Multi-Technology Approach to Carbon Dioxide Capture and Sequestration: A Strategy for Global Warming and Greenhouse Gas Mitigation

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Abstract- **The Intergovernmental Panel on Climate Change (IPCC) Fourth Assessment report states that the most potential cause of global warming is the emission of greenhouse gases due to human activity. The main greenhouse gas generated by human activities is carbon dioxide (CO_2). It is generated mainly due to the combustion of fossil fuels in the energy sector. CO_2 is also generated in various process industries e.g., natural gas processing, hydrogen purification, cement and steel industries and emitted by the transportation sector. Projections by International Energy Agency (IEA) indicate that fossil fuels, coal and hydrocarbon, will remain the major source of energy until 2030 and most likely beyond then. Hence, it is increasingly important that efficient mitigation technologies are developed for significant reduction in CO_2 emission in the entire energy sector to make use of fossil fuels sustainable.**

Keywords — CO_2 capture, Flue gas, Absorption, Adsorption, Membrane separation.

I. INTRODUCTION

The Intergovernmental Panel on Climate Change warned that CO_2 emission may to be doubled in the year 2050, if no special attentions are taken now. Undue growth in energy consumption and stringent environmental regulations makes the CO_2 capture more important today than ever. If emissions are to be mitigated through capture and sequestration, then capture technologies far more efficient than the conventional amine scrubbing systems, which could increase the cost of power from these plants by as much as 80%, must be developed [1, 2]. To meet these challenges extensive R&D activities are going on globally towards development of hybrid and activated solvents [3], biphasic solvents and ionic liquids for CO_2 capture by absorption, amine-functionalized and hyper-branched amine tethered adsorbents for CO_2 capture by adsorption [4], newer membranes with high permeability and good selectivity for low cost CO_2 separation from flue gas streams as well as for membrane absorbers for better absorption capture of CO_2 [5, 6]. Hence, emphasis has been laid on separation of CO_2 from power plant flue gases.

We need advanced processing technology for mitigating CO_2 emission so as to suppress global warming and improvement in the energy sector [7]. There are three main approaches to capture CO_2 from coal thermal power plants. These are (i) Oxy-combustion (ii) Pre-combustion and (iii) Post-combustion CO_2 capture [8]. The first two approaches required extensive redesign of existing power plant and thus can be applicable for new power plant. Hence, post-combustion CO_2 capture would be an effective way to capture and concentrate CO_2 up to the target specifications for transportation and storage from large point sources such as existing coal-based power plants. This work intends to analyse the challenges and prospects of various technologies options for CO_2 capture and sequestration projects.

II. CO_2 SEPARATION FROM FLUE GAS: TECHNOLOGY OPTIONS

The CO_2 concentration in the flue gas varies from as low as 4% by volume (turbine plant) to as high as 30% by volume (cement and steel plants). The coal based power plant flue gas contains typically about 13-15% CO_2. Most of the post-combustion CO_2 capture studies using amines are focused on the process modeling [9] and economics since the process has already been demonstrated on large scale CO_2 capture from natural gas and syn-gas. The limitations of the amine process are (a) expensive steam (b) SOx removal (c) amine loss and (d) corrosion of equipment. Within the PCC, there can be many CO_2 separation techniques, such as absorption, adsorption, cryogenic distillation and membrane separation [10]. Figure 1 shows the available technologies for CO_2 separation. Out of these the most widely practised technology for CO_2 removal from gas streams is regenerative chemical absorption of CO_2 into aqueous solutions of alkanolamines [8, 11].

