

Review

CO₂ capture and separation technologies for end-of-pipe applications – A review

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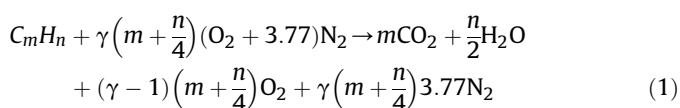
ABSTRACT

Carbon capture from point source emissions has been recognized as one of several strategies necessary for mitigating unfettered release of greenhouse gases (GHGs) into the atmosphere. To keep GHGs at manageable levels, large decreases in CO₂ emissions through capturing and separation will be required. This article reviews the possible CO₂ capture and separation technologies for end-of-pipe applications. The three main CO₂ capture technologies discussed include post-combustion, pre-combustion and oxyfuel combustion techniques. Various separation techniques, such as chemical absorption, physical absorption, physical adsorption, cryogenics, membrane technology, membranes in conjunction with chemical absorption and chemical-looping combustion (CLC) are also thoroughly discussed. Future directions are suggested for application by oil and gas industry. Sequestration methods, such as geological, mineral carbonation techniques, and ocean dump are not covered in this review.

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1. Introduction

Environmental issues due to emissions of pollutants from combustion of fossil fuels have become global problems, including air toxics and greenhouse gases (GHGs). The use of fossil fuels for energy contributes to a number of environmental problems globally. According to the Intergovernmental Panel on Climate Change (IPCC) [1], approximately three-fourths of the increase in atmospheric CO₂ is attributable to burning fossil fuels. Table 1 shows the harmful pollutants released into the atmosphere from burning of fossil fuels. If the carbon in all of the estimated fossil fuel reserves were emitted to the atmosphere, the carbon concentration would rise to more than 5 times pre-industrial levels [2]. The generic combustion reaction for hydrocarbon fuel is represented by the chemical equation below (eqn. (1)), where γ is the molar ratio of air required in excess of stoichiometric oxygen required.



Studies have shown that increased GHG levels in atmosphere are believed to cause global warming. Among these GHGs, CO₂ makes up a high proportion in respect of its amount present in the atmosphere, contributing 60 percent of global warming effects [3], although methane and chlorofluorocarbons (CFC's) have much

higher global warming potential as per mass of gases. There are increasing concerns for global warming caused by the effects of GHGs, particularly CO₂. Going by the prediction of IPCC, by year 2100, the atmosphere may contain up to 570 ppm of CO₂, causing a rise of mean global temperature of around 1.9 °C and an increase in mean sea level of 3.8 m [4]. The IPCC special report [5] on CO₂ capture and storage gives global CO₂ emission in 2000 at 23.5 GT with nearly 60% of this attributed to 7887 sources above 100,000 tonne/year including 4942 electrical power stations which emitted 10.5 GT/year CO₂. The remaining 40% emissions were mainly from transportation systems.

Reduction of anthropogenic CO₂ emissions into the atmosphere can be achieved by variety of means, which has been summarized by Professor Yoichi Kaya of the University of Tokyo and can be expressed as:

$$CO_2^{\uparrow} = POP \times \frac{GDP}{POP} \times \frac{BTU}{GDP} \times \frac{CO_2^{\uparrow}}{BTU} - CO_2^{\downarrow} \quad (i)$$

where CO_2^{\uparrow} is the total CO₂ released to the atmosphere, POP is population, GDP/POP is per capita gross domestic product and is a measure of the standard of living, BTU/GDP is energy consumption per unit of GDP and is a measure of energy intensity; CO_2^{\uparrow}/BTU is the amount of CO₂ released per unit of energy consumed and is a measure of carbon intensity; and CO_2^{\downarrow} is the amount of CO₂ stored or sequestered in biosphere and geosphere sinks. Of the first two measures, reducing the population or the standard of living is not likely to be considered. Consequently, the only three remaining options of reducing total CO₂ emission into the atmosphere are: (1) reducing energy intensity; (2) reducing carbon intensity, i.e. use of

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Table 1

Fossil fuel emission levels (pounds/billion BTU of energy input).

Pollutant	Natural gas	Oil	Coal
Carbon dioxide	117,000	164,000	208,000
Carbon monoxide	40	33	208
Nitrogen oxides	92	448	457
Sulphur dioxide	1	1122	2591
Particulates	7	84	2744
Mercury	0.00	0.007	0.016
Total	117,140	165,687.007	214,000.016

Source: EIA – [6].

carbon-free fuel; and (3) enhancing the sequestration of CO₂. 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 CO₂. It is clear that implementation of all the above-mentioned options will be necessary if CO₂ emission abatement becomes a serious global priority. However, at the current state of development, and the levels of risks and cost of non-fossil fuel energy alternatives such as nuclear, biomass, solar energy, etc, these energy sources cannot meet our need for energy fed by fossil fuels. Additionally, any rapid change to non-fossil energy sources, even if were possible would result in large disruptions to the existing energy supply infrastructure with substantial consequences to the global economy. Thus to meet mid-to long-term CO₂ reduction targets, cost-effective CO₂ capture from fossil fuel uses and subsequent sequestration options need to be evaluated, in view of the growing world demand for energy. This paper provides a status review of the existing and emerging technology options for the separation and capture of CO₂ from point source emissions.

To enhance the sequestration of CO₂, carbon dioxide capture and storage (CCS) technologies must be improved with development of new approaches of CO₂ separation and capture. Active CCS technologies require carbon emissions to be captured and stored in a form or location that is isolated from the atmosphere on a millennial time scale.

2. Carbon capture technologies

Capturing CO₂ from flue gas streams is an essential parameter for the carbon management for sequestration of CO₂ from our environment. Irons et al. [7] show that CO₂ emissions can be reduced for power generation by three capture technologies: post-combustion, pre-combustion decarbonization and oxyfuel combustion as illustrated in Fig. 1. The concentration of CO₂ in the gas stream, the pressure of the gas stream and the fuel type (solid or gas) are important factors in selecting the capture system. The current status and potential of these technologies are summarized in Tables 2 and 3 respectively.

2.1. Post-combustion CO₂ capture

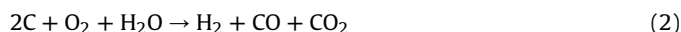
This involves separating CO₂ from the flue gas produced by fuel combustion. Post-combustion capture is a downstream process and in many respects is analogous to flue gas desulphurization (FGD), which is widely used to capture SO₂ from flue gas in coal and oil fired power plants. This method requires separating the CO₂ from other flue gases because sequestration of combustion gases is not feasible due in part to the cost of gas compression and storage.

The low concentration of CO₂ in power-plant flue gas (typically 4–14%) means that a large volume of gas has to be handled, which results in large equipment sizes and high capital costs. Post-

combustion capture offers a significant design challenge due to the relatively low partial pressure of the CO₂ in the flue gas. In addition, the relatively high temperature of the flue gases offers an additional design challenge. A further disadvantage of the low CO₂ concentration is that powerful chemical solvents have to be used and regeneration of the solvents to release the CO₂ will require a large amount of energy. There are several separation technologies that can be employed within this category. Chemical absorption, gas-separation membranes and low temperature distillation are among the separation technologies discussed in this review.

2.2. Pre-combustion carbon capture

In pre-combustion capture, fuel is reacted with oxygen or air, and in some cases steam, to give mainly carbon monoxide and hydrogen. This process is known as gasification, partial oxidation or reforming. The mixture of mainly CO and H₂, is passed through a catalytic reactor, called a shift converter, where the CO reacts with steam to give CO₂ and more H₂. The CO₂ is separated and the H₂ is used as fuel in a gas turbine combined-cycle plant. This technology is usually used for coal gasification (IGCC), however it could be applied to liquid and gaseous fuel. Typical reaction for IGCC is shown in the following equations [8].



Biomass and natural gas can also be used for pre-combustion capture technology. As gasification of biomass is similar to IGCC, for gasification of natural gas, several methods, which include steam reforming, partial oxidation and autothermal reforming are used. Steam reforming method converts CH₄ and water vapor into CO and H₂ (eqn. (5)), the process is endothermic and needs temperatures from 700 °C to 850 °C. Partial oxidation uses exothermic reaction of oxygen and methane (eqn (6)), while autothermal is combination of both methods [9].



After shift reaction, gas mixture is cooled and Selexol acid gas removal unit separates CO₂ and sulphur compound steams [8].

The profit of pre-combustion capture is based on transformation of carbon fuel to carbonless fuel. Gasification process uses chemical energy of carbon and transforms it to chemical energy of hydrogen. Hydrogen combustion doesn't emit any sulphur dioxide. Hydrogen seems to be useful fuel, as it could be used for gas boilers, gas turbines, fuel cells and other technologies. The CO₂ concentration and pressure are both higher in pre-combustion capture than in post-combustion capture, so the CO₂ capture equipment is much smaller and different solvents can be used, with lower energy penalties for regeneration.

Pre-combustion capture offers a more moderate energy penalty of 10% based on gasification or steam reforming. The high partial pressure of CO₂ could allow for the use of more efficient capture technologies (i.e, physical absorption), which would further reduce the energy penalty. Pre-combustion capture also has more potential for future use. The primary disadvantage of pre-combustion capture is that total capital costs of the generating facility are very high.

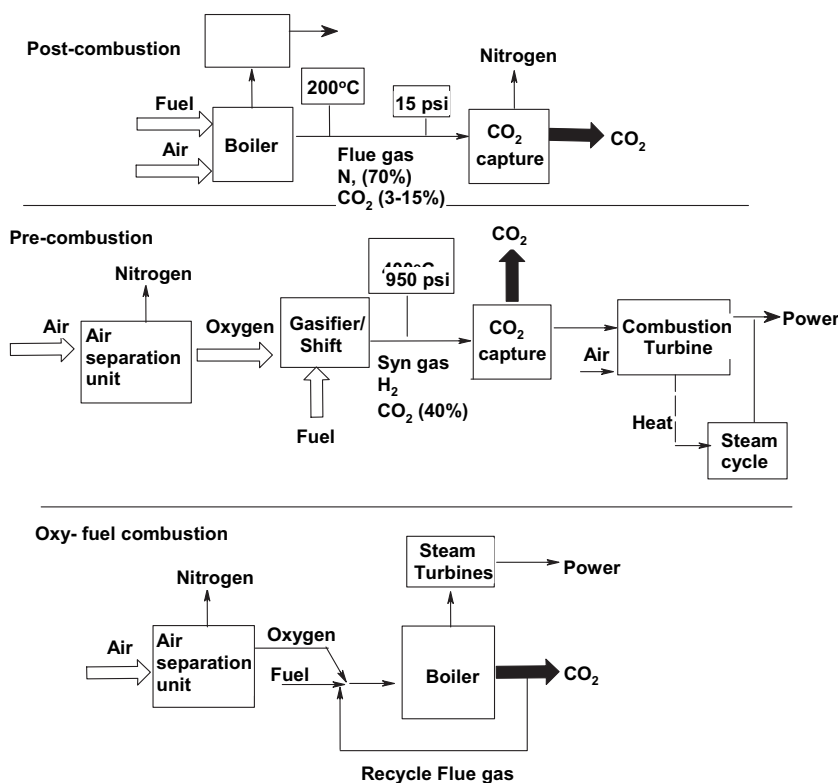


Fig. 1. Block diagrams illustrating post-combustion, pre-combustion and oxyfuel combustion techniques.

2.3. Oxyfuel combustion

Oxyfuel combustion is actually modified post-combustion method. Fuel is combusted in almost pure oxygen instead of air, which results in high concentration of CO₂ in flue gases. If fuel is burnt in pure oxygen, the flame temperature is excessively high, so some CO₂-rich flue gas would be recycled to the combustor to make the flame temperature similar to that in normal air-blown combustor. The advantage of oxygen-blown combustion is that the flue gas has a CO₂ concentration of over 80%, so only simple CO₂ purification is required. Another advantage is that NO_x formation is suppressed, with attendant benefits in the post-combustion removal of NO_x, and the volume of the gas to be treated in the flue gas desulphurization plant is greatly reduced. Additionally, other than a need for the gas desulphurization, oxyfuel combustion relies mainly on physical separation processes for O₂ production and CO₂ capture thereby avoiding the use of any reagent and/or solvents that contribute to operating costs and environmental disposal of any related solid or liquid wastes. The main disadvantage of oxyfuel combustion is that a large quantity of oxygen is required, which is expensive, both in terms of capital cost and energy consumption.

Table 2
Current status of CO₂ capture technologies.

Post-combustion capture	Pre-combustion capture	Oxyfuel combustion
Amine scrubbing is well established for natural gas. Solvent degradation is a problem. Some small power plants operating.	Integrated gasification combined cycle (IGCC) and ammonia production are well established. Physical solvent separation is well established. Gas turbines must be capable of using H ₂ -rich fuel.	Oxygen production is well established. Small scale combustor test rigs operating.

Advances in oxygen production processes, such as new and improved membranes that can operate at high temperatures could improve overall plant efficiency and economics [10]. Oxyfuel combustion has so far only been demonstrated in small scale test rigs [11]. The pros and cons of each of these capture technologies are presented in Table 4.

3. Sources of carbon

The pathways for carbon capture derived from three potential sources are given in Fig. 2. Many industrial processes produce highly concentrated streams of CO₂ as a by-product. Although limited in quantity, these by-products constitute a good capture target, because the captured CO₂ is integral to the total production process, resulting in low incremental capture costs. For example, natural gas ensuing from wells often contains a significant fraction of CO₂ that can be captured and stored. Other processes that lend themselves to carbon capture include ammonia manufacturing, fermentation process and hydrogen production during oil refining.

The largest potential sources of CO₂ today are fossil-fueled power production plants (Table 1). Power plants emit more than one-third of the CO₂ emissions worldwide. These plants are usually built in large centralized units, typically delivering 500–1000 MW of electrical power. A 1000-MW pulverized coal-fired power plant emits between 6 and 8 Mt/yr of CO₂, an oil fired single-cycle power plant emits about two-thirds of that and a natural gas combined-cycle power plant emits about one-half of that (Table 1).

Future opportunities for CO₂ capture may also arise from decarbonization, i.e., production of hydrogen from carbon-rich feedstock, such as natural gas, coal and biomass. The CO₂ by-product will be relatively pure, thus lowering the incremental cost of carbon capture. The hydrogen can be used in fuel cells and other hydrogen fuel-based technologies.

Table 3Potential of CO₂ capture technologies.

