-combustion capture is to use chemical absorption, such as monoethanolamine (MEA) absorption. This technique has been widely used in natural gas industry for over 60 years. Another advantage of this technique is it produces a relatively pure CO_2 stream. Although the size and cost of the required absorber would be comparable to those of an SO_2 scrubber, the absorber would consume one-quarter to one-third of the total steam produced by the plant, reducing its generating capacity by the same amount. Also the footprint of the host plant is increased by 60% (Elwell and Grant, 2006). The National Energy Technology Laboratory (NETL) estimated in 2000 that this scheme would increase the cost of electricity production by 70% (Elwell and Grant, 2006). An alternative post-combustion CO_2 capture method is the use of membrane gas separation technologies.
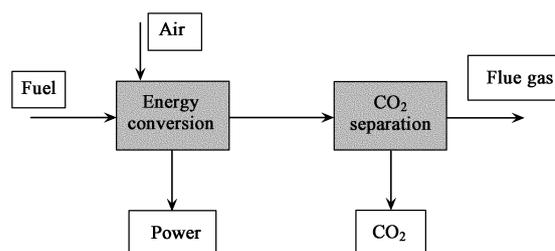
Fig. 2 Pulverized coal combustion CO_2 capture (Feron and Hendriks, 2005).

1.2 Gasification CO$_2$ separation and capture process

In this pre-combustion process, fuels are first converted into a mixture of CO$_2$ and H$_2$ through a reforming (natural gas) or gasification (coal) process and the subsequent shift-reaction. CO$_2$ can be separated from the conversion product stream and H$_2$ can then be burned in gas turbine or be used by fuel cell. Fig.3 shows this process flow (Feron and Hendriks, 2005). Gasification partially oxidizes coal to produce a gaseous fuel, which is essentially a hydrogen and carbon monoxide mixture. When syngas is used to fuel a plant similar to a traditional combined-cycle power plant, the process is referred to as integrated gasification combined-cycle (IGCC).

Several methods can be used to capture CO$_2$. The leading option for CO$_2$ capture is an absorption process, in which the solvent can be a chemical one, such as MEA absorption process, or physical one, such as pressure swing adsorption (PSA). Physical absorption is a mature technology and has been used in the Great Plains Synfuels plant in North Dakota, U.S. for 20 years (Elwell and Grant, 2006). This synfuel plant consume lignite coal and produces synthetic natural gas. Membrane technology has been used in the FutureGen power plant (Elwell and Grant, 2006).

Pre-combustion capture is potentially less expensive than post-combustion capture. IGCC power plants applying pre-combustion capture are more efficient than pulverized coal-fired plants and would be the choice for new plants. U.S. Department of Energy (DOE) estimated in 2000 that the use of pre-combustion capture would increase the cost of electricity production by 25%. The long-term goal is to reduce the production penalty to 10% (Elwell and Grant, 2006).

1.3 Oxy-combustion CO$_2$ separation and capture process

In the oxy-firing process, pure O$_2$ is separated from air and sent to energy conversion unit and combines with partially recycled flue gas of concentrated CO$_2$ to keep the furnace temperature below the allowable point. The combustion takes place in an environment of O$_2$/CO$_2$ mixture. The resulting flue gas is high-purity CO$_2$ stream. Fig.4 shows this process flow (Feron and Hendriks, 2005).

The exhaust gas stream is free of nitrogen components. Particulates and sulfur compounds are first removed from the exhaust stream using widely adopted techniques. After SO$_2$ removal, the exhaust gas stream is approximately 90% CO$_2$ by volume on a dry basis. Further separation of CO$_2$ is not necessary. CO$_2$ can then be compressed for storage or transportation.
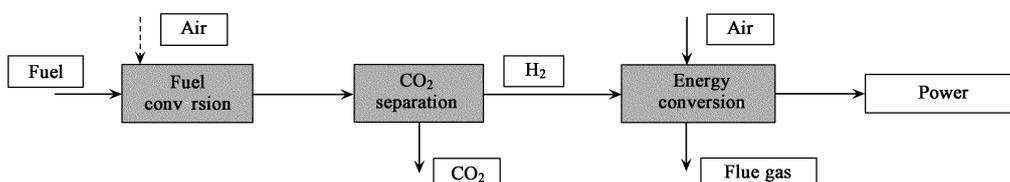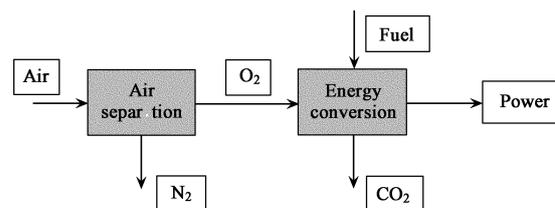

Fig. 4 Oxy-firing CO$_2$ capture process (Feron and Hendriks, 2005).

The main advantage of this technology is the elimination of NO$_x$ control equipment and the CO$_2$ separation step. The boiler size can be reduced because only oxygen is supplied for combustion. The size of subsequent equipments, such as SO$_2$ scrubber, can also be reduced. The disadvantage is the corrosion of equipment by increased SO$_2$ concentration in the exhaust gas stream.

This technology is not mature and its operating and maintenance and capital costs would be comparable to that of post-combustion technology. The capital cost is estimated to be USD $2,040/kW (Elwell and Grant, 2006). Specifically, the oxygen separation plant would consume about 23% to 37% of the total plant output and costs about the same as a chemical absorber.

1.4 Chemical-looping combustion process

Chemical-looping combustion (CLC) is a novel process with inherent CO$_2$ capture. It has also been called unmixed combustion since direct contact between fuel and combustion air is avoided. Instead, an oxygen carrier brings oxygen from air to fuel. Suitable oxygen carriers are small particles of metal oxide such as Fe$_2$O$_3$, NiO, CuO or Mn$_2$O$_3$. A basic CLC system is shown in Fig.5 (Rydén and Lyngfelt, 2006). The CLC has two reactors, one for air and one for fuel. The oxygen carrier circulates between the
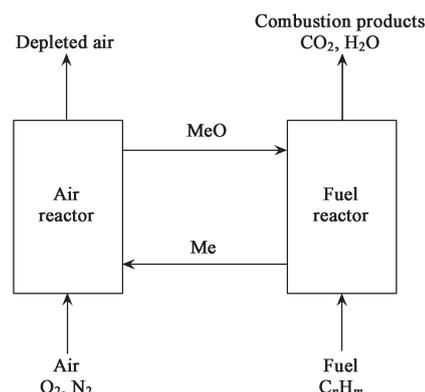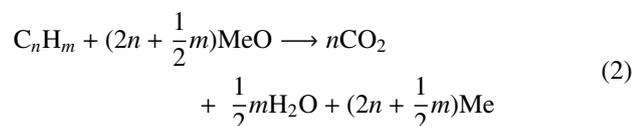

Fig. 5 Chemical-looping combustion (Rydén and Lyngfelt, 2006). Me: metal; MeO: metal oxide as oxygen carrier.