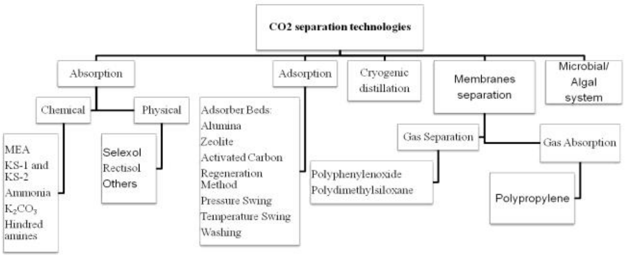


Fig. 1: Process technologies for post combustion CO_2 capture

A. *Chemical Absorption*

The most commonly used chemical solvents for the chemical absorption processes are aqueous alkanolamines, aqueous carbonates, etc. [12]. Amine based cyclic regenerative absorption process is one of the potential options for CO_2 capture [13]. Alkanolamines contain both amino and hydroxyl groups, and hence, are suitable as solvents for chemical absorption. The hydroxyl group reduces vapour pressure and increases water solubility, while the amino group provides the required alkalinity in aqueous solution to react with CO_2. Primary amines like monoethanolamine (MEA) and secondary amines like diethanolamine (DEA) have been the most widely employed acid gas treating solvents [10]. However, the drawback of using primary or secondary amines for CO_2 capture is that the reactions of CO_2 with these amines are highly exothermic. As a result, substantial energy input is necessary in the regeneration step to reverse the reaction and strip the CO_2 from the CO_2-rich amines. Besides, these carbamate forming amines have lower equilibrium capacity for CO_2. In recent years, methyldiethanolamine (MDEA), a tertiary amine, has been used as gas treating solvent because of its low heat of reaction and high equilibrium capacity. However, the MDEA-CO_2 reaction is slow because CO_2 cannot react directly with MDEA. Before reacting with any tertiary or sterically hindered amine, CO_2 must react with water to form carbonic acid which is a slow reaction. Sterically hindered amines such as AMP and piperazine (a cyclic diamine) belong to a special class of primary/ secondary amines with bulky groups attached to the nitrogen atom of the amine molecule so as to partially shield the amine group from the reacting acid gas [14]. Alternatively, blended amine solvents, which consist of a mixture of a primary/secondary amine with higher reaction rate, and a tertiary/sterically hindered amine with higher equilibrium capacity, can be used to realize the advantage of both. MEA has been blended either with amines that are less corrosive and require less steam to regenerate, or with the additive piperazine (PZ) that is of high reaction rate and higher resistance to thermal and oxidative and allows use of lower MEA concentrations [15]. A CO_2 separation process flowsheet is represented by Fig.2 [16]

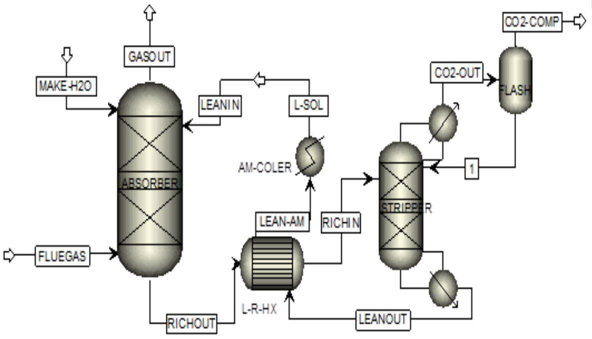


Fig. 2: Process flowsheet of Absorption

B. *Physical Absorption*

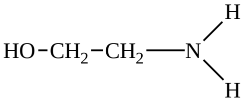
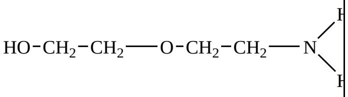
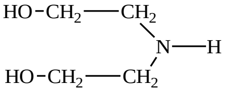
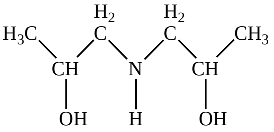
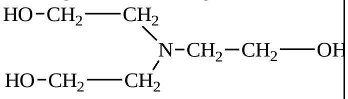
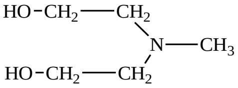
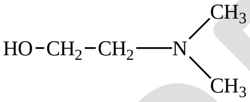
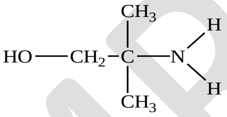
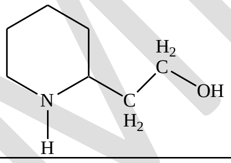
In physical absorption, the flue gas is contacted with a solvent which normally does not involve any chemical reaction. Physical absorption is preferred when the CO_2 partial pressure is high (>1.5 MPa) and it is a preferred choice for pre-combustion CO_2 capture which is typically operated near 40 °C [17]. When the CO_2 partial pressure is low, the preferred method is chemical absorption [18]. A brief summary of commonly used physical and chemical solvents for CO_2 removal is appendix presented in Table 1. Structural formulas for some important amines for CO_2 capture are presented in Table 2. Physical solvents are commercially used to remove CO_2 from natural gas, ammonia synthesis gas and hydrogen [8]. Some commercially used physical solvents include dimethyl ether and polyethylene glycol (Selexol), tetramethylene sulfone (Sulfolane), N-methyl-2-pyrrolidone (NMP) and cold methanol (Rectisol) [19]. Due to the low CO_2 partial pressure in flue gas, application of physical absorption for post combustion CO_2 capture is not feasible. In some cases, blends of physical and chemical solvents, known as hybrid solvents, are used to take advantages of high CO_2 solubility physical and high CO_2 reactivity chemical solvents for CO_2 absorption.