Post-combustion	Pre-combustion decarbonization	Oxyfuel combustion
Applicable to the majority of existing coal-fired plants. Low CO ₂ partial pressure. Significantly higher performance or circulation volume is required for high capture levels. CO ₂ produced at low pressure compared to sequestration requirements. Retrofit technology option. Efficiency and cost penalties for coal-fired power plants (IGCC) with conventional MEA scrubbing are reasonably well known. Improved solvents may reduce energy losses. Significant cost savings are possible.	Generally higher CO ₂ concentration than for post-combustion capture Higher driving force for CO ₂ separation. Fuel processing is needed. Potential for reduction in compression costs/loads. For coal plants, efficiency and cost penalties are generally lower than for post-combustion capture. Barriers to commercial application of gasification are common to pre-combustion capture. Extensive supporting systems requirements.	Very high CO ₂ concentration in flue gas. Combustors would be fairly conventional. Large cryogenic oxygen production requirement may be cost prohibitive. Need to recycle large quantities of flue gas to avoid excessively high combustion temperatures. CO ₂ is recycled to the compressor to provide the expansion medium, instead of air. Novel turbine cycles have been proposed including IGCC, which eliminates shift reaction/fuel gas CO ₂ separation. Potential for advanced oxygen separation membranes with lower energy consumption. Retrofit and repowering technology option. Decreased process efficiency.

4. Review of possible CO₂ separation techniques

Capture of CO₂ contributes 75% to the overall CCS cost and CCS increases the electricity production cost by 50% [12]. Although these numbers may vary with different CCS schemes, reducing 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 CO₂ separation techniques from a flue gas. There are many options for CO₂ separation, and these include absorption, adsorption, membrane and cryogenics. The optimum CO₂ capture scheme could be determined by analyzing costs or the context of power generation. The captured CO₂ is used for various industrial and commercial processes, e.g., urea production, fertilizer production, foam blowing, carbonation of beverages and dry ice production. A wide range of technologies currently exist for separation of CO₂ from gas streams (Fig. 3), although they have not been designed for power-plant scale operations [13]. They are based on different physical and chemical processes including absorption, adsorption, cryogenics and membranes [14,15]. The choice of a suitable technology depends on the characteristics of the flue gas stream, which depend mainly on the power-plant technology. The conditions for CO₂ separation in pre-combustion capture processes will be quite different from those in post-combustion capture. For example, in a coal IGCC process, modified for capture, the CO₂ concentration would be about 35–40% at a pressure of 20 bar or more. In that case, physical solvents, such as Selexol, could be used for pre-combustion capture

of CO₂, with the advantage that the CO₂ can be released mainly by depressurization, thereby avoiding the high heat consumption of amine-scrubbing processes. However, depressurization of the solvent still results in a significant energy penalty. Various CO₂ separation techniques are discussed below; and the summary of their current status is given in Table 5.

4.1. Chemical absorption technology

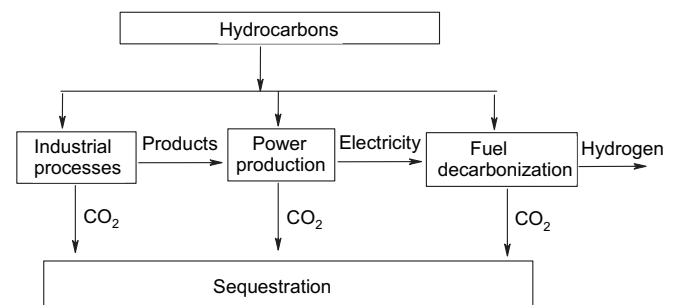
Chemical absorption is preferred for low to moderate CO₂ partial pressures. Because CO₂ is an acid gas, chemical absorption of CO₂ from gaseous streams such as flue gases depends on acid–base neutralization reactions using basic solvents. The CO₂ reacts with chemical solvents to form a weakly bonded intermediate compound, which is then broken down by the application of heat, regenerating the original solvent and producing a pure CO₂ stream.

Specialized solvents were developed more than 60 years ago to remove CO₂ from impure natural gas, and natural gas operations continue to use these solvents today. In addition, several power plants and other industrial plants use the same or similar solvents to recover CO₂ from flue gases for applications in the food processing and chemical industries. Finally, a variety of alternative methods are used to separate CO₂ from flue gas mixtures during production of hydrogen for petroleum refining, ammonia production and in other chemical industries [16].

The selection of a technology for a given capture application depends on many factors, i.e. partial pressure of CO₂ in the gas stream, extent of CO₂ recovery required, regeneration of the solvent, sensitivity to impurities, such as acid gases, particulates, purity of the desired CO₂ product, capital and operating costs of the process, the cost of additives necessary to overcome fouling and corrosion and where applicable, the environmental impacts [17]. A

Table 4Pros and cons of CO₂ capture technologies.

Capture technology	Pros	Cons
Post-combustion capture	Existing Technology Retrofit to existing power-plant designs Extra removal of NO _x and SO _x	Energy penalty due to solvent regeneration. Loss of solvent
Pre-combustion capture	Existing Technology Very low emissions	Cooling of gas to capture CO ₂ is necessary. Efficiency loss in water–gas shift section
Oxyfuel combustion capture	Existing Technology Absence of nitrogen eliminates NO _x emissions. Absence of nitrogen provides low volume of gases and so reduced size of entire process	High energy input for air separation. Combustion in pure oxygen is complicated.

**Fig. 2.** Sources of CO₂ for sequestration.

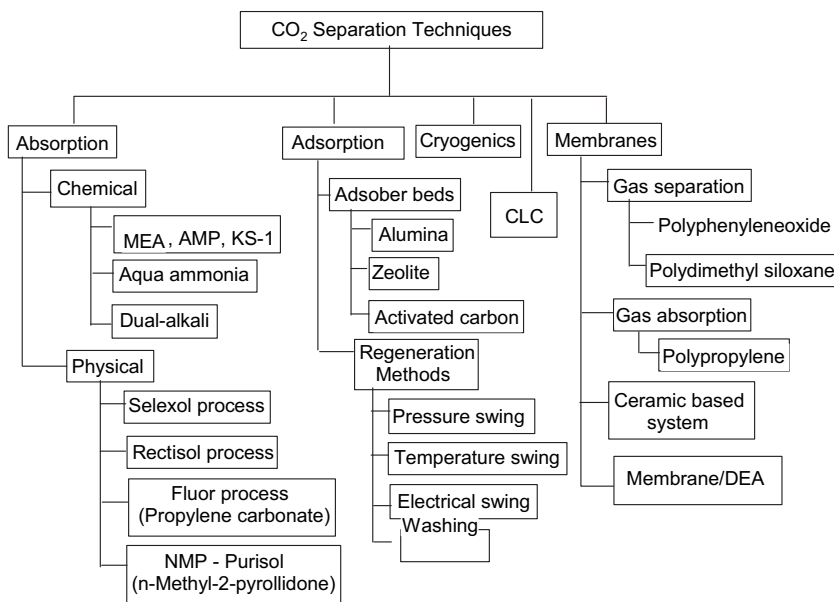
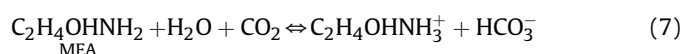


Fig. 3. Technology options for CO₂ separation.

schematic of a chemical absorption technology for power-plant flue gas is depicted in Fig. 4.

4.1.1. Amine absorption technology

The absorption/stripping technology, using amine solution such as monoethanolamine (MEA), is a commercialized technology used in natural gas industry for 60 years and is regarded as the most mature technology. Natural gas industry uses MEA to absorb CO₂ from natural gas. There are commercial MEA absorption processes with which CO₂ is removed from combustion flue gas stream. Such processes allow the MEA solution to be contacted with flue gas in an absorber where CO₂ is absorbed by the solution. When used in a power plant to capture CO₂, the flue gas is bubbled through the solvent in a packed absorber column, where the solvent preferentially removes the CO₂ from the flue gas. Afterward, the solvent passes through a regenerator unit, where the absorbed CO₂ is stripped from the solvent by counterflowing steam at 100–200 °C. Water vapor is condensed, leaving a highly concentrated (over 99%) CO₂ stream, which may be compressed for commercial utilization or storage. The lean solvent is cooled to 40–65 °C and is recycled into the absorption column [4]. The process is generally uneconomical as it requires large equipment size and intensive energy input. The CO₂ recycle rate is 98% for MEA [3]. The fundamental reaction for this process is:



During the absorption process, the reaction proceeds from left to right; during regeneration, the reaction proceeds from right to left.

The MEA process suffers the following disadvantages for CO₂ separation from flue gases: (1) low carbon dioxide loading capacity (g CO₂ absorbed/ g absorbent); (2) high equipment corrosion rate; (3) amine degradation by SO₂, NO₂, HCl and HF and oxygen in flue gas which induces a high absorbent makeup rate; and (4) high energy consumption during high temperature absorbent regeneration [18–20]. When capturing CO₂ from coal or petroleum-derived combustion flue gas, the MEA process requires that SO₂ be removed first from the flue gas stream, since MEA is degraded by SO₂ and oxygen, forming irreversible degradation products [21] as shown in reaction Scheme 1:

The cost of MEA makeup is high because of degradation, even after most of the SO₂ is removed from the flue gas in an upstream flue gas desulphurization unit. NO_x must also be eventually removed from the flue gas before it is discharged into the air in order to meet present and future gaseous emission limits.

Besides MEA, diethanolamine (DEA) and methyl diethanolamine (MDEA) are often used as absorbents. The proposed mechanism of reactions between CO₂ and amines are shown below (Scheme 2) [22]. According to this mechanism, the majority of the CO₂ 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-CO₂ for the formation of stable bicarbonate compounds resulting in the capture of CO₂.

Mixed amines have been reported to maximize the desirable qualities of the individual amines. Idem et al. [23] reported 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. They compared the performance of aqueous 5 kmol/m³ MEA with that of an aqueous MEA/MDEA (4/1 molar ratio) of 5 kmol/m³ total amine concentration as a function of the operating time using two pilot CO₂ 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 5
Summary of current status of CO₂ separation techniques.

Separation techniques	Type	Status
Chemical absorption	MEA KS-1	Commercially available
Physical adsorption	PSA method PTSA method	Under research
Membranes	Polymeric Inorganic Zeolite Silica	Commercially available
Amine and membranes	Amine solvent + membrane	Under research
CLC	MeO (Me = Ni, Cu, Mn or Fe)	Commercially available
Cryogenic	Cryogenic	Commercially available

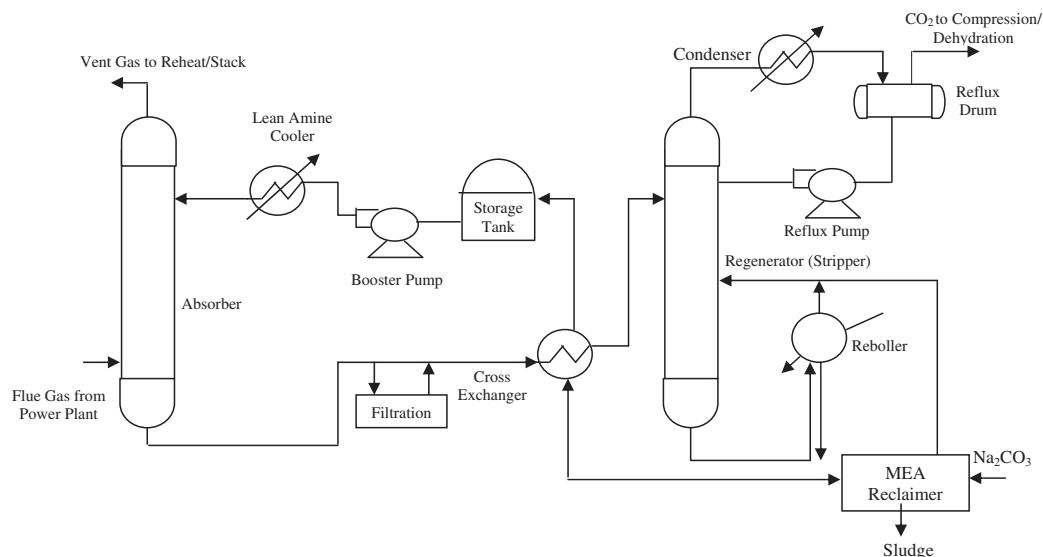


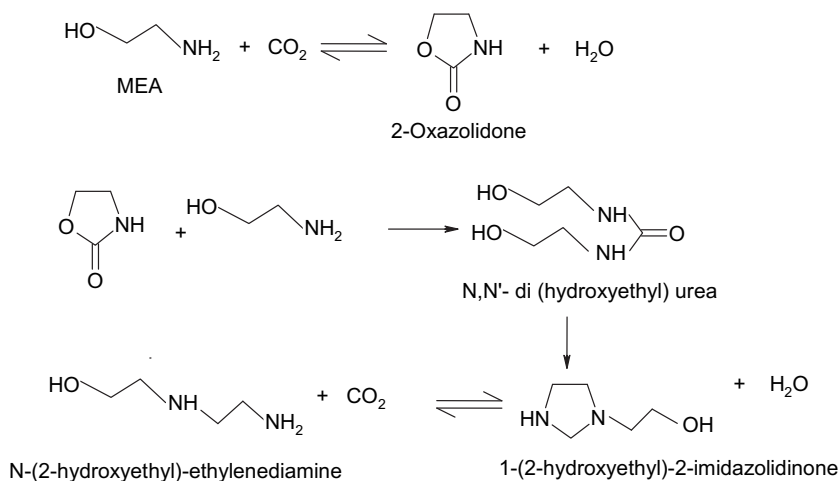
Fig. 4. Process flow diagram of a typical chemical absorption system for CO₂ recovery from flue gas.

an industrial environment of a CO₂ capture plant, although this benefit depends on whether the chemical stability of the solvent can be maintained.

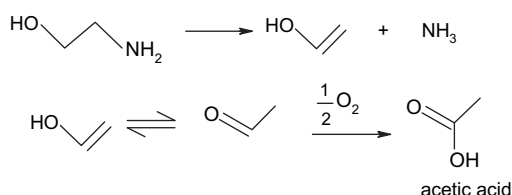
In recent years, a lot of effort has been put to develop new absorption solutions with enhanced CO₂ absorption performance. The use of sterically hindered amines, including aminoethers, aminoalcohols, 2-substituted piperidine alcohols and piperazine

derivatives, in solution to remove carbon dioxide from acidic gases by scrubbing process has been the focus in chemical absorption technology [24]. Sterically hindered amines have an amino group attached to a bulky alkyl group, e.g. 2-amino-2-methyl-1-propanol (NH₂–C(CH₃)₂CH₂OH). The nitrogen reacts rapidly and directly with CO₂ to bring the CO₂ into solution according to the following reaction sequence:

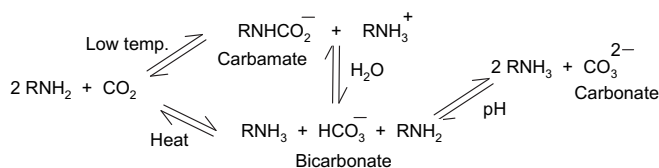
CO₂ - induced MEA Degradation :



O₂ - induced MEA Degradation:



Scheme 1. Degradation MEA by CO₂ and O₂.