Fig. 3 Gasification CO$_2$ capture process (Feron and Hendriks, 2005).

reactors. In the air reactor, the carrier is oxidized by oxygen according the following Reaction (1). In the fuel reactor, the metal oxide is reduced by fuel, which is oxidized to CO_2 and H_2O, according to the following Reaction (2).

$$O_2 + 2Me \longrightarrow 2MeO \tag{1}$$

$$C_nH_m + (2n + \frac{1}{2}m)MeO \longrightarrow nCO_2$$
$$+ \frac{1}{2}mH_2O + (2n + \frac{1}{2}m)Me \tag{2}$$

The amount of energy released or required in the reactors depends on these two reactions, as well as the temperature of reactions. Normally, Reaction (1) is strongly exothermic. Reaction (2) is usually endothermic but for some combinations of fuel and oxygen carrier it may be slightly exothermic. In principle, all major fuels can be utilized in a CLC.

CLC has several advantages compared with conventional combustion. The exhaust gas stream from air reactor is harmless, consisting mainly of N_2. In a well-designed system, there should be no thermal formation of NO_x since the regeneration of oxygen carrier takes place without flame and at moderate temperatures. The exhaust gas from the fuel reactor consists of CO_2 and H_2O. Separation of CO_2 can be done by a condenser. This is the major advantage with CLC which avoids the huge energy penalty necessary in traditional amine scrubbing process to capture CO_2.

2 Carbon fixation

There are both natural and artificial ways to capture or fix the carbon to avoid or delay emission into the atmosphere, such as forestation, ocean fertilization, photosynthesis, mineral carbonation, and hydrate. Geological injection and direct ocean dump are not covered.

2.1 Forestation

It is estimated that 1.4±0.7 Gt-carbon is captured by terrestrial systems from atmosphere via photosynthesis (Yamasaki, 2003). Increasing this carbon flux is achieved by forestation, reforestation of arid lands and greening of deserts. At the beginning of this sequestration, the carbon flow to terrestrial vegetation is positive and the "stock" of carbon is increased. When fully developed, the net capture becomes zero because the balance of capturing and release. The potential capacity for carbon sequestration in terrestrial systems is estimated to be 5-10 Gt-carbon annually (Yamasaki, 2003).

2.2 Ocean fertilization

Ocean stores more CO_2 than terrestrial vegetation. The ocean contains about 38,000 Gt-carbon, and about 1.7±0.5 Gt is taken up annually from the atmosphere (Yamasaki, 2003). The production of phytoplankton at 50–100 Gt-carbon annually is much higher than that of terrestrial vegetation (Yamasaki, 2003). Part of the carbon would be released back into the atmosphere by respiration process, and the remaining would descend into the deeper ocean

in the form of particulate organic matter either by the death of phytoplankton or after grazing. This sequestration process could be enhanced by ocean fertilization. Ocean fertilization refers to the practice of increasing limiting nutrients to stimulate the production of phytoplankton. Ocean fertilization has been challenged to interfere with the marine ecosystem which could lead to fatal impact. In addition, the decomposition of sinking organic matters could produce other stronger greenhouse gases, such as methane or nitrogen monoxide. This method needs to be further studied before it is put into practice.

2.3 Photosynthesis process

Most of the current CCS options offer short- to mid-term solutions with associated drawbacks. For instance, geologic and oceanic injection only delays the release of CO_2 into atmosphere. Authors believe that only by switching to renewable fuels can solve the CO_2 emission problem. Biological carbon sequestration using technologies such as controlled photosynthetic reactions may help to alleviate GHG problems in a sustainable way.

Stewart *et al.* studied a system that combines solar energy collection and delivery through a fiber optic system to stimulate the growth of biological organisms in a bio-generator to produce useful by-products from carbon dioxide (Stewart and Hessami, 2005).

The photo-bioreactor system makes use of the natural photosynthesis process to convert light, heat and carbon dioxide to useful products, such as carbohydrates, hydrogen and oxygen. The type of product depends on the biological strains used in the photo-bioreactor. The following equation illustrates a photosynthetic reaction:

$$6CO_2(aq) + 6H_2O(l) + light + heat \longrightarrow$$
$$C_6H_{12}O_6(aq) + 6O_2(g) \tag{3}$$
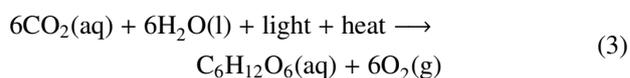
Cyanobacteria or micro-algae have been suggested to perform the role of photosynthesis. In order to promote uniform growth of the organisms, the distribution of light flux in the wavelength range of 400–700 nm needs to be delivered to the bioreactor. The efficient distribution of light throughout the photo-bioreactor will affect the carbon dioxide uptake rates. Despite 50 years of development of closed-system photo-bioreactor systems, commercial viability has not yet been achieved. At present, open pond systems produce around 100 t of biomass annually at a cost of around USD $10,000/metric ton (Stewart and Hessami, 2005).

2.4 Mineral carbonation, natural or biomimetic

Another major CO_2 fixation process in nature is the chemical weathering of rocks, such as silicates, containing calcium or magnesium. The silicate rocks could be turned into carbonates by reacting with CO_2 following this mechanism (Maroto-Valera *et al.*, 2005):

$$(Mg,Ca)_xSi_yO_{x+2y} + xCO_2 \rightarrow x(Mg,Ca)CO_3 + ySiO_2 \tag{4}$$
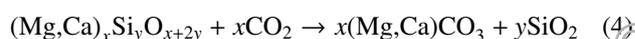
Mineral carbonation results in the storage of CO_2 in solid form as a stable, environmentally benign mineral

carbonate. The energy state of mineral carbonate is 60 to 180 kJ/mol lower than CO_2, which is 400 kJ/mol lower than carbon (Maroto-Valera *et al.*, 2005). Consequently, sequestration in the form of a carbonate ensures long-term fixation of CO_2 rather that temporary storage. Also avoided is the risk of any accidental release of stored CO_2 leaking from underground.

The weathering of rocks happens in nature over geologic time scales. Artificial ways were first proposed by Seifritz in 1990 to emulate this natural process (Liu *et al.*, 2005). Two methods are possible to accelerate the reaction rates, i.e., to enhance the dissolution of mineral ions using stronger acids, or to react under higher CO_2 pressure. This artificial process is called CO_2 mineralization, or mineral carbonation. Many researchers studied the mineral carbonation process (Druckenmiller and Marotovaler, 2005; Haywood *et al.*, 2001; Liu *et al.*, 2005; Maroto-Valera *et al.*, 2005; Stolaroff *et al.*, 2005). The capacity of this fixation is huge, even though the use of acid may cause problems in both the reaction facilities and in the environment, and higher CO_2 pressure consumes intensive energy.