Table 1: Commercial CO_2 scrubbing solvents used in gas treating industry

Process Type	Solvent	Trade Names
Physical absorption		
	Chilled methanol	Rectisol
	N-Methyl-2-pyrolidone (NMP)	Purisol
	Dimethylether of polyethylene glycol	Selexol
	Propylene carbonate	Flour solvent
Chemical absorption *Organic (amine based)*		
	Monoethanolamine (MEA) (20-35 wt% in water)	SNPA
	Diethanolamine (DEA) (30 wt% in water)	SNPA
	Diglycolamine (DGA) (30 wt% in water)	Econamine
	N-Methyl diethanolamine (MDEA)	Ucarsol HS, SIPM
	Diisopropanolamine	ADIP
	Hindered amine	Flexsorb, KS-1, KS-2
Inorganic	Promoted potassium carbonate	Benfield, Catacarb, Giammarco vetrocoke
Hybrid Solvent		
	Mixture of MDEA or DIPA, water and tetrahydothiopene dioxide or diethylamine	Sulfinol – M, Sulfinol – D
	Mixture of MEA, DEA, methanol and tetrahydothiopene dioxide or diethylamine	Amisol
	AMP-sulfolane-water	Flexsorb PS

Rate activator	Piperazine

Table 2: Structural formulas for some important amines in CO_2 capture

Class	Name	Structural Formula
Primary amine	Monoethanolamine (MEA)	
	Diglycolamine (DGA)	
Secondary amine	Diethanolamine (DEA)	
	Diisopropanolamine (DIPA)	
Tertiary amine	Triethanolamine (TEA)	
	N-Methyldiethanolamine (MDEA)	
	Dimethylethanolamine (DMEA)	
Hindered amine	2-Amino-2-methyl-1-propanol (AMP)	
	2-Piperidine ethanol (PE)	

C. Adsorption Using Solid Sorbents

A number of solid adsorbents, such as activated carbon and zeolites can be used for adsorption of CO_2 from flue gas streams. For years solid sorbents designed for CO_2 capture have been used to purify breathing air in confined spaces, such as space shuttles and submarines [5]. Examples of commonly used adsorbents are alumina or silica. Recent research is focusing towards CO_2 adsorption in amine coated active carbon molecular sieves, metal organic frameworks (MOFs), amine grafted zeolites and supported amine sorbents. Common used reactants along with adsorbents include amines such as polyethylenimine [20] or Na_2CO_3 sorbents to capture CO_2 from flue gas streams [21]. However, implementation of this pathway for CO_2 capture from flue gas is difficult due to the elevated pressure of the adsorption process.

The development of an alternate adsorption based technique for CO_2 capture is mostly driven by synthesis of novel adsorbent materials which can selectively adsorb reasonable amounts of CO_2 [22]. MOFs are being widely investigated for their potential to efficiently remove CO_2 from process streams. Some MOFs such as DOBDC series have shown good CO_2 adsorption uptake and selectivity over other gases like N_2, CH_4, and so forth at the desired process conditions. But poor stability toward moisture makes them unrealistic for any practical separation application. Like other members of the MIL series, MIL-53 MOFs are among the few which are readily stable toward moisture. Considerable amount of research work is published on these materials due to their fascinating breathing behaviour and good stability [23].