Scheme 2. Proposed reaction sequence for the capture of carbon dioxide by liquid amine-based systems [22]; ($R = \text{CH}_2\text{CH}_2\text{OH}$ for MEA).



where R is an alkanol group.

The above reaction is the cornerstone of the present invention, as it is the one accelerated by carbonic anhydrase. The carbamate reaction product (RNHCOO^-) can then be hydrolyzed to bicarbonate (HCO_3^-) according to the following reaction:



Reactions (8) and (9) play major roles on the CO_2 absorption process using sterically hindered amines. The idea behind hindered amines is based on attaching a bulky substitute to the nitrogen atom of the amine molecule. This molecular configuration plays an important role in process performance, by affecting the capacity of absorption and desorption temperature. In the case of CO_2 removal, and in contrast with the alkanolamines, the rotation of the bulky alkyl group around the aminocarbamate group is restricted in sterically hindered amines; and these result in considerably low stability of the carbamate compound. The carbamate compound is thus likely to react with water and forms free amine and bicarbonate ions (eqn. (9)). Stoichiometrically from eqn. (3); 1 mol. of the sterically hindered amines instead of 2 mol. of alkanolamine is required to react with 1 mol. of CO_2 . The overall reaction for sterically hindered amine can be written as follows:



The International CO_2 capture centre in Regina, Saskatchewan, Canada has developed a series of proprietary designer solvents designated as PSR solvents [25]. The PSR solvents have been designed specifically for the separation of CO_2 from flue gas streams. The key features claimed for the PSR solvents are lower regeneration temperature, lower solvent circulation rate, lower solvent degradation rate and lower corrosion rate.

Major players in the amine arena include Mitsubishi Heavy Industries (MHI) and Fluor, which offers its Econamine FG process. The development of sterically hindered amine is seen as a breakthrough because of the significant number of advantages it offers, which include an exceptionally low corrosive nature; and unlike MEA, does not require a corrosive inhibitor. Additionally, it offers superior CO_2 absorption and regeneration, lower degradation, lower circulation rate and has less solvent loss when compared to other amine-based systems. All of these features lead to decreased operating cost. Examples of sterically hindered amines include 2-amino-2-methyl-1-propanol (AMP), and the proprietary solvents marketed by Mitsubishi Heavy Industries, KS-1, KS-2 and KS-3 [17]. A large research effort is being directed at improved solvents to improve the CO_2 loading, reduce the energy requirement for solvent circulation and regeneration and to overcome solvent degradation [26–29]. There is evidence that the capture process efficiency can be substantially improved by careful design of a mixture of solvents [17,30].

4.1.2. Aqua ammonia process

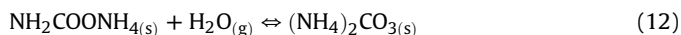
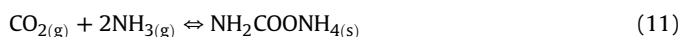
It is envisioned that the widely utilized MEA process could be replaced with aqueous ammonia process to capture all three major acid gases (SO_2 , NO_x , CO_2) plus HCl and HF , which may co-exist in the flue gas. Since SO_2 and NO_x emissions must comply with certain emission limits, a single process to capture all acidic gases is expected to reduce the total cost and complexity of emission control systems. Unlike the MEA process, the Aqua Ammonia Process (AAP) is not expected to have absorbent degradation problems that are caused by sulphur dioxide and oxygen in flue gas nor is it expected to cause equipment corrosion. The application of ammonia for simultaneous reduction of SO_2 , NO_x and mercury has also been reported [31].

The major by-products from the aqueous ammonia process include ammonium bicarbonate, ammonium nitrate and ammonium sulfate. Ammonium sulfate and ammonium nitrate are well known fertilizers for certain crops. Ammonium bicarbonate has been utilized by certain developing countries as a crop fertilizer for over 30 years with proven results in farmland practice which enhanced crop root development and leaf growth [32].

Research reports in the usage of ammonia for CO_2 capture are scanty, but the most noted ones are from Bai and Yeh [33] and Yeh and Bai [34]. Also reported by Bai [35] was a crystalline solid of NH_4HCO_3 , which was obtained by sparging CO_2 loading capacity into ammonium hydroxide solution and data published were comparing maximum CO_2 loading capacity in MEA and in ammonium hydroxide solution on equal weight of absorbent basis. It was concluded that the maximum CO_2 removal efficiency by NH_3 absorbent can reach 99% and the CO_2 loading capacity can approach 1.20 g CO_2/g NH_3 . On the other hand, the maximum CO_2 removal efficiency and loading capacity by MEA absorbent are 94% and 0.409 g CO_2/g MEA respectively under the same test conditions.

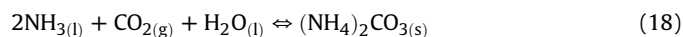
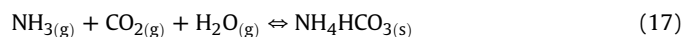
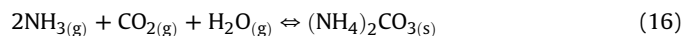
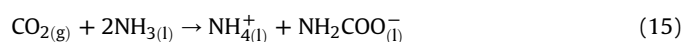
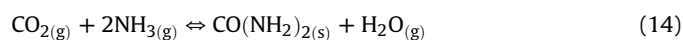
Preliminary research on aqueous ammonia scrubbing of CO_2 in a packed bed absorber produced similar CO_2 removal results [36] as compared to Yeh et al. [20]. The aqueous ammonia scrubbing technology seems to have avoided the shortcomings of the MEA process. In comparison, aqueous ammonia scrubbing technology has high loading capacity, does not pose a corrosion problem, tolerance to oxygen in the flue gas, low cost, there is no absorbent degradation problem, thus reducing absorbent makeup rate; and the energy requirement for absorbent regeneration is predicted to be much lower than in the MEA process. There is also the possibility of reaction with SO_x and NO_x – criteria pollutants found in flue gas – to form fertilizer (ammonium sulfate and ammonium nitrate) as a salable by-product.

4.1.2.1. Process chemistry of aqueous ammonia scrubbing technology. The absorption chemistry of CO_2 in aqueous ammonia solutions can be described by equations (6)–(8). The reaction with CO_2 and NH_3 in the dry condition occurs very easily and forms the ammonium carbamate ($\text{NH}_2\text{COONH}_4$), which is very soluble in water. Under moist air, it can form ammonium carbonate ($(\text{NH}_4)_2\text{CO}_3$) under room temperature [36], and then converts to ammonium bicarbonate (NH_4HCO_3). The above reactions are as follows:



The actual steps of the chemical reaction are complex and must pass through several intermediate reaction steps. Under the state of

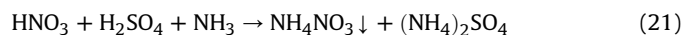
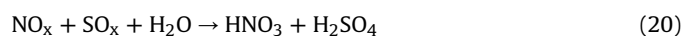
the ammonia injection, the reaction with CO₂, H₂O and NH₃ is as follows:



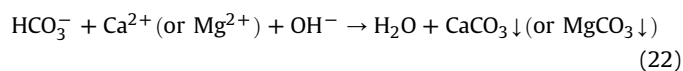
Under high pressure and with temperature greater than 140 °C, the CO₂–NH₃ reaction is directed to the formation of urea [CO(NH₂)₂] [37]. At room temperature and atmospheric pressure, the formation of ammonium (NH₄⁺) and carbamate (NH₂COO[−]) ion is very fast, and reaction equation (15) is irreversible [38]. On the other hand, reaction equations (16)–(19) are reversible; with ammonium carbonate [(NH₄)₂CO₃] and ammonium bicarbonate (NH₄HCO₃) as products [39]. The forward reactions are dominant at room temperature [40,41]. The backward reactions occur at temperatures of around 38–60 °C [42,43]. The solid ammonium carbonate and bicarbonate can either be dry powders or exist in an aqueous solution as crystalline solids.

Although reaction equation (14) may also be used to reduce CO₂ emission from flue gas since concentration of CO₂ in flue gas is high, the process needs a large amount of NH₃, which leads to the increase of operation cost. When the concentration of CO₂ in the flue gas is high, it will explode with the dry CO₂–NH₃ reaction if the process is not properly designed. The explosive limit for NH₃ gas is 15–28% (v/v) [44]. Therefore, for the sake of safety and simplicity, the wet method (i.e. using ammonia scrubbing instead of ammonia injection) is the most probable, as represented by reactions (18) and (19), for CO₂ removal by NH₃ scrubbing.

Spraying aqueous ammonia into flue gas not only captures CO₂ but also absorbs traces of SO_x and NO_x from the flue gas in accordance with the following chemical equations:



The product formed in equation (21), i.e ammonium bicarbonate (NH₄HCO₃) has been used as a nitrogen fertilizer in China for over 30 years. It has been well demonstrated that when NH₄HCO₃ is placed into deep soil, its nitrogen fertilization effect on crops is similar to that of other nitrogen fertilizers, such as (NH₄)₂SO₄ and urea [45]. It is also known that carbonates can react with alkaline earth metals such as calcium and magnesium, and be deposited as carbonate minerals. The bicarbonate HCO₃[−] from NH₄HCO₃ can neutralize alkaline species and reduce salt content by forming stable species as follows:



Solid products like CaCO₃ (or MgCO₃) are perfectly stable form of sequestered CO₂. Furthermore, soils could potentially serve as

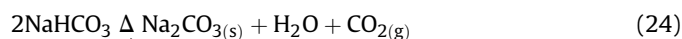
a “smart” screening material that will retain NH₄⁺ but allow HCO₃[−] to percolate with natural rainfall and/or irrigation down into groundwater, which is often rich in alkaline mineral species such as Ca²⁺ or Mg²⁺.

4.1.3. Dual-alkali absorption approach

A modified Solvay dual-alkali approach was proposed [46]. The Solvay process employs a dual-alkali approach with ammonia (primary alkali) as a catalyst to aid the reaction of CO₂ with sodium chloride for the production of sodium carbonate. The reaction was performed by first saturating brine with ammonia, and then with carbon dioxide.



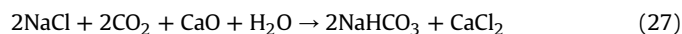
Product sodium carbonate is obtained by heating sodium bicarbonate.



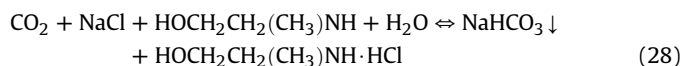
The ammonia is recovered by reacting ammonium chloride with lime (Ca(OH)₂), a secondary alkali, where limestone serves as the source of lime.



However, this scheme poses several drawbacks when applied to capture CO₂ from flue gas. The use of limestone for the regeneration of ammonia renders the process ineffective because of the consumption of limestone, production of CO₂ and extensive energy requirement during calcinations. In the Solvay process, for every two moles of CO₂ captured from flue gas, one mole of CO₂ is released from calcinations of limestone as given in the following overall reaction.



To circumvent the drawbacks of the Solvay process, a new dual-alkali method was developed using monoethanolamine (MEA) to replace ammonia as primary alkali. The monoethanolamine (MEA) was used as an effective primary alkali with the following reaction.



The CO₂ absorption capacity of methylaminoethanol (MAE) (0.75 mol-CO₂/mol-MAE) is greater than that of MEA (0.5 mol-CO₂/mol-MEA). The maximum CO₂ absorption capacity of an amine is 0.5 mol-CO₂/mol-amine if the reaction product is carbamate and 1.0 if the reaction product is bicarbonate. So theoretically, the CO₂ absorption capacity of an amine increases with an increase of bicarbonate in the products.

The second step of the dual-alkali approach involves a secondary alkali to regenerate the first alkali. In order to regenerate ammonia, and to make the process effective, activated carbon (AC) was replaced with limestone to serve as secondary alkaline to regenerate ammonia, the primary alkaline in the Solvay process, at ambient temperature (25 °C), according to the following equation.



The basicity of the activated carbon is responsible for the adsorption of HCl molecules from NH₄Cl solution with the liberation of ammonia. The by-product being HCl adsorbed on AC. This group of

researchers had not identified the secondary alkali to regenerate the primary alkali, MAE.

4.2. Physical absorption process

For physical absorption, CO₂ is physically absorbed in a solvent according to Henry's Law, which means that they are temperature and pressure dependent. Physical solvent processes use organic solvents to physically absorb acid gas components rather than reacting chemically. Removal of CO₂ by physical absorption processes are based on the solubility of CO₂ within the solvents and the solubility depends on the partial pressure and on the temperature of the feed gas. Higher CO₂ partial pressure and lower temperature favor the solubility of CO₂ in the solvents (Absorbent). The solvents are then regenerated by either heating or pressure reduction. The interaction between CO₂ and the absorbent is weak relative to chemical solvents; decreasing the energy requirement for regeneration. Physical absorption is used commercially to remove acid gas, (CO₂ + H₂S), from natural gas and to remove CO₂ from syngas in the production of hydrogen, ammonia and methanol. Physical solvents scrubbing of CO₂ are commercially available. Selexol (dimethylether of polyethylene glycol), a liquid glycol based solvent, has been used for decades to process natural gas, both for bulk CO₂ removal and H₂S removal [47]. Glycol is effective for capturing both CO₂ and H₂S at higher concentration. The Rectisol process, based on low temperature methanol (cold methanol), is another physical solvent process that has been used for removing CO₂. Glycol carbonate is interesting because of its high selectivity for CO₂ but it has relatively low capacity [48]. Other physical solvents for CO₂ removal include propylene carbonate (FLUOR process) and N-methyl-2-pyrrolidone (Purisol). The physical absorption process is illustrated in figure below (Fig. 5). CO₂ dissolved in the solvent is recovered by reducing pressure in various flash drums. No heat is required to release CO₂ due to the low heat of absorption. After depressurization, pure CO₂ streams are released at different pressures.

Some CO₂ capture applications benefit from a mixture of physical and chemical solvents. The most commonly used examples are Sulfinol, a mixture of the physical solvent sulfolane and the amines such as diisopropyl amine (DIPA) or methyl diethanolamine (MDEA); and Amisol, a mixture of methanol and secondary amines. These hybrid solvents attempt to exploit the positive qualities of each constituent under special conditions.