The carbonation of silicate minerals by mechanochemical process was investigated by University of Utah and University of Idaho (Nelson, 2004; Nelson and Prisbrey, 2004). Natural and synthetic silicate compounds were ground for a range of times in the presence of gaseous CO_2. Studied materials include naturally-occurring materials, such as forsterite, lizardite, and wollastonite. Synthetic material magnesium silicate was also studied. It was shown that a significant change takes place in the lizardite variety of serpentine after 15 to 20 min of intense grinding in the presence of gaseous CO_2. Analyses showed that small amounts of carbon are fixed by grinding lizardite, forsterite, and wollastonite, and magnesium silicate, in the presence of gaseous CO_2. Considering the energy input to grind the materials to a size that can fix CO_2, this technology should have limited use in practice.

Maroto-Valer *et al.* studied mineral carbonation through surface activation to promote and accelerate carbonation reaction rates and efficiencies at moderate reaction conditions (Maroto-Valera *et al.*, 2005). Their results indicate that the surface area of the raw serpentine can be significantly increased through physical and chemical activation methods. The chemical activations were more effective than physical activation at increasing the surface area. Sulfuric acid was found to be the most effective acid used during the chemical activation. The steam activation promotes the CO_2 capture by serpentine. The most promising results came from the carbonation of the extracted $Mg(OH)_2$ solution, where the carbonation efficiency was estimated to be at least 53 percent.

Liu *et al.* developed a biomimetic process, in which a biological catalyst, the enzyme carbonic anhydrase, was used to accelerate an aqueous processing route to carbonate formation (Liu *et al.*, 2005). The enzyme was immobilized on chitosan-alginate beads. Simulated brine containing calcium was used to provide cations for carbonate formation. Results show carbonic anhydrase is a promising enzyme to increase the rate of precipitation of carbonate mineral, with industrial wastewater as a cation source.

According to a study performed by Haywood *et al.*, without radical alteration to the various process routes, it seems unlikely that CO_2 sequestration within a stable mineral carbonate is a realistic proposition (Haywood *et al.*, 2001). Widespread application of this technology will require a huge supply of metal oxides–sufficient to cause major impacts upon iron, manganese, chromium and nickel mining industries.

2.5 *In-situ* CO_2 capture

Hughes *et al.* explored the *in-situ* CO_2 capture using carbonation mechanism at high temperature (–700°C) at atmosphere pressure in a dual fluidized bed combustion system (Hughes *et al.*, 2005). The following reactions take place inside the reactors:

$$CaO + CO_2 \rightleftharpoons CaCO_3 \qquad (5)$$

Similar to CLC, there are two reactors in this system. Primary fuel combustion take place in the carbonator and sorbent CaO reacts with CO_2 in the same reactor achieving *in-situ* CO_2 capture. $CaCO_3$ is heated to regenerate CaO in calciner and the heat is provided by burning a secondary fuel such as petroleum coke. The overall thermal efficiency has been shown to be comparable to that of a current combustion system without CO_2 capture. CANMET has extensively studied similar approaches (Sun *et al.*, 2007; Manovic and Anthony, 2007; MacKenzie *et al.*, 2007).

2.6 Hydrate-based separations

Hydrate-based separation as a promising option is worth mentioning. This process begins by forming the hydrate by exposing the exhaust gas streaming containing CO_2 to water under high pressure. As the hydrate forms, the CO_2 is capture. Thy hydrate is then separated and dissociated, thereby releasing CO_2. This technology has an energy penalty as small as 7% (Elwell and Grant, 2006).

3 Carbon separation technical options

Capture of CO_2 contributes 75 percent to the overall CCS cost and CCS increases the electricity production cost by 50 percent (Feron and Hendriks, 2005). Although these numbers may vary with different CCS schemes, cutting the capture cost is the most important issue for the CCS process to be acceptable to the energy industry. Hence, this article mainly focuses on the progress in technologies of CO_2 separation and capture from a gas mixture from the chemical conversion point of view. There are many options for CO_2 separation and capture, and these include adsorption, absorption, membrane and biotechnology. The optimum CO_2 capture scheme could be determined by analyzing costs in the context of power generation.

The absorption/stripping process, using amine solutions such as MEA, is a commercialized technology used in natural gas industry for 60 years and is regarded as the

most mature process. The CO_2 recovery rate is 98% for MEA (Yamasaki, 2003). The stability of the amines and the energy consumption of the stripping process have large room of further improvement.

The adsorption process is based on the same principle but using porous solid adsorbents such as zeolites and activated carbon, and chemical reactions between the adsorbent and CO_2 may or may not occur during the separation process. Both pressure swing adsorption and temperature swing processes are widely used.

CO_2 adsorption/absorption capacity data from various references are summarized in Table 2.

The large-scale membrane separation process has an advantage over other processes. Membrane materials with high selectivity for CO_2 over oxygen or nitrogen have been developed, including polymeric materials and inorganic materials. Porous membranes with supporting amine solutions could be effective for the separation of CO_2 (Yamasaki, 2003). At present stage, a sufficiently high selectivity with a large flux has not been realistic for membrane separation process.

3.1 Amine absorption process

MEA absorption process is the most extensively studied CO_2 absorption system. Various aspects of MEA absorption were recently studied, such as modifying the absorbents, improve the process design, or optimizing the process operation (Abanades *et al.*, 2004; Aboudheir *et al.*, 2006; Al-Juaied and Rochelle, 2006; Bello and Idem, 2006; Goff and Rochelle, 2006; Idem *et al.*, 2006; Jassim and Rochelle, 2006; Lawal and Idem, 2006; Ma'mun *et al.*, 2006; Oyenekan and Rochelle, 2006; Ramachandran *et al.*, 2006; Rao and Rubin, 2006; Silva and Svendsen, 2006; Supap *et al.*, 2006; Tanthapanichakoon *et al.*, 2006; Tobiesen and Svendsen, 2006). This paper summarizes only representative studies.

Natural gas industry uses MEA to absorb CO_2 from natural gas. There are commercial MEA absorption processes with which CO_2 is removed from combustion flue gas stream. Such processes allow the MEA solution to be contacted with flue gas in an absorber where CO_2 is absorbed by the solution. MEA reacts with CO_2 in the gas stream to form MEA carbamate. The CO_2-rich MEA solution is then sent to a stripper where it is reheated to release almost pure CO_2. The MEA solution is then recycled to the absorber (Stewart and Hessami, 2005). This process is generally uneconomic as it requires large equipment size and intensive energy input. It is widely known that the heat

duty for solvent regeneration can constitute up to 70% of the total operating costs in a CO_2 capture plant (Idem *et al.*, 2006). The MEA process disadvantages include: (1) low carbon dioxide loading capacity; (2) high equipment corrosion rate; (3) amine degradation by SO_2, NO_2, HCl, HF, and oxygen in flue gas which induce a high absorbent makeup rate; (4) high energy consumption during high temperature absorbent regeneration (Fauth *et al.*, 2005; Resnik *et al.*, 2004; Yeh *et al.*, 2005).