D. Cryogenic Separation

CO_2 can be separated from other gases by cooling and condensation. Cryogenic separation is widely used commercially for streams that already have high CO_2 concentrations (typically > 90%) but it is not used for dilute CO_2 streams [10]. The major disadvantage of this technology are the high energy requirement to provide the needed refrigeration for the process, particularly for dilute gas streams. Another disadvantage is that some components, such as water, have to be removed before the gas stream is cooled, to avoid blockages. Cryogenic separation has the advantage that it enables direct production of liquid CO_2, which is needed for certain transport options, such as transport by ship. Cryogenics would normally be applied to high concentration, high pressure gases, such as in pre-combustion capture processes or oxy-fuel combustion.

E. Membrane Separation

A membrane is a selective barrier between two phases. The molecules or small particles can transport from one phase to the other through the membrane. A CO_2 selective membrane can be utilized in CO_2 separation process for CO_2 capture and to enhance the hydrogen/electricity generation [24]. The selective nature of a membrane can be attributed to one or more of the following mechanisms: (a) Knudson diffusion; (b) surface diffusion; (c) capillary condensation; (d) molecular sieving; (e) solution diffusion; and (f) facilitate transport. Most CO_2 selective membranes are based on either solution diffusion or facilitate transport mechanism since the CO_2 molecule is significantly larger. An amine based carrier is often used to facilitate the transportation of CO_2 from the retentate side to the permeate side [25]. As a result, a hydrogen selective membrane can be made of metallic, inorganic (ceramic), porous carbon, polymer, or hybrid materials while most of the CO_2 selective membranes for separating CO_2 from hydrogen are polymeric. The desirable features of a membrane include good permeability, selectivity, reliability, and tolerance to contaminants. For commercial applications in gasification processes, it should also be affordable, thermally stable, and durable. Of all the H_2-selective membranes, metallic membranes and ceramic membranes are the most extensively studied. [26, 27]. The metallic H_2-selective membranes generally have a very high selectivity and thermal stabilities. The potential candidates include palladium, platinum, tantalum, niobium, and vanadium [26, 27].

Although it is still in the developmental stage, gas separation membranes can be used for removing CO_2 from flue gas streams. There are many different types of gas separation membrane, including porous inorganic membranes, polymeric membranes that are used for separation of gas mixture [10]. Another type of membrane is being developed, called an absorption membrane. These membranes are impregnated with a liquid that selectively reacts with the CO_2 [28]. Membrane separation process has certain advantages. It has no moving parts. Its other advantages are its modularity, small footprint, and no regeneration energy requirement. Current membranes are either not selective enough towards CO_2 or not permeable enough, hence, cannot usually achieve high degrees of separation, so multiple stages and/or recycle of one of the streams is necessary [29]. This leads to increased complexity, energy consumption and costs. More recently, some researchers have focused on developing hybrid processes in which membrane separation is combined with another separation process such as chemical absorption [30]. However, further development is needed before membranes could be used on a large scale for CO_2 capture from in power plant flue gas streams.

Polymer membranes have been used successfully in a number of industrial applications, including the production of high-purity nitrogen, gas dehydration and recovery of hydrogen from process streams for recycle. However, successful use of a polymer membrane in post-combustion CO_2 capture process requires a membrane that is thermally, chemically, and mechanically stable at high temperature. Unfortunately, the commercially available polymeric materials currently employed are not stable in such demanding environments to the degree required. Current commercial membrane have CO_2/N_2 separation factors of around 18-19 and work at relatively low temperature. The process design study has to explore at this stage the interplay between the operational energy requirement and cost of installation for a set of data. Any increased energy requirement for the capture process will indeed increase the secondary CO_2 emission, which has obviously to be minimized. Thus, the energy efficiency of a capture process is a key issue. Typically a 4GJ/ton of recovered CO_2 (CO_2 capture cost of about \$60/ton CO_2) is reported by the first generation post-combustion capture process using monoethanolamine solvents. A 2GJ/ton is often considered as a major target in order to achieve acceptable CO_2 capture costs [31].