4.2.1. Selexol process

Selexol has been used since 1969 to sweeten natural gas, both for bulk CO₂ removal and H₂S removal. The Selexol process uses

Union Carbide Selexol solvent, a physical solvent made of dimethylether polyethylene glycol [CH₃(CH₂CH₂O)_nCH₃]; where *n* is between 3 and 9 [49]

Absorption takes place at low temperature (0–5 °C). Desorption of the rich Selexol solvent can be accomplished either by letting down the pressure (CO₂ removal) or by stripping with air, inert gas or steam. The solvent can be used to selectively or simultaneously remove sulphur compounds, carbon dioxide, water as well as aromatic compounds (BTX). Dehydration of the feed gas is required before entering the Selexol unit.

4.2.1.1. Advantages of Selexol process.

- (i) The heat rise of the solvent in the absorber is low since there is no heat of chemical reaction
- (ii) The sweet gas from the absorber comes out dry because of the high affinity of Selexol solvent with water
- (iii) The initial plant and operating costs are minimal
- (iv) Regeneration of the solvent is by air stripping, it required no re-boiler's heat
- (v) Selexol process allows for construction of mostly carbon steel due to its non-aqueous and inert chemical characteristics.
- (vi) The process could be operated at low pressure

4.2.1.2. Disadvantages of Selexol process.

- (i) The solvent has high affinity to heavy hydrocarbon which will be removed with CO₂ and essentially result to hydrocarbon losses.
- (ii) The process is more efficient at high operating pressure

4.2.2. Rectisol process

Rectisol has mainly been used to treat synthesis gas, hydrogen and town gas streams and removes most impurities. Rectisol process uses chilled methanol as a solvent, because of high vapor pressure of methanol, the process is normally operated at temperature range of –30 to –100°F. The process is best suited where there are limited quantities of ethane and heavier components [50]. There are many possible processes configurations for Rectisol process depending on process requirement/specifications and scalability. Rectisol process is extensively used in natural gas industry to remove CO₂ [51].

4.2.2.1. Advantages of Rectisol process.

- (i) The solvent (methanol) does not foam and completely miscible with water and thus reduces losses.
- (ii) They have high thermal and chemical stability
- (iii) It is non-corrosive
- (iv) There are no degradation problems
- (v) The carbon steel can be widely used for the equipment
- (vi) The rich solvent can be easily regenerated by flashing at low pressure, therefore eliminate the need for re-boiler's heat.

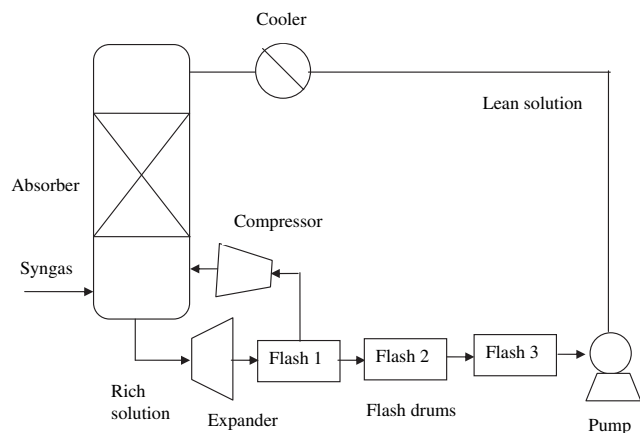


Fig. 5. Physical absorption to capture CO₂ from syngas.

4.2.2.2. Disadvantages of Rectisol process.

- (i) Chilled methanol solvent used is capable of absorbing metallic trace components such as mercury (Hg) to form amalgams in the low temperature of the process
- (ii) Rectisol complex scheme and the need to refrigerate the solvent result in high capital and operating cost of the plant

4.2.3. Fluor process

The Fluor solvent process is one of the most attractive processes for gas treating when the feed gas CO₂ partial pressure is high (>60 psig), or where the sour feed gas is primarily CO₂. The process is based on the physical solvent propylene carbonate (FLUOR™) for the removal of CO₂. Propylene carbonate (C₄H₆O₃), is a polar solvent with high affinity for CO₂.

4.2.3.1. Advantages of fluor process.

- (i) Fluor process required no fired duty for solvent regeneration
- (ii) The FLUOR solvent has high CO₂ solubility and enhance CO₂ loading
- (iii) It required no makeup water
- (iv) The operation is simple and a dry gas as output product
- (v) Since propylene carbonate freezes at −57°F, winterization modification is minimal
- (vi) Modification for increasing CO₂ in the feed is low

4.2.3.2. Disadvantages of Fluor process.

- (i) Solvent circulation for the FLUOR solvent process is high
- (ii) The FLUOR solvent is very expensive
- (iii) The solvent has high affinity to heavy hydrocarbons which will be removed with CO₂ and essentially results to hydrocarbon losses.

4.3. Physical adsorption

Adsorption relies on the thermodynamic properties of a substance to shift from the gas phase to attach itself to a solid material. This attachment can be either physical (physisorption) or chemical (chemisorption). Adsorption encompasses the selective removal of CO₂ from a gas stream to the adsorbent (zeolite or charcoal), followed by regeneration (desorption), which can be achieved either by reducing pressure (Pressure-Swing Adsorption or PSA), or by increasing temperature (Temperature Swing Adsorption, or TSA) or by passing an electric current through the adsorbent (Electrical Swing Adsorption, or ESA) or process hybrids (PTSA) or washing.

4.3.1. Molecular sieve adsorption

Molecular sieves are a range of specially designed sieves that separate molecules based on their molecular mass or molecular size. This technology is believed to be cost-effective and can be adapted to a variety of carbon sequestration schemes [4]. There

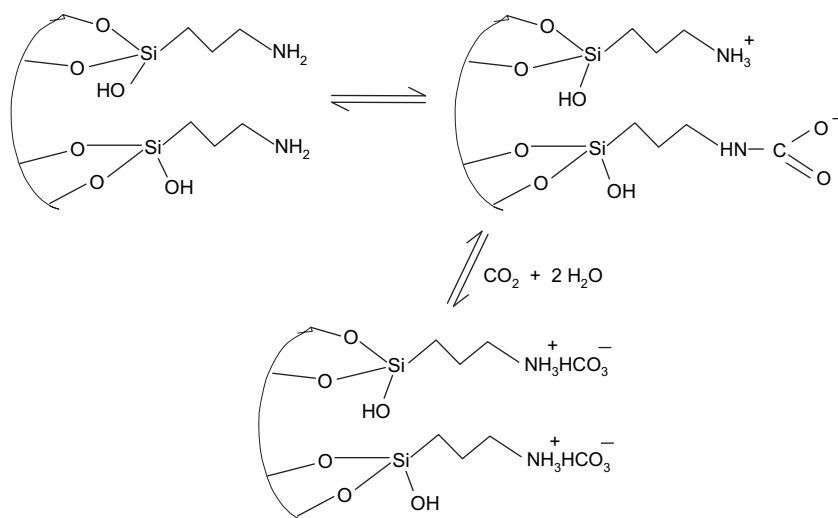
were many research activities targeted at improving the CO₂ adsorption by chemical modification of the molecular sieve surface. Adsorbents based on high surface area inorganic supports that incorporate basic organic groups, usually amines, are of particular interest. The interaction between the basic surface and acidic CO₂ molecules is thought to result in the formation of surface ammonium carbamates under anhydrous conditions and in the formation of ammonium bicarbonate and carbonate species in the presence of water as given in the scheme of reactions below (Scheme 3) [52]. Similar to amine absorption process, the CO₂ adsorption capacity is 0.5 mol CO₂/mol surface-bound amine group without the presence of water, 1.0 mol CO₂/mol surface-bound amine with the presence of water. Mesoporous substrates, such as silica [52,53], SBA-1 [54], SBA-15 [22], MCM-41 [54–56] and MCM-48 [46] are attractive because they possess pores that are large enough to be accessed by molecules with amino groups. Both the porosity and surface functionalized groups facilitate the capture of CO₂.

Chaffee et al. [57] also developed novel adsorbents for vacuum swing adsorptive (VSA) based CO₂ separation from flue gas. The adsorbents are insensitive to moisture and capable of operation at above ambient temperature. The authors focused on development of inorganic–organic hybrid adsorbents where the mesoporous inorganic substrate provides both substantial pore volumes and high surface area into and onto which basic organic group can be incorporated [52,53,58,59]. The amine groups react with the acidic CO₂ in the absence of water to form surface-bound ammonium carbamates (zwitterionic ammonium carbamate) with an apparent stoichiometric limit of 1 CO₂ molecule for every 2 N atoms (Scheme 3). However, in the presence of water, the adsorption capacity is sometimes improved further, towards a theoretical limit of 1 CO₂ molecule for every N atom via the formation of bicarbonates (ammonium bicarbonates) after proton exchange. Thus, the chemistry is analogous to that which occurs by absorption in solution. The mechanism of adsorption involves chemical bond formation and is therefore quite different to conventional adsorbents which operate according to the principle of physisorption.

4.3.2. Adsorption by activated carbon

Activated carbons have well developed micro- and mesoporosities which are applied in a wide range of industrial and technological processes [60]. The surface chemistry of activated carbons is governed by the presence of heteroatoms, such as oxygen, nitrogen etc. These heteroatoms exist in the form of acidic, basic or neutral organic functional groups [61]. Delocalized π electrons of aromatic rings and unsaturated valences also contribute to the basicity of carbonaceous sorbents. In order to enhance the specific adsorbate–adsorbent interaction, the surface chemistry can be modified by the incorporation of heteroatoms such as nitrogen. The presence of nitrogen within the carbon matrix causes an increase in the number of basic groups, which changes the charge distribution in the grapheme layers. The adsorption capacity of activated carbons to adsorb CO₂, which is based on physical adsorption, can be increased by introducing nitrogen functional groups into their structure [62,63]. The incorporation of these functionalities may be achieved by impregnating the surface with appropriate chemicals or introducing nitrogen into the carbon structure.

Maroto-Valer et al. [64] studied the CO₂ capture behavior of steam-activated anthracite. The adsorption capacity of the activated anthracite decreases rapidly with increasing adsorption temperature. The highest CO₂ adsorption capacity was 65.7 mg CO₂/g adsorbent for the anthracite activated at 800 °C for 2 h with a surface area of 540 m²/g. The anthracite with the highest surface area of 1071 m²/g only had a CO₂ adsorption capacity of 40 mg CO₂/g adsorbent. Also, chemical modification with NH₃



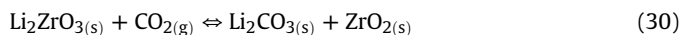
Scheme 3. Surface reaction of amine groups with CO₂ [52].

and polyethylenimine (PEI) impregnation increased the CO₂ capture capacity of the activated anthracite at higher temperature, due to the introduction of alkaline nitrogen groups on the surface.

Pevida et al. [65] reported that any surface modifications of commercial activated carbons should be carefully performed, so that nitrogen functionalities that promote the CO₂ capture capacities of adsorbents can be incorporated without altering the textural properties of the parent carbon.

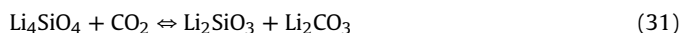
4.3.3. Adsorption based on lithium compounds

Lithium zirconate (Li₂ZrO₃), with favorable CO₂ sorption characteristics, has been investigated as a high temperature CO₂ absorbent [18]. This technology, based on the chemical reaction using Li₂ZrO₃ to capture CO₂, is illustrated in the following reaction:



The reaction is reversible in the temperature range of 450–590 °C; and the direction is reversible easily by a simple temperature swing approach. The formation of eutectic carbonate composed of Li₂CO₃ and K₂CO₃ can accelerate the CO₂ absorption reaction. A number of binary and ternary eutectic salt-modified lithium zirconate sorbents were identified and evaluated for high temperature CO₂ capture [66]. Their results showed that the combination of binary alkali carbonate, binary alkali/alkali earth carbonate, ternary alkali carbonate and ternary alkali carbonate/halide eutectic to Li₂ZrO₃ significantly improved the CO₂ uptake rate and CO₂ sorption capacity. Formation of a eutectic molten carbonate layer on the outer surface of reactant Li₂ZrO₃ particles facilitates the transfer of gaseous CO₂ during the sorption process.

Lithium silicate (Li₄SiO₄) was also studied for their CO₂ adsorption behaviors [67,68]. They found that the capacity of lithium silicate is much larger than that of lithium zirconate. Lithium silicate adsorbs CO₂ below 720 °C and releases CO₂ above 720 °C by the following mechanism:



Features, such as large capacity, rapid absorption, wide range of temperature and concentrations of CO₂ and stability, make lithium silicate a strong candidate for developing commercially competitive CO₂ adsorbent.

4.4. Cryogenics

The cryogenic method of purification involves the separation of the gas mixtures by fractional condensation and distillation at low temperature. Low temperature distillation (cryogenic separation) is a commercial process commonly used to liquefy and purify CO₂ from relatively high purity (> 90%) sources. It involves cooling the gases to a very low temperature (lower than –73.3 °C) so that the CO₂ can freeze out/liquefied and separated. The process has the advantage that it allows recovery of pure CO₂ in the form of a liquid, which can be transported conveniently or pumped to the injection site for enhance oil recovery (EOR) or enhance coal-bed methane (ECBM).

Hart and Gnanendran [69] reported cryogenic CO₂ capture in natural gas. The authors had researched into CryoCell CO₂ removal technology, tested in a demonstration plant and successfully demonstrated in a field trial. The CryoCell technology uses a cryogenic process to remove CO₂ from the natural gas, while avoiding the shortcomings of the conventional acid gas treatment process. The CryoCell technology eliminates water consumption, usage of chemicals and corrosion related issues. The field test programme has demonstrated the technical viability of solid phase CO₂ separation and cost comparison studies with amine absorption process indicate improved economic viability for high CO₂ gas field developments.

4.5. Membrane technology

A relatively novel capture concept is the use of selective membranes to separate certain components from a gas stream, which can be CO₂ from flue gas (post-combustion system), CO₂ from natural gas (natural gas processing), and CO₂ from hydrogen (pre-combustion systems) or oxygen from nitrogen (in oxyfuel combustion system).