Besides MEA, diethanolamine (DEA) and methyl-diethanolamine (MDEA) are often used as absorbents. The proposed mechanism of reactions between CO_2 and amines are shown in Fig.6. According to this mechanism, the majority of the CO_2 captured will result in the formation of bicarbonate in the liquid amine capture system. In aqueous media, there is a requirement of 2 mol-amine/mol-CO_2 for the formation of stable bicarbonate compounds resulting in the capture of CO_2.
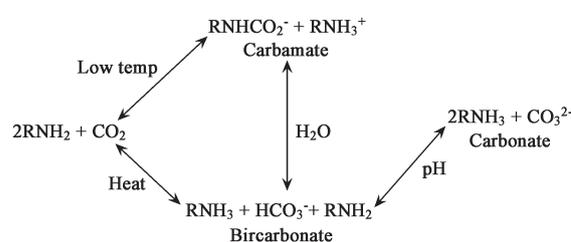

Fig. 6 Proposed reaction sequence for the capture of carbon dioxide by liquid amine-based systems (Gray *et al.*, 2005).

Mixed amines have been reported to maximize the desirable qualities of the individual amines. The use of mixed amines is to have a solution consisting of tertiary and primary amines or tertiary plus secondary amines that retains much of the reactivity of primary amines or secondary amines at similar or reduced circulation rates but offers low regeneration costs similar to those of tertiary amines. There are reports of substantial reduction in energy requirements and modest reduction in circulation rates for amine blends relative to the corresponding single amine system of similar total amine concentration (Idem *et al.*, 2006). Idem *et al.* compared the performance of aqueous 5 kmol/m^3 MEA with that of an aqueous 4/1 molar ratio MEA/MDEA blend of 5 kmol/m^3 total amine concentration as a function of the operating time using two pilot CO_2 capture plants. Their results indicate that a huge heat duty reduction can be achieved by using a mixed MEA/MDEA solution instead of a single MEA solution in

Table 2 CO_2 sorbent performance reported by references

| Sorbent	Capacity	Flue gas composition	References
Aqueous ammonium	1.20 g CO_2/g NH_3	15 vol% CO_2, 85 vol% N_2	Resnik *et al.*, 2004; Yeh *et al.*, 2005
Aminated mesoporous silica	0.45–0.6 mol CO_2/mol amine	100% CO_2	Knowles *et al.*, 2005
Aminated SBA-15	1528–4188 μmol CO_2/g sorbent	10% CO_2, 90% He, with about 2% H_2O	Gray *et al.*, 2005
PEI-impregnated MCM-41	45 ml (STP) CO_2/g adsorbent	15% CO_2, 4% O_2, 81% N_2	Xu *et al.*, 2005
PEI-impregnated MCM-41	246 mg CO_2/gPEI or 82 mg CO_2/g sorbent	N/A	Song, 2006; Xu *et al.*, 2002
Anthracite activated carbon	65.7 mg CO_2/g adsorbent	N/A	Maroto-Valer *et al.*, 2005
Lithium silicate	360 mg CO_2/g sorbent	100% CO_2	Kato *et al.*, 2005

an industrial environment of a CO_2 capture plant, although this benefit depends on whether the chemical stability of the solvent can be maintained.

3.2 Ammonium absorption process

Yeh *et al.* reported the Aqua Ammonia Process which avoids the drawbacks of the MEA processes (Resnik *et al.*, 2004; Yeh et al., 2005). This process uses aqueous ammonia as CO_2 sorbent with the capability of multi-component control. Flue gas needs to be pretreated by oxidizing SO_2 and NO to SO_3 and NO_2, respectively. The flue gas then reacts with aqueous ammonia in a wet scrubber. The regeneration of ammonium requires heat input to thermally decompose ammonium bicarbonate and ammonium carbonate. They estimated that this process saves energy up to 60 percent compared to MEA process. The major by-products from this process include ammonium sulfate, ammonium nitrate, ammonium bicarbonate. Ammonium sulfate and ammonium nitrate are well-known fertilizers. The market for ammonium bicarbonate is uncertain but can be thermally decomposed to recycle ammonium. This process potentially promotes the burning of cheap and abundant high-sulfur coals.

### 3.3 Dual-alkali absorption approach

A modified Solvay dual-alkali approach was proposed (Huang *et al.*, 2001). The Solvay process employs a dual-alkali approach with ammonia (primary alkali) as a catalyst to aid the reaction of CO_2 with sodium chloride for the production of sodium carbonate:

$$CO_2 + NaCl + NH_3 + H_2O \longrightarrow NaHCO_3^- \downarrow + NH_4Cl \tag{6}$$
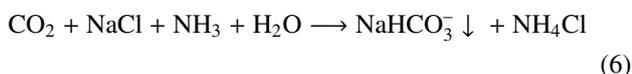
Product sodium carbonate is obtained by heating sodium bicarbonate. The ammonia is recovered by reacting ammonium chloride with lime (secondary alkali), where limestone serves as the source of lime.

$$2NH_4Cl + Ca(OH)_2 \longrightarrow 2NH_3 + CaCl_2 + 2H_2O \tag{7}$$

When applying this process to capture carbon dioxide from flue gas, several drawbacks are obvious. The use of limestone for the regeneration of ammonia renders the process ineffective mainly because of the consumption of limestone, production of CO_2, and intensive energy requirement during calcination. Also for every two moles of CO_2 captured, one mole of CO_2 is released from calcination of limestone. This can be seen from the overall reactions:

$$CaCO_3 \longrightarrow CaO + CO_2 \tag{8}$$

$$2NaCl + 2CO_2 + CaO + H_2O \longrightarrow 2NaHCO_3 + CaCl_2 \tag{9}$$
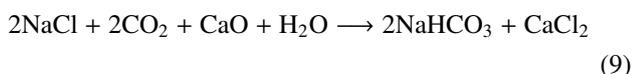
In this study, methylaminoethanol (MAE) was chosen as an effective primary alkali with the following reaction:

$$CO_2 + NaCl + HOCH_2CH_2(CH_3)NH + H_2O \longleftrightarrow$$
$$NaHCO_3^- \downarrow + HOCH_2CH_2(CH_3)NH \cdot HCl \tag{10}$$
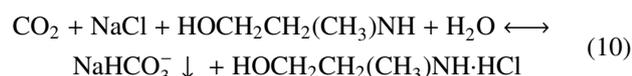
The CO_2 absorption capacity of MAE (0.75 mol-CO_2/mol-MAE) is greater than that of MEA (0.5 mol-CO_2/mol-MEA). The maximum CO_2 absorption capacity of an amine is 0.5 mol-CO_2/mol-amine if the reaction product is carbamate and 1.0 if the reaction product is bicarbonate. This group of researchers had not identified the secondary alkali to regenerate the primary alkali MAE.