It has been concluded that the membrane process will be cost effective if the CO_2/N_2 selectivity is about 140 for a CO_2 permeance of 3000 GPU (Gas Permeation Unit) at 1 bar feed pressure with a 0.2 bar sweep side pressure. CO_2-facilitated transport membrane can achieve high selectivity and permeability based on the reversible reaction of the target gas with the active carrier incorporated into the membrane. Hence, use of novel amine carriers for the synthesis of CO_2-selective thin-film membrane is an attractive option for post-combustion CO_2 capture [32, 33]

F. Other Approaches

The main point of concern of regenerating chemical absorption process for CO_2 removal is the large energy requirement in solvent regeneration. In addition, thermal and oxidative degradation of the solvents result in large solvent make-up, besides producing products that are corrosive. Hence, chemical absorption processes with newer amine solvents, such as sterically hindered amines, amine based ionic liquids, and activated amine solvents which have a higher selectivity for CO_2, a higher degradation resistance, and lower energy requirement for regeneration, are presently the subject of global R&D.

In addition to absorption, adsorption and membrane-based systems, there are other variety of approaches under development such as microalgae system, ionic liquids, etc. Microalgae systems, which have long been under investigation for CO_2 capture from air, are especially attractive because they consume CO_2 in photosynthesis. This obviates the need for CO_2 compression and sequestration. Furthermore, the algae biomass can serve as animal feed or an effectively carbon-neutral fuel [34].

Another area that has demonstrated great potential and in which there is currently a great deal of interest is the field of ionic liquids. Ionic liquids are organic salts with melting points usually near room temperature, below 100°C. An unexpectedly large solubility of CO_2 gas in ionic liquids was first reported by [35]. In general, ionic liquids are characterized by extremely low vapor pressures, non-flammability, thermal stability, tunable polarity, good electrolytic properties and easy recycling [36]. These attributes make them attractive candidate sorbents for CO_2 capture and separation from post-combustion flue gases from coal-fired power plants. However, desorption of CO_2 from ionic liquids and regeneration of the sorbent requires significant thermal energy [37]. In addition, the viscosity of ionic liquids is relatively high, about 5-fold higher than that of a conventional aqueous solution of MEA and increases with CO_2 loading, leading to an additional energy penalty in pumping the sorbent [38].

III. CONCLUSION

Carbon dioxide emission due to industrial and human activity has been increasing at an alarming rate posing a great threat to the environmental ecology. About 80% of world primary energy demand is met by fossil fuels and their use is expected to grow, causing CO_2 emission to be doubled in the year 2050, if no special attentions are taken now. Hence, emphasis has been laid on capture of CO_2 from power plant flue gases. We need advanced processing technology for mitigating CO_2 emission so as to suppress global warming and utilization of clean energy. Three main approaches to capture CO_2 are Oxy-combustion, Pre-combustion and Post-combustion CO_2 capture. The first two approaches required extensive redesign of existing power plant and thus can be applicable for new power plants only and also not suitable to treat large amount of flue gas. Hence, post-combustion CO_2 capture would be an effective way to capture and compress CO_2 up to the specified condition for transportation and storage. In the contrary lower energy efficiency and high cost of process and equipments are the two major barriers for implementation of CCS processes industrially. Hence, the future research focus must be on the development of solvents which require less energy for CO_2 absorption and solvent regeneration. To achieve the purpose we intend to use absorbents with less corrosion effect, less solvent viscosity, low vapor pressure, rapid reaction rate at low CO_2 pressure, high CO_2 absorption capacity etc. The major parameters which should be considered while using the amine-based absorption process are solvent flow rate, CO_2 loading capacity, solvent degradation rate and energy requirement for regeneration. There should be attention on optimization for energy efficient CO_2 capture process at pilot plant scale using high gas-to-liquid mass transfer rates in absorber and stripper, to reduce equipment and capital cost, to prevent solvent degradation by SO_x, NO_x, and oxygen, and to develop an efficient model for the scale up using modelling and simulation. There is no solvent which can have all the required properties, but by setting process parameters at proper conditions it is possible to take maximum benefit of the mixed amines and other potential CO_2 capture fluids.

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