Membranes are semi-permeable barriers able to separate substances by various mechanisms (solution/diffusion, adsorption/diffusion, molecular sieve and ionic transport). They are available in different material types, which can be either organic (polymeric) or inorganic (carbon, zeolite, ceramic or metallic) and can be porous to non-porous. 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. 6 below. Two characteristics dictate membrane performance; permeability, that is the flux of a specific gas through

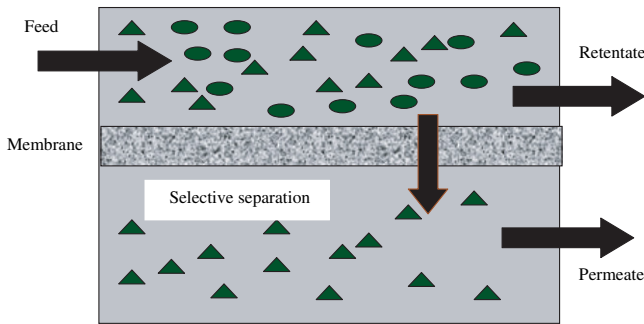


Fig. 6. Schematic of gas-separation membrane.

the membrane, and selectivity, the membrane's preference to pass one gas species over the other.

There are five possible mechanisms for membrane separation [70–73], they are Knudsen diffusion, molecular sieving, solution–diffusion separation, surface diffusion and capillary condensation, of which the first three are schematically shown below (Fig. 7).

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. The relationship between permeability, diffusivity and solubility can be described by:

$$P = DS \quad (\text{ii})$$

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 (cm^2s^{-1}), the mobility of molecules within the membrane and S is the solubility coefficient ($\text{cm}^3(\text{STP})\text{cmHg}^{-1}$), which measures the solubility of gas molecules within the membrane.

For ideal gas, the driving force across a gas-separation membrane is the pressure differential (Δp) between the feed side and the permeate side, as given by Fick's law:

$$J_i = \frac{P_i}{l} A_m (x_i p_f - y_i p_p) = \frac{P_i}{l} A_m \Delta p \quad (\text{iii})$$

where J_i is the flux across the membrane ($\text{cm}^3(\text{STP})\text{s}^{-1}$), P_i is the permeability value for component i , l is the membrane thickness [m], A_m is the membrane area [m^2], x_i and y_i are the mole fractions of the component i in the feed and the permeate sides respectively; p_f and p_p are the pressures in the feed side and the permeate side respectively.

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

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

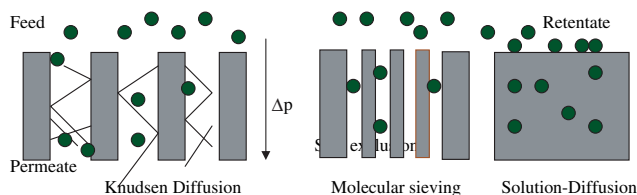


Fig. 7. Schematic representation of three of the different possible mechanisms for membrane gas separation, Knudsen diffusion, molecular sieving and solution–diffusion.

One option for achieving the driving force across the membrane is to set the permeate stream at atmospheric pressure and compress the feed gas to a higher pressure. This has been the assumption of the majority of previous studies that have investigated the feasibility of membrane technology for CO_2 capture [74–76].

Although membranes have several advantages over absorption and adsorption processes (no regeneration energy required, simple modular systems, no waste streams), membranes cannot always achieve high degrees of separation, which makes multiple stages or recycling necessary. Another disadvantage of membranes is the sensitivity to sulphur compounds and other trace elements. Membranes can be used for separation only, but can also be integrated with chemical reactors, benefiting often both separation and reaction characteristics as will be discussed in the later section.

4.5.1. Polymeric membrane

Generally, the transport of gas molecules through a polymeric membrane is by a solution–diffusion mechanism. Others include molecular sieve effect and Knudsen diffusion mechanisms [77]. Polymeric membranes are classified as rubbery or glassy, dependent on operating temperature relative to the glass transition temperature of the polymer [78]. 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 :

$$C_D = K_D f \quad (\text{v})$$

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 that 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 adsorbed gas within glassy membrane (C_T) can be described by the following equation [72]:

$$C_T = C_D + C_H \quad (\text{vi})$$

where C_H is the standard Langmuir relationship;

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

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

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

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

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

Membrane permeability is inversely proportional to the membrane area required for separation. Thus high permeability leads to lower cost. However, for most membranes, there is trade-off between selectivity and permeability. A highly permeable membrane tends to have low selectivity, and vice versa. Robeson [79] has suggested that this trade-off may be represented as an

upper bound to membrane performance. Overcoming of this upper bound is the focus of many researchers in polymeric membranes, because achieving both high carbon dioxide permeability and selectivity is desirable.

Improving the performance of the CO₂-selective polymeric membrane is achievable by two approaches; first is by increasing the solubility of carbon dioxide in the membrane through changes in polymeric composition, and secondly, increasing the diffusion of carbon dioxide by altering the polymer packing within the membrane. The combination of these approaches has produced a wide range of polymeric membranes with reasonable permeability and selectivity to provide good carbon dioxide separation. Polymers studied by various researchers include polyacetylenes [80], polyaniline [81], poly(arylene ether)s [82], polyarylates [83], polycarbonates and polyphenylene ethers [84], polyetherimides [85], poly(ethylene oxide) [86], polyimides [87], polypyrrolones [88] and polysulfones [89]. They all have reasonable permeability and selectivity, with some achieving performance around Robeson's upper bound. Fig. 8 shows the molecular structures of some commonly used polymers.

Ostwal et al. [90] recently reported the transport and sorption properties of poly (fluoroalkoxyphosphazene) (PFAP) membranes for carbon dioxide and nitrogen in both pure and mixed gas experiments. The CO₂ permeability was reported to decrease from

336 to 142 Barrers with an increase in the CO₂/N₂ ideal separation factor from 12 to 21 as the membrane temperature was decreased from 303 K to 258 K at feed pressure of 209 bars. Their report compares favorably well with that of Stewart et al. [91], who also reported CO₂ permeability of 376 Barrers and CO₂/N₂ ideal separation factor of 17 for PFAP at 303 K.

The performance of some polymeric membranes is summarized in Table 6, mainly separating post-combustion flue gas with CO₂/N₂ being the main components [77]. Single-stage membrane systems are not capable of high capture efficiency and CO₂ can be further concentrated by a second membrane stage.

4.5.2. Inorganic membrane

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 [92] or oxygen through perovskite systems [93]. In porous inorganic membranes, a porous thin top layer is casted on a porous metal or ceramic support, which provides mechanical strength but offers minimum mass-transfer resistance. Porous inorganic membranes are generally cheaper but less selective.

Alumina, carbon, glass, silicon carbide, titania, zeolite and zirconia membranes are mainly used as porous inorganic

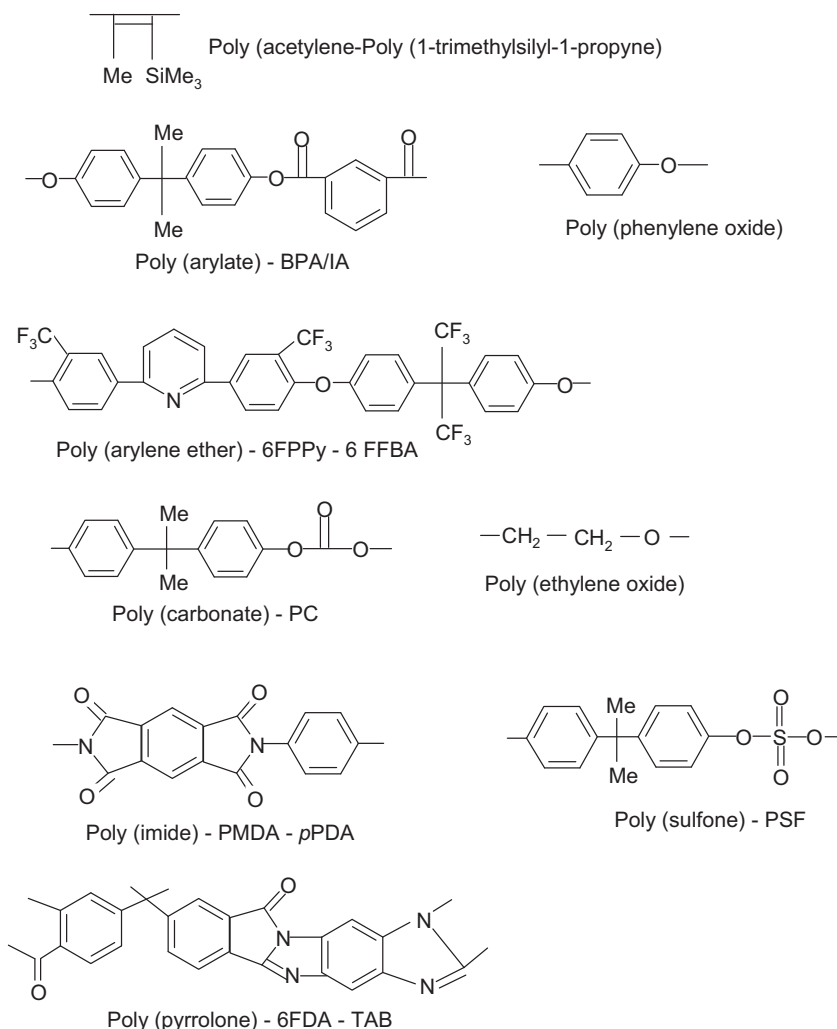


Fig. 8. Examples of polymer molecular structures used for CO₂ separation.

Table 6
Performance of polymeric membranes separating CO₂/N₂.

Material	Permeance [m ³ /(m ² Pa s)]	Selectivity %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

Source: Powell and Qiao [77].

membrane supported on different substrates such as α -alumina, γ -alumina, 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. These functional groups have a high chemical affinity for carbon dioxide and therefore the pore walls become saturated, which increases the permeability. These membrane performances approach Robeson's upper bound for carbon dioxide separation and are therefore compatible with polymeric membranes.

4.5.3. Zeolite membrane

Zeolites are inorganic crystalline structures with uniform-sized pores of molecular dimensions. Small-, medium-, and large-pore zeolites have been used to prepare membranes that separated CO₂ from CH₄ [94–98]. Because both CO₂ (0.33 nm kinetic diameter) and CH₄ (0.38 nm) molecules are much smaller than the pores of large-pore and medium-pore zeolites, separation with these membranes was mainly based on competitive adsorption. For ZSM-5 membranes, the CO₂/CH₄ separation selectivity at room temperature was 2.4–5.5 [99]. For Y-type membranes, CO₂/CH₄ separation selectivities were ~ 10 [100], for X-type membranes, CO₂/CH₄ separation selectivities as high as 28 were obtained [96]. Sebastian et al. [101] also prepared MFI-type zeolite membranes (Na-ZSM-5 and B-ZSM-5) on γ -alumina and stainless steel tubular supports, and were tested for separation of CO₂/N₂ mixtures. The separation between CO₂ and N₂ was reported to take place because of the preferential adsorption of CO₂, which hinders the permeation of N₂ through the zeolite pore network. Boron substituted ZSM-5 (B-ZSM-5) membrane prepared over a porous stainless steel support was reported to give the best results, with CO₂/N₂ separation selectivities of 13 and a CO₂ permeance of 2.66×10^{-7} mol/(m² s Pa).

In contrast, the small-pore molecular sieves such as zeolite T (0.41 nm pore diameter), DDR (0.36 \times 0.44 nm) and SAPO-34 (0.38 nm) have pores that are similar in size to CH₄ but larger than CO₂. High CO₂/CH₄ selectivities were observed for these membranes due to a combination of differences in diffusivity and competitive adsorption. Cui et al. [102] using a T-type zeolite membrane, obtained a CO₂/CH₄ separation selectivity of 400 and a CO₂ permeance of 4.6×10^{-8} mol/(m² s Pa) at 308 K for a trans-membrane pressure drop of 0.1 MPa and a vacuum on the permeate side. Tomita et al. [103] using DDR zeolite membrane on porous alumina tubes, obtained a CO₂/CH₄ selectivity of 220 and a CO₂ permeance of 7×10^{-8} mol/(m² s Pa) at 301 K for pressure drop of 0.5 MPa. Some authors have also reported that SAPO-34 membranes selectively separate CO₂ from CH₄ [94,97,104]. The SAPO-34 is a silicoaluminophosphate having the composition: Si_x-Al_yP_zO₂, where $x = 0.01$ –0.98; $y = 0.01$ –0.60; $z = 0.01$ –0.52; and $x + z = y$ [98]. Li et al. [104] reported that SAPO-34 membranes had a CO₂/CH₄ selectivity of 67 and a CO₂ permeance of 1.6×10^{-7} mol/(m² s Pa) at 297 K. Adsorption isotherm showed that CO₂ adsorbs

more strongly than CH₄ on SAPO-34 crystals and thus, preferential adsorption of CO₂ is partially responsible for the CO₂/CH₄ selectivity. These membranes were reported to be selective for CO₂ in the presence of H₂O, N₂, C₂H₄, C₃H₈ and *n*-C₄H₁₀ impurities. In the presence of the five impurities in the feed, Li et al. [104] reported that the CO₂/CH₄ selectivity was 48 and the CO₂ permeance was 0.88×10^{-7} mol/(m² s Pa) at 297 K.

4.5.4. Silica membrane

Amorphous silica with pores smaller than 1 nm is suitable as a material for highly selective membranes. However, diffusion through such narrow pores is usually slow. In order to improve both the performance and the selectivity of silica membranes, a number of studies have been reported on attempts to control the pore structures. Chemical vapor deposition (CVD) and sol–gel methods are used to prepare silica membranes, which provide pore properties that, are appropriate for gas separation. The latter is frequently adopted in membrane synthesis or membrane pore modification because of its controllability and homogeneity [105–107]. Gas permeation rates through inorganic membranes prepared by sol–gel process are relatively high, because of the very thin top layers of 50–200 nm thick. Brinker et al. [108] and Raman and Brinker [109] used methyltriethoxysilane (MTES) to modify silica membranes that were formed by using tetraethoxysilane (TEOS) and reported that the resulting membranes showed both high CO₂ permeances and CO₂/CH₄ selectivities.

4.5.5. Membranes in conjunction with chemical absorption

The combination of chemical absorption and selective membranes has also been suggested, so as to perform absorption and desorption in a single unit [110,111]. Guha et al. [112] modeled and measured the permeabilities and separation factors through a liquid membrane for a CO₂–N₂ system over a wide range of CO₂ partial pressures. In their approach, an immobilized liquid membrane (ILM, also referred to as supported liquid membrane or SLM) and an aqueous solution of diethanolamine (DEA) was used. In this system, DEA was immobilized in the pores of hydrophobic microporous polypropylene membrane, and helium gas was used as the sweep. Their combined CO₂ absorption and desorption into a single unit that require no external energy was reported to achieve CO₂/N₂ separation factors of 230–516. The model developed by Guha et al. [112] was adopted by Bao and Trachtenberg [113] to evaluate the performance of hollow fiber, contained liquid membrane (HFCLM) permeator for the separation of CO₂ from a CO₂–air mixture, using a DEA solution as the liquid membrane by means of both experimental and numerical methods. A permeance of 1.51×10^{-8} mol/m² s Pa was reached and CO₂/N₂ selectivity of 115, with a 20% (wt) DEA liquid membrane and a feed of 15% CO₂ in CO₂–air mixture at atmospheric pressure. Their model predictions compared well with the experimental results at CO₂ concentrations of industrial importance.