3.4 Molecular sieve adsorbent

Molecular sieves are a range of specially designed sieves that separate molecules based on their molecular weight or molecular size. This technology is believed to be cost-effective and can be adapted to a variety of carbon sequestration schemes (Stewart and Hessami, 2005). There were many research activities aiming to improve the CO_2 adsorption by chemically treat the molecular sieve surface.

Adsorbents based on high surface area inorganic supports that incorporate basic organic groups, usually amines, are of particular interest. The interaction between the basic surface and acidic CO_2 molecules is thought to result in the formation of surface ammonium carbamate under anhydrous conditions and in the form of ammonium bicarbonate and carbonate species in the presence of water. Refer to Fig.7 for a schematic of reactions between CO_2 and amines within an adsorbent environment. Similar to amine absorption process, the CO_2 adsorption capacity is 0.5 mol CO_2/mol surface-bound amine group without the presence of water, 1.0 mol CO_2/mol surface-bound amine
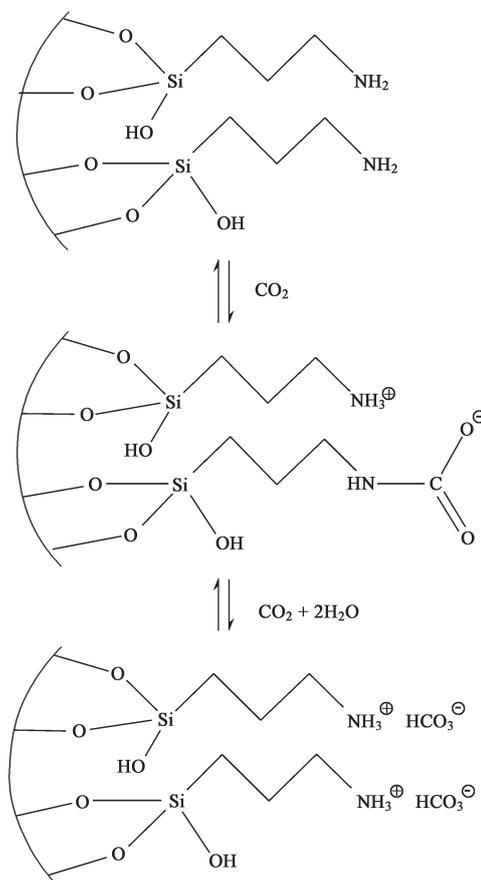

Fig. 7 Surface reactions of amine groups with CO_2 (Knowles *et al.*, 2005).

with the presence of water. Mesoporous substrates, such as silica (Knowles *et al.*, 2005; Knowles *et al.*, 2006), SBA-1 (Yoshitake *et al.*, 2003), SBA-15 (Gray *et al.*, 2005), MCM-41 (Song, 2006; Xu *et al.*, 2005; Yoshitake *et al.*, 2003) and MCM-48 (Huang *et al.*, 2003), are attractive because they possess pores that are large enough to be accessed by molecules with amino groups. Both the porosity and surface functional groups facilitate the capture of CO_2. A typical study is summarized below.

3.5 "Molecular basket" adsorbent for CO_2 separation

Song (2006) and Xu *et al.* (2002) studied a novel CO_2 "molecular basket" adsorbent. This adsorbent is based on mesoporous molecular sieve of MCM-41 impregnated with polyethylenimine (PEI). Fig.8 shows the structures of MCM41 and PEI. Fig.9 shows the concept of this molecular basket. With the increase in PEI loading, the surface area, pore size and pore volume of the loaded MCM-41 decrease. When the loading is higher than 30 wt.%, the mesoporous pores began to be filled with PEI and the adsorbent shows a synergetic effect on the adsorption of CO_2 by PEI. At PEI loading of 50 wt.%, the highest CO_2 adsorption capacity of 246 mg/g PEI is obtained, which is 30 times higher than that of MCM-41 and is about 23 times that of the pure PEI. Chemical impregnation proved to be a better way to prepare the molecular basket. This study also shows that this molecular basket can selectively capture CO_2 for the separation of CO_2 from simulated flue gas, the separation of CO_2 from natural gas-fired and coal-fired boiler flue gas (Song, 2006).

3.6 Adsorption by activated carbon

Anthracites are known to produce high surface area activated carbon. Maroto-Valer *et al.* studied the CO_2 capture behavior of steam-activated anthracite (Maroto-Valer *et al.*, 2005). They found that CO_2 capture does not show a linear relationship with the surface area. The highest CO_2 adsorption capacity was 65.7 mg CO_2/g adsorbent for the anthracite activated at 800°C for 2 h with a surface area of 540 m^2/g. The anthracite with the highest surface area of 1,071 m^2/g only had a CO_2 adsorption capacity of 40 mg CO_2/g adsorbent. This could be explained by certain size pores being effective for CO_2 adsorption. Also the NH_3 treatment and PEI impregnation increased the CO_2 capture
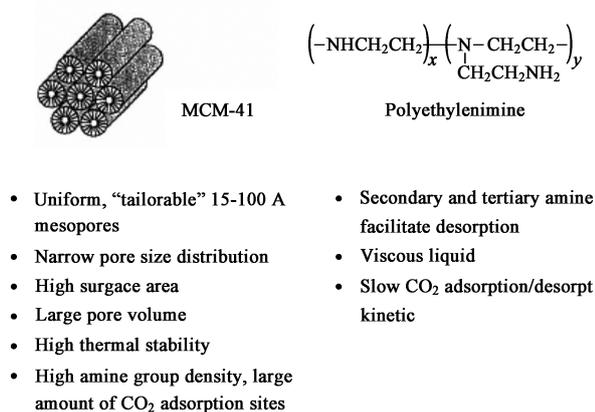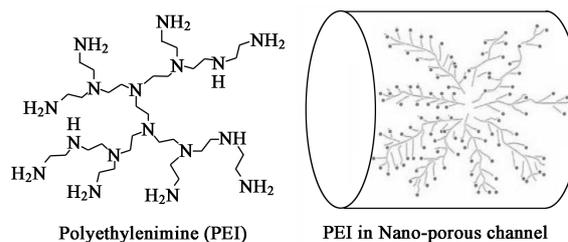

- Uniform, "tailorable" 15-100 A mesopores
- Narrow pore size distribution
- High surgace area
- Large pore volume
- High thermal stability
- High amine group density, large amount of CO_2 adsorption sites

- Secondary and tertiary amine facilitate desorption
- Viscous liquid
- Slow CO_2 adsorption/desorpt kinetic

Fig. 8 Structures of MCM-41 and PEI (Song, 2006).