4.6. Chemical-looping combustion

Chemical-looping combustion (CLC), proposed by Richter and Knoche in 1983 [114], divides combustion into intermediate oxidation and reduction reactions that are performed separately with a solid oxygen carrier circulating between the separated sections. Suitable oxygen carriers are small particles of metal oxide such as Fe₂O₃, NiO, CuO or Mn₂O₃. A basic CLC system is shown in Fig. 9 [115]. The CLC has two reactors, one each for air and fuel. The oxygen carrier circulates between the reactors. In the air reactor, the carrier is oxidized by oxygen according to reaction (32). In the fuel reactor, the metal oxide is reduced by the fuel, which is oxidized to CO₂ and H₂O according to reaction (33).

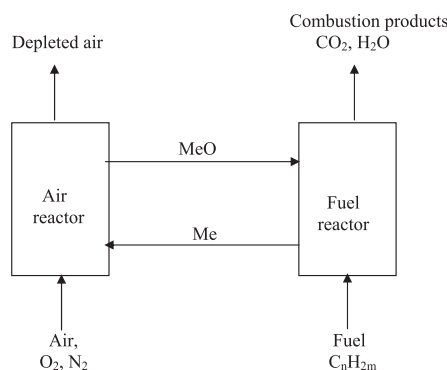
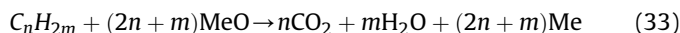


Fig. 9. Chemical-looping combustion [113].



The amount of energy released or required in the reactors depends on these two reactions, as well as the temperature of reactions.

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, a major advantage with CLC which avoids the huge energy penalty necessary in traditional amine-scrubbing process to capture CO_2 , and thus leads to less operational cost.

Research in metal oxide air separation is focused on cost and the physical and chemical stability of the oxygen carriers over many cycles. The particles usually consist of a reactive oxide and a supporting inert oxide. While various oxygen carrier particles are under consideration, copper, iron, manganese and nickel are the most promising reactive metals [116]. No large-scale demonstration has been performed but models predict that a power system utilizing metal oxide air separation has significant advantages. The lower irreversibilities associated with the regeneration step relative to conventional combustion add to the already low energy requirement of the inherent separation of CO_2 from nitrogen. Brandvoll and Bolland [117] reported that the resulting overall energy penalty could be as low as 400 kJ/kg CO_2 for a natural gas combined-cycle plant, assuming idealized chemical stability of the oxygen carrier.

The pros and cons of CO_2 separation techniques discussed above is summarized in Table 7.

5. Technical and economic barriers of CO_2 capture and separation technologies

Carbon capture and separation each have many technical barriers remaining to be scaled in the future. The idea of separating and capturing CO_2 from the flue gas of power plants did not start with concern about the greenhouse effect. Rather, it gained attention as a possible economic source of CO_2 , especially for use in enhanced oil recovery (EOR) operations where CO_2 is injected into oil reservoirs to increase the mobility of the oil and, therefore, the productivity of the reservoir. The three main general technological approaches discussed in this review for CO_2 capture include post-combustion, oxyfuel combustion and pre-combustion

decarbonization. Each technology has advantages and disadvantages. Some have been proven in the chemical production industry and others, while holding much future promise, are still in the laboratory development stage.

Post-combustion CO_2 capture is the most straightforward technique. End-of-pipe treatment of flue gases produced by conventional fossil fuel-fired plants belongs to this category. However, the technique's economic efficiency is rather low. The huge volumes of the flue gas containing relatively little CO_2 must be handled by conventional absorption processes requiring very large and expensive equipment. Though the efficiency penalty that the technique imposes on the power plant is huge, on the order of 25–35% [118]; yet post-combustion capture seems eminently suitable for retrofitting to existing facilities because it does not affect the upstream (fuel) part of the plant.

The second approach to carbon capture is oxyfuel combustion, which is also called oxyfuel decarbonization or O_2/CO_2 firing. It is a much more elegant technique than post-combustion CO_2 capture because pure oxygen is used as the oxidant instead of air. Nitrogen is completely eliminated from the process. Oxyfuel combustion is much more promising for new installations than post-combustion CO_2 capture. Although the air separation (oxygen generation) unit consumes a lot of energy, its overhead is mitigated by the elimination of the need for final CO_2 separation. There is a broad, ongoing and worldwide R&D effort to reduce the cost of oxygen generation. Most advanced processes being investigated are based on operating membranes at high temperatures. Scale-scale test rigs have confirmed that overall plant efficiency and economics can be improved by oxyfuel combustion; and it appears that oxyfuel combustion could be retrofit to existing steam power plants without incurring exorbitant costs [118].

The third carbon capture option, pre-combustion decarbonization, involves removal of the carbon prior to the combustion stage of an IGCC plant. First, a fossil fuel is transformed to a synthetic gas (syngas), essentially a mixture of $\text{CO} + \text{H}_2$. Next, the CO in the syngas is converted to $\text{H}_2 + \text{CO}_2$ by a water–gas shift (WGS) reactor. Finally, the CO_2 is separated by conventional methods. The big advantage of pre-combustion carbon removal is that the CO_2 separation step consumes much less energy than in other processes because it takes place in a smaller reaction volume and at lower volumetric flow rates, elevated pressure and higher component concentration. The higher concentrations make the capture process far less energy-intensive. The energy generation penalty, typically 10–16%, is roughly half that of post-combustion CO_2 capture. Pre-combustion carbon capture is a lot more cost-effective than post-combustion capture and slightly more effective than oxyfuel capture [118]. The primary disadvantage of pre-combustion capture is that total capital costs of generating facility are very high. Operating costs are higher than for standard plants due to the energy penalty, but they are lower than for post-combustion capture. Affordable pre-combustion capture will require significant Research and Development investment. Hot gas cleanup technology and improved oxygen production processes are the two areas of development. While several carbon capture methods are commercially mature for use, application on a scale necessary to impact global CO_2 emission may lead to unacceptable increases in the costs of plant operations unless current technologies can be significantly improved upon or new approaches are developed. Wright et al. [119] has carried out simulations to evaluate the use of sorption-enhanced-water–gas shift (SEWGS) for power generation from natural gas with carbon capture. Their modeling results show that using SEWGS process could significantly reduce the cost of capturing CO_2 versus a reference design that uses amine absorption. van Selow et al. [120] also developed a technology using potassium-promoted hydrtalcite-based

Table 7Pros and cons of CO₂ separation technologies.

CO ₂ separation technology	Pros	Cons
<i>Chemical absorption technology</i>		
Ammonia process	<ul style="list-style-type: none"> • Lower heat of regeneration than MEA • Higher net CO₂ transfer capacity than MEA • Stripping steam not required • Offers multipollutant control 	<ul style="list-style-type: none"> • Ammonium bicarbonate decomposes at 140°F, so temperature in the absorber must be lower than 140°F • Ammonia is more volatile than MEA and often provides an ammonia slip into the exit gas. • Ammonia is consumed through the irreversible formation of ammonium sulfates and nitrates as well as removal of HCl and HF.
Amine scrubbing	<ul style="list-style-type: none"> • Applicable to CO₂ partial pressures. • Recovery rates of up to 95% and product purity >99 vol. % can be achieved. 	<ul style="list-style-type: none"> • Process consumes considerable energy. • Solvent degradation and equipment corrosion occur in the presence of O₂. • Concentrations of SO_x and NO_x in the gas stream combine with the amine to form nonregenerable, heat-stable salt. • Rectisol refrigeration costs can be high.
<i>Physical absorption</i>	<ul style="list-style-type: none"> • Low utility consumption • Rectisol uses inexpensive, easily available methanol. • Selexol has a higher capacity to absorb gases than amines. • Selexol can remove H₂S and organic sulphur compounds. • Both provide simultaneous dehydration of the gas stream 	<ul style="list-style-type: none"> • Hydrocarbons are coabsorbed in Selexol, resulting in reduced product revenue and often requiring recycle compression. • Refrigeration is often required for the lean Selexol solution. • More economical at high pressures.
<i>Membrane technology</i>	<ul style="list-style-type: none"> • No regeneration energy is required • Simple modular system • No waste streams 	<ul style="list-style-type: none"> • Membranes can be plugged by impurities in the gas stream. • Preventing membrane wetting is a major challenge. • Technology has not been proven industrially
CLC	<ul style="list-style-type: none"> • Exhaust gas stream for air reactor is harmless • No thermal formation of NO_x • Avoids huge energy penalty; and thus less operational cost 	<ul style="list-style-type: none"> • No large-scale demonstration has been performed.

material; and has been shown to reversibly take up CO₂ at temperatures near 400 °C with associated promising breakthrough capacities of 1.3–1.4 mmol/g under realistic conditions. Total capacities for this material can exceed 8 mmol/g if feed partial pressures of CO₂ and H₂O are sufficiently high. However, this high capacity was presumably associated with formation of MgCO₃ and the kinetics of this chemisorption is too slow to exploit in a pressure-swing adsorption process such as SEWGS. Sorbent development reactor development and process improvement are imperative to meet cost targets for commercialization of the SEWGS technology in power plants and hydrogen production plants.

Various technologies have also been discussed for CO₂ separation, and these include chemical absorption using ammonia and amine, physical absorption, physical adsorption, membrane systems, cryogenic fractionation, chemical-looping combustion. Each of these technologies may be combined with various methods for fuel pre-processing and combustion. For example, the removal process may be applied directly to the flue gas from a conventional power plant; it may be combined with a coal gasifier as an add-on to an integrated coal gasifier combined facility; or it may be integrated into a system based on fuel cells. The precise form of the separated CO₂ (purity, solid, liquid or gaseous state; and the temperature and/or pressure) is a function of the total system design, including the disposal methods (deep oceans [121]; depleted oil and gas fields [122], deep saline formations (aquifers) and recovery of enhanced oil, gas and coal-bed methane [122] and mineral carbonation [123]). The costs of each of these individual technical approaches are highly uncertain, particularly at the scale of a modern fossil power plant. Moreover, costs estimates may differ greatly depending on the type of fossil fuel used.

By and large, opportunities for advances in materials to improve current capture technologies include higher capacity adsorbents and increased membrane selectivity. Research enabling improved compounds for chemical separation processes could reduce energy requirements and increase stability. Chemical solvent separation

could benefit from compound with high capacity and lower regeneration energy.

6. Improvement opportunities in CO₂ separation technology

The new demand from climate change concerns has stimulated research efforts to examine new opportunities in this area. Improvements to amine-based systems for post-combustion CO₂ capture are being pursued vigorously by a number of process developers; a few of these include Fluor, Mitsubishi Heavy Industry (MHI) and Cansolv Technologies. Fluor Econamine FG plus is a proprietary acid gas removal system that has demonstrated greater than 95% availability with natural gas fired power plants. It is currently the state-of-the-art commercial technology baseline and is used in comparing other CO₂ capture technologies. MHI has developed a new absorption process, referred to as KS-1. A key factor in this development is the utilization of a sterically hindered amine solvent for the capture of CO₂ from flue gas [124].

Cansolv Technologies, Inc., also proposes to reduce costs by incorporating CO₂ capture in a single column with processes for capturing pollutants, such as SO₂, NO_x and Hg. Their new DC103^R tertiary amine solvent has demonstrated fast mass transfer and good chemical stability with high capacity – a net of 0.5 mol of CO₂/mole of amine per cycle compared to 0.25 mol/mol for monoethanolamine (MEA) [125].

Research and Development pathways to improve amine-based systems include modified tower packing to reduce pressure drop and increase contacting, increased heat integration to reduce energy requirements, additives to reduce corrosion and allow higher amine concentrations and improved regeneration procedures.

Another ammonia-based system, under development by Alstom is Chilled ammonia process (CAP). This process uses the same AC/ABC absorption chemistry as the aqueous system described above, but differs in that no fertilizer is produced and a slurry of aqueous AC and ABC and solid ABC is circulated to capture CO₂ [126]. The process operates at near freezing temperatures

(32–50°F), and the flue gas is cooled prior to absorption using chilled water and a series of direct contact coolers. Technical barriers associated with the technology include cooling the flue gas and absorber to maintain operating temperatures below 50°F (required to reduce ammonia slip, achieve high CO₂ capacities, and for AC/ABC cycling), mitigating the ammonia slip during absorption and regeneration, achieving 90% removal efficiencies in a single stage, and avoiding fouling of heat transfer and other equipment by ABC deposition as result of absorber operation with a saturated solution. This process and aqueous ammonia scrubbing technology have the potential for improved energy efficiency over amine-based systems, if the barriers can be overcome.

Better improvement in gas–liquid contact can also reduce the size of absorber and costs; improve practical CO₂ loading and reduce the sorbent circulation and regeneration energy requirement. This becomes more important for new sorbents that have lower reaction rate constants along with their lower regeneration energy requirements. A study has indicated that structured packing in an absorber can provide a much higher overall mass-transfer coefficient than the currently used random packing [127]. Using the membrane technology can reduce absorber size because membranes provide large contact surface between the gas and the liquid. A study has also indicated that an absorber using membrane technology can reduce its size by 72% and its weight by 66% compared with a conventional absorption column [128].

Chemical modification of polymeric membranes is one of the most promising approaches for greatly enhancing separation performance. Therefore, further development of existing modification methods or invention of new modification technique for existing gas-separation materials may accelerate the commercialization of polymeric membranes for the hydrogen economy. However, long-term stability and performance of the polymeric membranes at elevated temperature are necessary to maintain the robustness of the membrane-based systems [129].

Biologically based capture systems are another potential avenue for improvement in CO₂ capture technology [130]. These systems are based upon naturally occurring reactions of CO₂ in living organisms. Carbozyme, Inc., has developed a biomimetic technology that promises significant cost and performance advantages over amine-scrubbing systems for the capture of CO₂ from combustion flue gases [131]. The Carbozyme technology has three key features: 1) a rapid catalyst, CA; 2) a high efficiency mass-transfer hollow fiber design; and 3) low energy requirement that does not use high value steam. The process, utilizing carbonic anhydrase (CA) in a hollow fiber contained liquid membrane, has demonstrated at laboratory scale the potential for 90% CO₂ capture followed by regeneration at ambient conditions. This is a significant technical improvement over the MEA temperature swing absorption process. The CA process has been shown to have a very low heat of absorption that reduces the energy penalty typically associated with absorption processes. Carbozyme biomimetic process can afford a 17-fold increase in membrane area or a 17 times lower permeance value and still be competitive in cost with MEA technology [132].