Polyethylenimine (PEI)   PEI in Nano-porous channel

- Large pore volume nano-porous support can store large amount of CO_2
- Branched CO_2-affinity polymers provide adsorption sites
- Branched amine facilitate the desorption
- Synergic effect on the CO_2 adsorption capacity and adsorption kinetic between nano-porous support and polyethylenimine

Fig. 9 "Molecular basket" concept for highly-selective high-capacity CO_2 adsorbent (Song, 2006).

capacity of the activated anthracites at higher temperature, due to the introduction of alkaline nitrogen groups on the surface.

3.7 CO_2 adsorbents based on lithium compounds

Lithium zirconate (Li_2ZrO_3), with a favorable CO_2 sorption characteristics, has been investigated as a high temperature CO_2 absorbent (Fauth *et al.*, 2005). This technology, based on the chemical reaction using Li_2ZrO_3 to capture CO_2, is illustrated in the following reaction:

$$Li_2ZrO_3(s) + CO_2(g) \longleftrightarrow Li_2CO_3(s) + ZrO_2(s) \qquad (11)$$
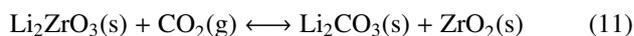
The reaction is reversible in the temperature range of 450–590°C. The direction can be easily reversed by a simple temperature swing approach. The formation of eutectic carbonate composed of Li_2CO_3 and K_2CO_3 can accelerate the CO_2 absorption reaction. A number of binary and ternary eutectic salt-modified lithium zirconate sorbents were identified and evaluated for high temperature CO_2 capture. The combination of binary alkali carbonate, binary alkali/alkaline earth carbonate, ternary alkali carbonate and ternary alkali carbonate/halide eutectic to Li_2ZrO_3 noticeably improved the CO_2 uptake rate and CO_2 sorption capacity. Formation of a eutectic molten carbonate layer on the outer surface of reactant Li_2ZrO_3 particles facilitates the transfer of gaseous CO_2 during the sorption process.

Lithium silicate (Li_4SiO_4) was studied by Nakagawa *et al.* for their CO_2 adsorption behaviors (Essaki *et al.*, 2004; Kato *et al.*, 2005). They found that the capacity of lithium silicate is much larger than that of lithium zirconate. Lithium silicate adsorbs CO_2 below 720°C and releases CO_2 above 720°C by the following mechanism:

$$Li_4SiO_4 + CO_2 \longleftrightarrow Li_2SiO_3 + Li_2CO_3 \qquad (12)$$
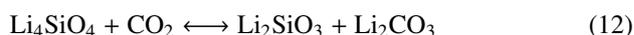
Desired features, such as large capacity, rapid absorption, wide range of temperature and concentrations of CO_2, and stability, make this compound a strong candidate for developing commercially competitive CO_2 adsorbent.

3.8 CO_2 capture based on membrane separation

Membranes have been widely used in various industrial separations for the last two decades. Industrial applications

are currently dominated by polymeric membranes. Recent research directed at the development and application of inorganic membranes is advancing faster because of the demand in new application fields, such as fuel cells, membrane reactors, and other high-temperature separations. Inorganic or polymeric membrane separation processes are expected to be more efficient that conventional CO_2 separation processes (Damle and Dorchak, 2001; Xu *et al.*, 2001).

Both polymeric and metallic membranes can be used to produce clean fuel from a syngas obtained either from coal gasification or reforming natural gas or methanol. Syngas containing H_2 is delivered at pressures and temperatures dependent on the type of fuel processor. Cooling is required for polymeric membranes. If the fuel gas is composed mainly of CO and H_2, various polymers can be used for hydrogen separation, but actual selectivities are lower due to polymer plasticization (Carapellucci and Milazzo, 2003). For inorganic membranes, palladium/silver alloys are the most efficient. Their 100 percent selectivity for hydrogen guarantees a pure hydrogen permeant. The separation based on metallic membranes is more efficient as the pressure drop across membrane is smaller.

The diffusional characteristics of a particular gas through a given membrane depend on membrane physical and chemical properties, the nature of the permeant species. The third factor, interaction between membrane and permeant, refers to the sorptivity or solubility of the gas in the membrane (Shekhawat *et al.*, 2003).

It is important to construct membranes into a practical configuration. Most polymeric membrane gas separation studies are performed on dense homogeneous membranes. Such a configuration provides the permeability with a closer relationship to the intrinsic permeability of the polymer. However, the construction of a gas separation module in practical applications requires a more complex membrane structure. Dense membranes tend to be significantly thicker than the selective layer of asymmetric membranes. This leads to dense membranes possessing considerably lower gas fluxes than alternative membrane structures. Often used is asymmetric composite hollow fiber or flat sheet configuration.

3.9 Polymeric membranes

Generally, gas molecules transport through a polymeric membrane by a solution-diffusion mechanism. Other mechanisms include a molecular sieve effect and Knudsen diffusion (Powell and Qiao, 2006). These transport mechanisms are briefly introduced in inorganic membrane section. The terms permeability and selectivity are used to describe the performance of a gas separation membrane. There appears to be a trade-off between selectivity and permeability. Gas molecules tend to move through free volumes–the gaps between polymeric structures. Because of the movement of the polymer chains, a channel between gaps can be formed allowing gas molecules to move from one gap to another and thus gas molecules can effectively diffuse through the membrane structure. Selective transport of gases can be achieved by use of a polymer which

forms channels of a certain size. Large channels will allow faster diffusion of gases through a membrane at the cost of less selectivity.

Membranes are a low cost means of separating gases when high purity is not vital. There are a number of issues associated with the capture of carbon dioxide from flue gas which limit the use of membranes. The concentration of carbon dioxide in flue gases is low, which means that large quantities of gases will need to be processed. The high temperature of flue gases will rapidly destroy a membrane, so the gases need to be cooled to below 100°C prior to membrane separation. The membranes need to be chemically resistant to the harsh chemicals contained within flue gases, or these chemicals need to be removed prior to the membrane separation. Additionally, creating a pressure difference across the membrane will require significant amounts of power.

Polymers studied in various studies include: polyacetylenes (Stern, 1994), polyaniline (Illing *et al.*, 2001), poly (arylene ether)s (Xu *et al.*, 2002), polyarylates (Pixton and Paul, 1995), polycarbonates (Aguilar-Vega and Paul, 1993), polyetherimides (Li and Freeman, 1997), poly (ethylene oxide) (Lin and Freeman, 2004), polyimides (Stern *et al.*, 1989), poly(phenylene ether) (Aguilar-Vega and Paul, 1993), poly(pyrrolone)s (Zimmerman and Koros, 1999) and polysulfones (Aitken *et al.*, 1992). Fig.10 shows molecular structures of some commonly used polymers.