7. Conclusion

The fundamentals of combustion and separation processes suggest that the capture of high purity, high concentrated CO₂ from fossil fuels require energy. Improved energy efficiency and fuel switching are thus clearly superior strategies for curtailing CO₂ emissions. The possibility of capturing carbon and fixing it as a solid (to be disposed of at low cost) or use it as a secondary product of commercial value, is also attractive. Carbon capture and separation from large point source such as power plants can be achieved

through continued research, development and demonstration. Research to develop technologies and processes that increase the efficiency of capture system with reduction in overall cost and energy efficiency is critical to creating a feasible GHG control implementation plan, covering not only power plant and industrial facilities but also the infrastructure required to support such implementation.

MEA has been the most commonly chosen solvent so far for absorption process, and has often been enhanced with additives to improve its performance. Improvement must still be made, however, for post-combustion solvent absorption/regeneration processes to be a competitive option for CO₂ capture. Aqueous ammonia scrubbing technology is a promising technology for CO₂ separation but the fate of bicarbonate after the spreading of ABC onto soil is a key issue. The use of sterically hindered amine, such as AMP or Mitsubishi Heavy Industry (KS-1, KS-2) provides another option which has an exceptionally low corrosive nature and unlike MEA, does not require a corrosion inhibitor. Gas-separation membranes have the potential to capture CO₂ from pre-combustion and post-combustion gas stream. However, improvements in membrane CO₂ permeability, CO₂/N₂ selectivity, membrane cost reductions, degradation of performance over times due to a variety of factors are some of the challenges that will be needed to overcome to make CO₂ separation using membrane technology a competitive option. Solvent assisted membranes are also being developed to combine the best features of membranes and solvent scrubbing. CLC, a novel capture technique whereby a fuel is contacted with a metal oxide which releases oxygen for combustion; and regenerating the oxide by reaction with air in a separate vessel. Degradation of the oxide material is a concern in CLC.

Utilization of technological options for separation and/or capture of CO₂ from combustion flue gas and other industrial effluents will make the world oil and gas industry realize their vision in future by moving from “CO₂ threatening”, due to the global warming potential (or “the greenhouse effect”) of CO₂ to “opportunities” from the use of the captured CO₂ as a secondary product to produce chemical substances through the application of organic chemistry, biofuels, etc or injecting the pure streams of CO₂ captured into the underground for enhanced oil recovery (EOR), enhanced gas recovery (EGR) and enhanced coal-bed methane (ECBM), although not covered in this review.

There are a lot of uncertainties about which technologies could lead to real improvements and which really have no real prospects for reducing the cost of capture. When reviewing the literature, it is difficult to compare technologies that have been studied by different groups of researchers because they each have different bases for analysis and optimism were often injected into their analysis. According to Steeneveldt et al. [133], IEA [134] and Irons et al. [7], post-combustion is the only most feasible technology to implement in near future especially for existing power plants with amine solvents. Technologies should be carefully and objectively analyzed, and efforts should be made to reduce uncertainty and bias before implementation.

References

- [1] IPCC. Climate change 2001: impacts, adaptation and vulnerability. Contribution of Working Group II to the Third Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge: Cambridge University Press; 2001.
- [2] O'Neill BC, Oppenheimer M. Climate change: dangerous climate impacts and the Kyoto protocol. *Science* 2002;296(5575):1971–2.
- [3] Yamasaki A. An overview of CO₂ mitigation options for global warming – emphasizing CO₂ sequestration options. *J Chem Eng Jpn* 2003;36(4):361–75.
- [4] Stewart C, Hessami M. A study of methods of carbon dioxide capture and sequestration – the sustainability of a photosynthetic bioreactor approach. *Energy Convers Manage* 2005;46:403–20.

- [5] IEA special report on carbon dioxide capture and storage. IPCC web site: www.ipcc.ch; 2005.
- [6] Natural gas issues and trends. Energy Information Administration (EIA); 1998.
- [7] Irons R, Sekkapan G, Panesar R, Gibbins J, Lucquiaud M. CO₂ capture ready plants. IEA Greenhouse Gas R & D Programme, www.ieagreen.org.uk; 2007.
- [8] Adams D, Davison J. Capturing CO₂. IEA Greenhouse Gas R & D program, ISBN 978-1-898373-41-4; 2007. 17p.
- [9] Hydrogen production and storage. International Energy Agency; 2006. 38p.
- [10] Armstrong PA, Bennett DL, Foster EP, Stein VE. Ceramic membrane development for oxygen supply to gasification applications, www.gasification.org.
- [11] Croiset E, Thambimuthu KV. Coal combustion in O₂/CO₂ mixtures compared to air. *Canad J Chem Eng* 2000;78:402–7.
- [12] Feron PHM, Hendriks CA. CO₂ capture process principles and costs. *Oil Gas Sci Technol Rev* 2005;60(3):451–9. IFP.
- [13] Desideri U, Corbelli R. CO₂ capture in small size cogeneration plants: technical and economic considerations. *Energy Convers Manage* 1998;339(9):857–67.
- [14] Jeremy D. Economic evaluation of leading technology options for sequestration of carbon dioxide. M.S thesis, MIT, Cambridge, MA; 2000.
- [15] Audus H. Leading options for the capture of CO₂ at power stations. Presented at the 5th international conference on greenhouse gas control technologies, 13–16 August, 2000, Cairns, Australia.
- [16] Anderson S, Newell R. Prospects for carbon capture and storage technologies. Washington, D.C.: Resources for the Future; 2003. 1–67.
- [17] White CM, Strazisar BR, Granite EJ, Hoffman JS. Separation and capture of CO₂ from large stationary sources and sequestration in geologic formations – coalbeds and deep saline aquifers. *J Air Waste Manage Assoc* 2003;53:645–715.
- [18] Fauth DJ, Frommell EA, Hoffman JS, Reasbeck RP, Pennline HW. Eutectic salt promoted lithium zirconate: novel high temperature sorbent for CO₂ capture. *Fuel Process Technol* 2005;86(14–15):1503–21.
- [19] Resnik KP, Yeh JT, Pennline HW. Aqua ammonia process for simultaneous removal of CO₂, SO₂ and NO_x. *Int J Environ Technol Manage* 2004;4(1–2):89–104.
- [20] Yeh JT, Resnik KP, Pygle K, Pennline HW. Semi batch absorption and regeneration studies for CO₂ capture by aqueous ammonia. *Fuel Process Technol* 2005;86(14–15):1533–46.
- [21] Strazisar BR, Anderson RR, White CM. Degradation pathways for monoethanolamine in a CO₂ capture facility. *Energy Fuel* 2003;17:1034–9.
- [22] Gray ML, Soong Y, Champagne KJ, Pennline H, Baltrus JP, Stevens RW, et al. Improved immobilized carbon dioxide capture sorbents. *Fuel Process Technol* 2005;86(14–15):1449–55.
- [23] Idem R, Wilson M, Tontiwachwuthikul P, Chakma A, Veawab A, Aroonwiles A, et al. Pilot plant studies of the CO₂ capture performance of aqueous MEA and mixed MEA/MDEA solvents at the University of Regina CO₂ capture technology development plant. *Ind Eng Chem Res* 2006;45(8):2414–20.
- [24] Yagi Y, Mimura T, Lijima M, Hida K, Yoshiyama R, Kamijo T, et al. Improvement of carbon dioxide capture technology from flue. In: Seventh international conference on greenhouse gas control technologies. Canada: Vancouver Convention Centre; 2004. p. E3–4.
- [25] Veawab A, Aroonwiles A, Chakma A, Tontiwachwuthikul P. Solvent formulation for CO₂ separation from flue gas streams. Presented at first national conference on carbon sequestration, Washington, DC, May 15–17; 2001.
- [26] Zheng XY, Diao YF, He BS, Chen CH, Xu XC, Feng W. Carbon dioxide recovery from flue gases by ammonia scrubbing. *Greenhouse gas control technologies*. In: Gale J, Kaya Y, editors. Proceedings of the 6th international conference on greenhouse gas control technologies (GHGT-6), 1–4, Oct., 2002, Kyoto, Japan. Oxford, UK: Elsevier Science Ltd.; 2003. p. 193–200.
- [27] Cullinane JT, Rochelle GT. Carbon dioxide absorption with aqueous potassium carbonate promoted by piperazine. In: Gale J, Kaya Y, editors. *Greenhouse gas control technologies*, vol. 11. UK: Elsevier Science; 2003. p. 1603–6.
- [28] Chakravarti S, Gupta A, Hunek B. Advanced technology for the capture of carbon dioxide from flue gases. In: Presented at first national conference on carbon sequestration, May 15–17, 2001, Washington, DC; 2001.
- [29] Mimura T, Nojo T, Iijima M, Yoshiyama T, Tanaka H. Recent developments in flue gas CO₂ recovery technology. *Greenhouse gas control technologies*. In: Gale J, Kaya Y, editors. Proceedings of the 6th international conference on greenhouse gas control technologies (GHGT-6), 1–4, Oct., 2002. Kyoto, Japan. Oxford, UK: Elsevier Science Ltd; 2003.
- [30] Melien TCCP. Final cost estimation and economics. Common economic model team summary report. In: Thomas DC, editor. Carbon dioxide capture for storage in deep geologic formations—results from the CO₂ capture project. Capture and separation of carbon dioxide from combustion sources, vol. 1. Elsevier; 2005. p. 47–87.
- [31] Joanna Duncan. Electro-catalytic oxidation (ECO): results from pilot scale testing of simultaneous NO_x, SO₂, Hg and PM_{2.5} removal at first energy's R.E. burger plant. In: Proceedings of 20th annual international Pittsburgh coal conference, Pittsburgh, PA; 2003.
- [32] NPCC. Study on CO₂ sequestration by spray concentrated aqueous ammonia and production of modified NH₄HCO₃ fertilizer – a proposal for US – China joint research. China: State Engineering Technology Research Centre of Combustion of Power Plants (NPCC); 2000. May.
- [33] Bai H, Yeh AC. Removal of CO₂ greenhouse gas by ammonia scrubbing. *Ind Eng Chem Res* 1997;36(6):2490–3.
- [34] Yeh AC, Bai H. Comparison of ammonia and monoethanolamine solvents to reduce CO₂ greenhouse gas emissions. *Sci Total Environ* 1999;228:121–33.
- [35] Bai H. Fundamental study of ammonia–carbon dioxide reactions to form solid particles. Ph.D. dissertation, University of Cincinnati, USA; 1992.
- [36] Brooks LA, Audrieth LF. Ammonium carbonate. *Inorg Synth* 1946;2:85–92.
- [37] Kucheryavii VI, Gorlovskii DM. Densities of coexisting phases in the equilibrium gas–liquid system NH₃–CO₂–CO(NH₂)₂–H₂O at high temperatures and pressures. *Zh Prikl Khim* 1970;43:1675–82.
- [38] Hatch TF, Pigford RL. Simultaneous absorption of carbon dioxide and ammonia in water. *Ind Eng Chem Fundam* 1962;1:209–18.
- [39] Brooks R. Manufacture of ammonium bicarbonate. British Patent 1953;742:386.
- [40] Pelkie JE, Concannon PJ, Manley DB, Poling BE. Product distributions in the CO₂–NH₃–H₂O system from liquid conductivity measurements. *Ind Eng Chem Res* 1992;31:2209.
- [41] Koubsky P, Hladky V. Equilibrium calculations in the system NH₃–CO₂–H₂O. *Int Chem Eng* 1976;16:392.
- [42] Shale CC, Simpson DG, Lewis PS. Removal of sulfur and nitrogen oxides from stack gases by ammonia. *Chem Prog Symp Ser* 1971;67:52.
- [43] Grayson M. Kirk–Othmer encyclopedia of chemical technology. 3rd ed., vol. 2. New York: John Wiley & Sons; 1978.
- [44] Merck K. Reagents-chemicals-diagnostics. Darmstadt, Germany: IRIODIN/AFFLAIR; 1996.
- [45] Xi Z, Shi X, Liu M, Cao Y, Wu X, Ru G. Agrochemical properties of ammonium bicarbonate. *Turang Xuebao* 1985;22(3):223–32.
- [46] Huang HY, Yang RT, Chinn D, Munson CL. Amine-grafted MCM-48 and silica xerogel as superior sorbents for acidic gas removal from natural gas. *Ind Eng Chem Res* 2003;42(12):2427–33.
- [47] Davison J, Freund P, Smith A. Putting carbon back into the ground. IEA Greenhouse Gas R & D Programme; 2001.
- [48] Kovvali AS, Sirkar KK. Carbon dioxide separation with novel solvents as liquid membranes. *Ind Eng Chem Res* 2002;41:2287–95.
- [49] Johnson JE, Homme Jr AC. Selexol solvent process reduces lean, high-CO₂ natural gas treating costs. *Energy Progr* 1984;4(4):241–8.
- [50] Weiss H. Rectisol wash for purification of partial oxidation gases. *Gas Sep Purif*; 1998:171–6.
- [51] Knapp H. Processing gas conditioning conference. Norman: Okla; 1968. p. C-1.
- [52] Knowles GP, Graham JV, Delaney SW, Chaffee AL. Aminopropyl-functionalized mesoporous silicas as CO₂ adsorbents. *Fuel Process Technol* 2005;86:1435–48.
- [53] Knowles GP, Delaney SW, Chaffee AL. Diethylenetriamine [propyl (silyl)-functionalized (DT) mesoporous silicas as CO₂ adsorbents. *Ind Eng Chem Res* 2006;45(8):2626–33.
- [54] Yoshitake H, Yokoi T, Tatsumi T. Adsorption of chromate and arsenate by amino-functionalized MCM-41 and SBA-1. *Chem Mater* 2003;15:4536–8.
- [55] Song C. Global challenges and strategies for control, conversion and utilization of CO₂ for sustainable development involving energy, catalysis, adsorption and chemical processing. *Catal Today* 2006;115:2–32.
- [56] Xu X, Song C, Miller BG, Scaroni AW. Adsorption separation of carbon dioxide from flue gas of natural gas-fired boiler by a novel nanoporous “molecular basket” adsorbent. *Fuel Process Technol* 2005;86(14–15):1457–72.
- [57] Chaffee AL, Knowles GP, Liang Z, Zhang J, Xiao P, Webley PA. CO₂ capture by adsorption: materials and process development. *Int J Greenhouse Gas Control* 2007;1:11–8.
- [58] Knowles GP, Beyton V, Chaffee AL. New approaches for the preparation of aminopropyl-functionalized silicas as CO₂ adsorbents. *Am Chem Soc, Div Fuel Chem Prepr* 2006;51:102–3.
- [59] Liang Z, Fadhil B, Schneider CJ, Chaffee AL. Mesoporous-bound melamine-type dendrimers and their CO₂ adsorption properties. *Am Chem Soc Div Fuel Chem; Prepr* 2006;51:159–61.
- [60] Bansal RC, Donnet J, Stoeckli F. Activated carbon. Marcel Dekker Inc.; 1998.
- [61] Arenillas A, Rubiera F, Parra JB, Ania CO, Pis JJ. Surface modification of low cost carbons for their application in the environmental protection. *Appl Surf Sci* 2005;252:619–24.
- [62] Drage TC, Arenillas A, Smith KM, Pevida C, Piippo S, Snape CE. Preparation of carbon dioxide adsorbents from the chemical activation of urea-formaldehyde and melamine-formaldehyde resins. *Fuel* 2007;86:22–31.
- [63] Plaza MG, Pevida C, Arias B, Fermoso J, Arenillas A, Rubiera F, et al. Application of thermogravimetric analysis to the evaluation of aminated solid sorbents for CO₂ capture. *J Therm Anal Cal* 2008;92:601–6.
- [64] Maroto-Valer MM, Tang Z, Zhang Y. CO₂ capture by activated and impregnated anthracites. *Fuel Process Technol* 2005;86(14–15):1487–502.
- [65] Pevida C, Plaza MG, Arias B, Fermoso J, Rubiera F, Pis JJ. Surface modification of activated carbons for CO₂ capture. *Appl Surf Sci* 2008;254(22):7165–72.
- [66] Yeboah YD, Xu Y, Sheth A, Godavarty A, Agrawal PK. Catalytic gasification of coal using eutectic salts: identification of eutectics. *Carbon* 2003;41:203–14.
- [67] Essaki K, Nakagawa K, Kato M, Uemoto H. CO₂ absorption by lithium silicate at room temperature. *J Chem Eng Jpn* 2004;37(6):772–7.
- [68] Kato M, Nakagawa K, Essaki K, Maezawa Y, Takeda S, Kogo R, et al. Novel CO₂ absorbents using lithium-containing oxide. *Int J Appl Ceramic Technol* 2005;2(6):467–75.
- [69] Hart A, Gnanendran N. Cryogenic CO₂ capture in natural gas. *Energy Procedia* 2009;1:697–706 (GHGT-9).

- [70] Shekhawat D, Luebke DR, Pennline HW. A review of carbon dioxide selective membrane – a topical report. National Energy Technology Laboratory, United States Department of Energy; 2003.
- [71] Luebke D, Myers C, Pennline H. Hybrid membranes for selective carbon dioxide separation from fuel gas. *Energy Fuels* 2006;20(5):1906–13.
- [72] Paul D, Yampol'skii YP. Polymeric gas separation membranes. Baton Rouge: CRC Press; 1994.
- [73] Frizsche A, Kurz J. The separation of gases by membranes. In: Porter MC, editor. *Handbook of industrial membrane technology*. William Andrew Publishing; 1990. p. 559–93.
- [74] Ho MT, Allinson G, Wiley DE. Comparison of CO₂ separation options for geo-sequestration. Are membranes competitive? *Desalination* 2006;192:288–95.
- [75] Ho MT, Leamon G, Allinson G, Wiley DE. Economics of CO₂ and mixed gas geo-sequestration of flue gas using gas separation membranes. *Ind Eng Chem Res* 2006;45:2546–52.
- [76] van Der Sluis JP, Hendriks CA, Blok K. Feasibility of polymer membranes for carbon dioxide recovery from flue gas. *Energy Convers Manage* 1992;33:429–36.
- [77] Powell CE, Qiao GG. Polymeric CO₂/N₂ gas separation membranes for the capture of carbon dioxide from power plant flue gases. *J Membr Sci* 2006;279:1–49.
- [78] 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. p. 115–208.
- [79] Robeson L. Correlation of separation factor versus permeability for polymeric membranes. *J Membr Sci* 1991;62:165–85.
- [80] Stern SA. Polymers for gas separations: the next decade. *J Membr Sci* 1994;94:1–65.
- [81] Illing G, Hellgardt K, Wakeman RJ, Jungbauer A. Preparation and characterization of polyaniline based membranes for gas separation. *J Membr Sci* 2001;184:69–78.
- [82] Xu ZK, Dannenberg C, Springer J, Banerjee S, Maier G. Novel poly (arylene ether) as membranes for gas separation. *J Membr Sci* 2002;205:23–31.
- [83] Pixton MR, Paul DR. Gas transport properties of polyarylates. Part 1: Connector and Pendant group effects. *J Polym Sci B: Polym Phys* 1995;33(7):1135–49.
- [84] Aguilar-Vega M, Paul DR. Gas transport properties of polycarbonates and polysulfones with aromatic substitutions on the bisphenol connector group. *J Polym Sci B: Polym Phys* 1993;31(11):1599–610.
- [85] Lin Y, Ding M, Xu J. Gas separation properties of aromatic polyetherimides from 1,4-bis (3,4-dicarboxyphenoxy)benzene dianhydride and 3,5-diaminobenzoic acid and its esters. *J Appl Polym Sci* 1997;63(1):1–7.
- [86] Lin H, Freeman BD. Gas solubility, diffusivity and permeability in poly (ethylene oxide). *J Membr Sci* 2004;239:105–17.
- [87] Stern SA, Mi Y, Yamamoto H, Clair AK. Structure/permeability relationships of polyimide membranes. Applications to the separation of gas mixtures. *J Polym Sci B: Polym Phys* 1989;27(9):1887–909.
- [88] Zimmerman CW, Koros WJ. Entropic selectivity analysis of a series of polypropylenes for gas separation membranes. *Macromolecules* 1999;32(10):3341–6.
- [89] Aitken CL, Koros WJ, Paul DR. Effect of structural symmetry on gas transport properties of polysulfones. *Macromolecules* 1992;25(13):3424–34.
- [90] Ostwal M, Lau JM, Orme CJ, Stewart FF, Way JD. The influence of temperature on the sorption and permeability of CO₂ in poly (fluoroalkoxy phosphazene) membranes. *J Membr Sci* 2009;344(1–2):199–203.
- [91] Stewart FF, Harrup MK, Orme CJ, Luther TA. Phosphazene membranes for gas separations. US 2006/0016331 A1, USA; 2006.
- [92] Hsieh H. Inorganic membranes. *Membr Mater Proc* 1990;84:91.
- [93] Shreiber EH, Eardley EP, Srinivasan V, van Hassal BA, Shah MM. US20026623714; 2002.
- [94] Li S, Falconer JL, Noble RD. Membranes for CO₂/CH₄ separation. *J Membr Sci* 2004;241:121–35.
- [95] Li S, Martinek JG, Falconer JL, Noble RD. High-pressure CO₂/CH₄ separation using SAPO-34 membranes. *Ind Eng Chem Res* 2005;44:3220–8.
- [96] Hasegawa Y, Tanaka T, Watanabe K, Jeong BH, Kusakabe K, Morooka S. Separation of CO₂–CH₄ and CO₂–N₂ systems using ion-exchanged FAU-type zeolite membranes with different Si/Al ratios. *Korean J Chem Eng* 2002;19:309–13.
- [97] Poshusta JC, Tuan VA, Pape EA, Noble RD, Falconer JL. Separation of light gas mixtures using SAPO-34 membranes. *Ind Eng Chem Res* 2000;46:779–89.
- [98] Poshusta JC, Noble RD, Falconer JL. Characterization of SAPO-34 membranes by water adsorption. *J Membr Sci* 2001;186:25–40.
- [99] Poshusta JC, Falconer JL, Noble RD. Temperature and pressure effects on CO₂ and CH₄ permeation through MFI zeolite membranes. *J Membr Sci* 1999;160:115–20.
- [100] Kusakabe K, Kuroda T, Murata A, Morooka S. Formation of a Y-type zeolite membrane on a porous α -alumina tube for gas separation. *Ind Eng Chem Res* 1997;36:649–56.
- [101] Sebastian V, Kumakiri I, Bredesen R, Menendez M. Zeolite membrane for CO₂ removal: operating at high pressure. *J Membr Sci* 2007;292:92–7.
- [102] Cui Y, Kita H, Okamoto KI. Preparation and gas separation performance of zeolite T membrane. *J Mater Chem* 2004;14:924–31.
- [103] Tomita T, Nakayama K, Sakai H. Gas separation characteristics of DDR type zeolite membrane. *Micropor Mesopor Mater* 2004;68:71–8.
- [104] Li S, Alvarado G, Falconer JL, Noble RD. Effects of impurities on CO₂/CH₄ separations through SAPO-34 membranes. *J Membr Sci* 2005;251:59–66.
- [105] Kim HS, Han JW, Chin KY, Shul YG, Joe YL. Synthesis of organic–inorganic composite membrane by sol–gel process. *Korean J Chem Eng* 1995;12:405–11.
- [106] Roh HS, Chang JS, Park SE. Synthesis of mesoporous silica in acidic condition by solvent evaporation method. *Korean J Chem Eng* 1999;16:331–9.
- [107] Lee KH, Cho YK, Han KW. Manufacture of alumina composite membranes for CO₂ sequestration. *Hwahak Konghak* 1995;33:570–2.
- [108] Brinker CJ, Sehgal R, Hietala SL, Deshpande R, Smith DM, Loy D, et al. Sol–gel strategies for controlled porosity inorganic materials, Alex Stern Honorary symposium on membrane-based gas separation. *J Membr Sci* 1994;94:85–92.
- [109] Raman NK, Brinker CJ. Organic template approach to molecular sieving silica membranes. *J Membr Sci* 1995;105:273–9.
- [110] Mano H, Kazama S, Haraya K. Development of CO₂ separation membrane (1) Polymer membrane. In: Gale J, Kaya Y, editors. *Greenhouse gas control technologies*. UK: Elsevier Science, Ltd.; 2003. p. 1551–4.
- [111] Okabe K, Matsumija N, Mano H, Teramoto M. Development of CO₂ separation membranes (1) Facilitated transport membrane. In: Gale J, Kaya Y, editors. *Greenhouse gas control technologies*. UK: Elsevier Science Ltd.; 2003. p. 1555–8.
- [112] Guha AK, Majumdar S, Sirkar KK. Facilitated transport of CO₂ through an immobilized liquid membrane of aqueous diethanolamine. *Ind Eng Chem Res* 1990;29:2093–100.
- [113] Bao L, Trachtenberg M. Modelling CO₂-facilitated transport across a diethanolamine liquid membrane. *Chem Eng Sci* 2005;60:6868–75.
- [114] Richter HJ, Knoche K. Reversibility of combustion processes, efficiency and costing – second law analysis of processes. *ACS Symp Ser* 1983;235:71–85.
- [115] Ryden M, Lyngfelt A. Using steam reforming to produce hydrogen with carbon dioxide capture by chemical – looping combustion. *Int J Hydrogen Energy* 2006;31:1271–83.
- [116] Lyngfelt A, Kronberger B, Adanez J, Morin J, Hurst P. The grace project: development of oxygen carrier particles for chemical looping combustion, design and operation of a 10 kW chemical-looping combustor. GHGT-7 Conference, Vancouver, BC, Canada, September 5–9, 2004.
- [117] Brandvoll O, Bolland O. Inherent CO₂ capture using chemical looping combustion in a natural gas fired power cycle. *J Eng Gas Turbines Power* 2004;126:316–21.
- [118] IMTE AG Consulting Engineers. Exploring the many carbon capture options. IM 090301; March 2009.
- [119] Wright A, White V, Hufton J, van Selow E, Hinderink P. Reduction in the cost of pre-combustion CO₂ capture through advancement in sorption-enhanced water–gas shift. *Energy Procedia* 2009;1:707–14 (GHGT-9).
- [120] van Selow ER, Cobden PD, van den Brink RW, Hufton JR, Wright A. Performance of sorption-enhanced water–gas shift as a pre-combustion CO₂ capture technology. *Energy Procedia* 2009;1:689–96 (GHGT-9).
- [121] US DOE. Carbon sequestration research and development. United States Department of Energy; 1999.
- [122] USGS; geologic sequestration of carbon dioxide – an average resource perspective. USGS Fact Sheet FS-026-03. United States Geological Survey; 2003.
- [123] Lackner KS. Carbonate chemistry for sequestering fossil fuel carbon. *Ann Rev Energy Environ* 2002;27:193–232.
- [124] BP America. CO₂ capture project technical report DE - FC26-O/NT41145. National Energy Technology Laboratory. Pittsburgh, PA: US Department of Energy; 2005.
- [125] Hakkala L. Cansolv Technologies Inc., Private communication; 2007.
- [126] Black S. Chilled ammonia scrubber for CO₂ capture. Cambridge, MA: MIT Carbon Sequestration Forum VII; 2006.
- [127] Aroonwilas A, Tontiwachwuthikul P. Mass transfer studies of high performance structured packing for CO₂ separation processes. *Energy Convers Manage* 1997;38(Suppl.):S75–80.
- [128] Falk-Petersen O, Dannstrom H. Separation of carbon dioxide from offshore gas turbine exhaust. *Energy Convers Manage* 1997;38(Suppl.):S81–6.
- [129] Shao L, Low BT, Chung TS, Greenberg AR. Polymeric membranes for the hydrogen economy: contemporary approaches and prospects for the future. *J Membr Sci* 2009;327(1–2):18–31.
- [130] Figueroa JD, Fout T, Plasynski S, McIlvried H, Srivastava RD. Advances in CO₂ capture technology – The U.S. Department of Energy's carbon sequestration program – Review. *Int J Greenhouse Gas Control* 2008;2:9–20.
- [131] Trachtenberg MC, Cowan RM, Smith DA, Horazak DA, Jensen MD, Laumb JD, et al. Membrane based, enzyme-facilitated, efficient carbon dioxide capture. *Energy Procedia*; 2009:353–60. GHGT-9.
- [132] Yang WC, Ciferno J. Assessment of carboxy enzyme-based membrane technology for CO₂ capture from flue gas. DOE/NETL 401/072606; 2006.
- [133] Steeneveldt R, Berger B, Torp TA. CO₂ capture and storage “closing the knowing-doing gap”. *Chem Eng Res Des* 2006;84(A9).
- [134] IEA. Capturing CO₂. IEA Greenhouse Gas R & D Programme, www.ieagreen.org.uk; 2007.