The performance of some polymeric membranes are summarized in Table 3 mainly separating post-combustion flue gas with CO_2/N_2 being the main components (Powell and Qiao, 2006). Single-stage membrane systems are not capable of high capture efficiency and CO_2 can be further concentrated by a second membrane stage.

Table 3   Performance of polymeric membranes separating CO_2/N_2 (Powell and Qiao, 2006)

Material	Permeance $(m^3/(m^2 \cdot Pa \cdot s))$	Selectivity α_{CO_2/N_2}
Polyimide	735	43
Polydimethylphenylene oxide	2750	19
Polysulfone	450	31
Polyethersulfone	665	24.7
Poly(4-vinylpyridine)/polyetherimide	52.5	20
Polyacrylonitrile with poly (ethylene glycol)	91	27.9
Poly(amide-6-b-ethylene oxide)	608	61

Materials for effective separation of gases can follow one of two overall strategies: increasing the rate of diffusion of carbon dioxide through the polymeric structure and increasing the solubility of carbon dioxide in the membrane. The introduction of mixed-matrix membranes may allow superior performance which combines the advantages of polymeric and inorganic membranes materials.

3.10 Inorganic membranes

Inorganic membranes can be classified into two categories based on structure: porous and dense. In porous inorganic membranes, a porous thin top layer is casted on a porous metal or ceramic support, which provides mechan-
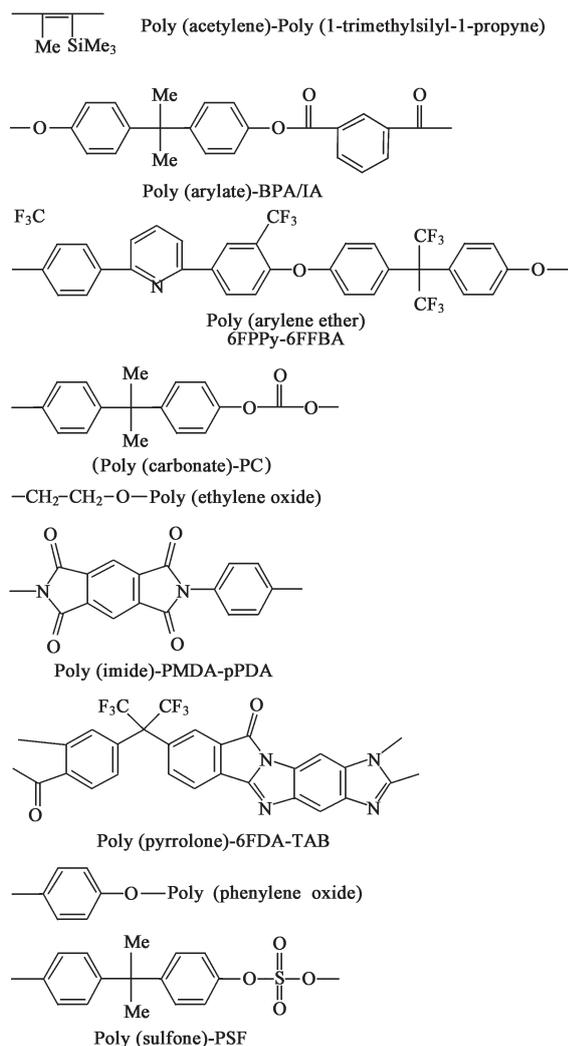
Fig. 10 Examples of polymer molecular structures used for CO_2 separation (Powell and Qiao, 2006).

ical strength but offers minimum mass-transfer resistance. Alumina, carbon, glass, silicon carbide, titania, zeolite, and zirconia membranes are mainly used as porous inorganic membranes supported on different substrates, such as α-alumina, γ-alumina, zirconia, zeolite, or porous stainless steel. Surface modification by covalently bonding a layer of selected compounds with appropriate functional groups is one of the more convenient ways to alter membrane performance. Such modification can increase the performances by changing the mean pore size and promoting an eventual specific interaction between the surface of the membrane and the permeating molecules to enhance permeation. The dense inorganic membranes consist of a thin layer of metal, such as palladium and its alloys, or solid electrolytes, such as zirconia. These membranes are highly selective for hydrogen or oxygen separation. Gas transport occurs via solution-diffusion mechanism or charged particles in dense membranes. The low permeability across the dense inorganic membranes limits its wide applications as compared to porous inorganic membranes.

There are four main transport mechanisms by which gas separation using porous inorganic membranes can be described, described by Fig.11, i.e. Knudsen diffusion,

surface diffusion, capillary condensation, and molecular sieving (Shekhawat et al., 2003; Luebke et al., 2006). Please refer to the references for detailed explanation.
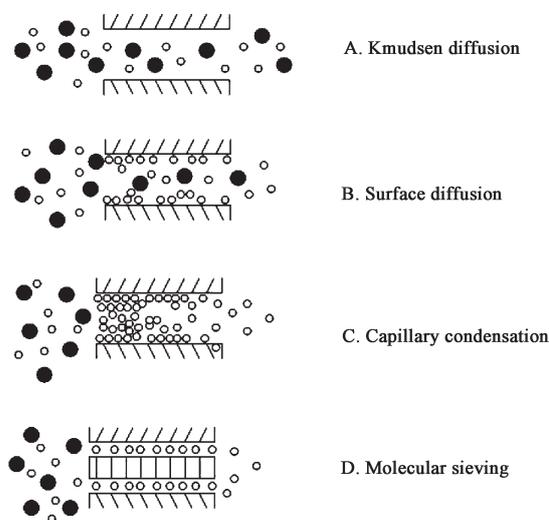
Fig. 11 Transport mechanism through microporous membranes (Shekhawat et al., 2003).

3.11 Carbon membranes

Carbon membranes for gas separations are typically produced by the pyrolysis of thermosetting polymers. The pyrolysis temperature, typically in the range of 500 to 1,000°C, depends upon the type of precursor material and dictates the separation performance of the carbon membranes (Shekhawat et al., 2003). Pyrolysis of polymeric compounds leads to carbon material with a narrow pore size distribution below molecular dimensions (< 1 nm), which makes it possible to separate gases with very similar molecular sizes. The predominant transport mechanism of most carbon membranes is molecular sieving. The selection of precursor polymer, the membrane preparation method, and the carbonization process determine the performance of carbon molecular sieve membranes. The mechanical stability can be improved by supporting a thin carbon membrane on a porous support material, such as α-alumina. The high thermal and chemical stability of these membranes provide hope in gas separation applications, such as separation of CO_2 in flue gas emissions from power plants.

3.12 Alumina membranes

The generally mesoporous structure of alumina dictates that transport within such membranes by a Knudsen diffusion mechanism (Shekhawat et al., 2003). With mixtures such as CO_2/N_2, where the gases have similar mass, and CO_2/H_2, where selectivity toward the heavier component is required, alumina is undesirable as a material for membrane separation layer. Alumina finds its use in the separation of gases mainly as support, where its sound structural properties, and chemical and hydrothermal stabilities beyond 1,000°C make it very desirable. A few attempts have been made to modify alumina membranes to facilitate CO_2 surface diffusion with limited success. In

order to achieve high separation factors in systems like CO_2/N_2, an interaction between one of the gases in the mixture and the membrane surface can be introduced by chemical modification of separation layers.

3.13 Silica membranes

Silica is a viable starting material for the fabrication of CO_2 selective membranes, primarily because of its innate stability and easy modification of its structures. Unlike alumina, which tends to undergo phase transition at relatively low temperature, or carbon, which can exhibit substantial changes in pore size in oxidizing environments, silica shows exceptional thermal, chemical, and structural stability in both oxidizing and reducing environment. Sol-gel method and chemical vapor deposition (CVD) technique are used to prepare silica membranes.

3.14 Zeolite membranes

Zeolites are crystalline aluminosilicates with a uniform pore structure and a minimum channel diameter range of 0.3 to 1.0 nm. The presence of molecular-sized cavities and pores make the zeolites effective as shape-selective materials for a wide range of separation applications. This ability to selectively adsorb molecules by size and polarity is the key to the unusual efficiency of synthetic zeolites as the basis for gas separation. Separation occurs in zeolite membranes by both molecular sieving and surface diffusion mechanisms.

Zeolite membranes are usually prepared by *in-situ* hydrothermal synthesis on porous stainless steel, α-alumina, or γ-alumina support tubes or disks for the gas permeation studies. Membranes of various zeolites, such as ZSM-5 (Kusakabe *et al*., 1996), Y type (Kusakabe *et al*., 1997), silicalite (Lin *et al*., 2000), A type (Aoki *et al*., 2000), P type (Dong and Lin, 1998), modernite (Bernal *et al*., 2000), and silicoaluminophosphate (Poshusta *et al*., 2000) have been synthesized on porous supports. Typically the heat of adsorption of gases on most zeolites increase in this order: $H_2 < CH_4 < N_2 < CO_2$ (Poshusta *et al*., 2000). This order is consistent with the electrostatic properties of each molecule. Carbon dioxide preferentially permeates in CO_2/N_2, CO_2/CH_4, and CO_2/H_2 mixtures at low temperatures, because CO_2 adsorbs more strongly on zeolites than the other gases. For the CO_2/N_2 and CO_2/CH_4 mixtures, CO_2 is smaller in size and thus permeates faster at elevated temperature. However, the selectivities are the same for the CO_2/N_2 or CO_2/CH_4 systems at elevated temperatures due to the absence of competitive adsorption.

3.15 Mixed-matrix and hybrid membranes

These molecular sieves possess superior gas transport properties, but have significant problems with their processibility. Incorporation of molecular sieves within a polymer membrane possibly provides both the processibility of polymers and selectivity of molecular sieves (Nomura *et al*., 1997). Many research direct at mixed-matrix membranes; the polymer-zeolite pairs include polydimethylsiloxane-silicalite (Tantekin-Ersolmaz *et al*., 2000), polyimide-carbon molecular sieve (Vu *et*

al., 2003), polyimide-silica (Kusakabe *et al*., 1996), Nafion-zirconium oxide (Apichatachutapan *et al*., 1996), HSSZ-13-polyetherimide (Husain and Koros, 2007), acrylonitrile butadiene styrene-activated carbon (Anson *et al*., 2004). It is known that the permeability of a gas through a zeolite-filled polymeric membrane depends on the intrinsic properties of the zeolite and the polymer (Tantekin-Ersolmaz *et al*., 2000). However, their performance suffers from defects caused by poor contact at the molecular sieves/polymer interface. This can allow the gases to flow non-selectively around the solid particles. Sonication and decantation techniques have been suggested to overcome this issue (Vu *et al*., 2003). The successful implementation of this membrane development depends on both, the selection of polymeric matrix and inorganic zeolite, and the elimination of interfacial defects (Anson *et al*., 2004).

A similar concept is hybrid membrane where a porous inorganic support material is surface-modified with chemicals which have good affinity with CO_2. Strictly speaking, the hybrid membrane might better be named surface-modified inorganic membrane so that not to be confused with mixed-matrix membrane. This helps CO_2 separation in two ways: porous inorganic materials allows large flux while the chemical provides selectivity (Luebke *et al*., 2006; Shekhawat *et al*., 2003). The studied chemical-inorganic pairs include polyether-silica (Kim *et al*., 2005), trichlorosilane-γ-alumina (Luebke *et al*., 2006), organosilane-Vycor glass (Singh *et al*., 2004), tetrapropylammonium-silica (Yang *et al*., 2002), titania-trimethoxysilaen (Abidi *et al*., 2006), γ-alumina-trimethoxysilane (Abidi *et al*., 2006), hexagonal mesoporous silica-aminopropylhydroxysilyl (Knowles *et al*., 2005; Chaffee, 2005).

3.16 Facilitated transport membranes

Facilitated transport membranes (FTM) have received a lot of attention in gas separations because they offer higher selectivity and larger flux (Shekhawat *et al*., 2003). Higher selectivity in FTM is achieved by incorporating a carrier agent into membrane, which reacts reversibly with the penetrating species. In addition to the solution-diffusion mechanism of the polymeric membranes, FTMs also involve a reversible complexing reaction. The permeating species dissolves in the up stream portion of the membrane and reacts with the carrier agent inside the membrane to form a complex. This complex diffuses across the membrane, and then releases the permeants on the downstream side of the membrane, while the carrier agent is simultaneously recovered and diffuses back to the feed side. FTMs can be in a form of fixed carrier membranes, solvent-swollen polymer membrane, and mobile carrier membranes (Shekhawat *et al*., 2003).

4 Conclusions

Fossil fuels continue to be the primary energy source, at least for this century. There are many technical options for separation and/or capture of CO_2 from combustion flue gas and other industrial effluents. Other than geological

injecting and direct ocean dump, forestation and ocean fertilization can be utilized to avoid or delay the carbon emission into atmosphere. Mineral carbonation should have limited applications. Amine absorption process is mature but has large room of improvement. Adsorption provides another option although it has many problems need to be addressed. Membrane separation processes provide several advantages over other conventional separation techniques; a membrane combining high flux, high selectivity and high stability is not realistic at this stage but mixed-matrix membranes provide hopes.

Although emerging technologies, such as zero-emission power plant, significantly reduce the complexity of separating CO_2, many other industrial processes still emit substantial amounts of carbon dioxide which needs to be separated; CO_2 separation and capture technologies will continue to evolve. Membrane process as energy-saving, space-saving, easy to scale-up, could be the future technology for CO_2 separation.

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