Progress and trends in CO₂ capture/separation technologies: A review

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A B S T R A C T

Coal-fired thermal power plants are the major source of CO₂ emission among fossil fuel power plants. In thermal power plants, coal combustion produces flue gas containing a number of gases including hazardous pollutants, such as CO₂, mercury (Hg), sulfur dioxide (SO₂), and oxides of nitrogen (NOₓ). Among all, CO₂ is the largest contributor to global warming. CO₂ capture and separation are therefore essential to keep the environment safe and secure. The present paper delineates the existing literature to examine the current status of various methods and technologies used for CO₂ capture and separation from thermal power plant flue gas. Various emerging technologies like, chemical-looping combustion, integrated gasification combined cycle, enzyme based separation, dual-alkali absorption approach, facilitated transport membrane, hydrate based separations, mixed matrix membrane and, calcium looping are also thoroughly discussed.

1. Introduction

Increasing CO₂ emissions in environment leads to global warming which is an issue of great concern today. The climate of the earth is varying continuously due to various factors, viz., change in the Earth’s orbit, change in the Sun’s intensity, change in ocean currents, volcanic emissions and increase in greenhouse gas (GHG) concentrations. The greenhouse effect is the phenomenon where water vapor, carbon dioxide (CO₂), methane and other atmospheric gases absorb outgoing infrared radiation causing an increase of Earth’s temperature [1]. Excessive greenhouse gases in the atmosphere are responsible for various environmental problems like continuous rise of water-level in sea, the increasing number of ocean storms, floods, etc. [2]. Among the GHGs, CO₂ is the major contributor for global warming and it has the greatest adverse impact which accounts approximately 55% of the observed global warming. CO₂ alone is responsible for about 64% of the enhanced greenhouse effect [3]. According to the prediction of Intergovernmental Panel on Climate Change (IPCC), by the year 2100, the atmosphere may contain up to 570 ppmv 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.

Currently 85% of total world demanded energy is supplied by fossil fuel thermal power plant including coal, oil and gas. Fossil fuel power plants account roughly 40% of total CO₂ emission and coal-fired power plant is the main contributor among them [4]. The capture of CO₂ from power plant flue gas accounts three quarter of the total cost of carbon capture and storage. It has become an important research issue of global perspectives as more international attention is focused on global warming [5]. To achieve mid to long term CO₂ reduction targets, cost effective CO₂ capture from fossil fuel power plant and subsequent sequestration options need to be evaluated keeping in view of world’s growing demand of energy. There are several technologies available for CO₂ capture such as absorption, adsorption, gas separation, membrane, cryogenic separation, etc.

This paper briefly reviews the existing and emerging technologies for the separation and capture of CO₂ from point source emissions. The aim of this literature review is to provide a current understanding of the present development of various capture technologies, existing technological options and the remaining development challenges of the main capture technologies.

2. Various options for CO₂ capture

Depending upon different plant configurations, CO₂ emissions from thermal power plant flue gas can be reduced by any of the following methods:

- Pre-combustion capture
- Post-combustion capture
- Oxyfuel combustion

2.1. Pre-combustion capture

Pre combustion process is related to the treatment of synthesis gas (syngas) composed principally of CO and hydrogen [6]. Pre-
Combustion rate is premised on the production of syngas, removal of CO₂ and combustion of H₂ [7]. In some ways it is oxymoron because CO₂ is obviously not normally available for capture prior to combustion, as CO₂ is a product of coal combustion, not a natural precursor. All types of fossil fuels can be gasified (partially combusted, or reformed) with sub stoichiometric amount of oxygen at elevated pressures typically in the range of 30–70 atm to produce a syngas predominantly CO and H₂. Thereafter steam is added to syngas and passed through the bed packed with catalysts, onto which water gas shift reaction takes place that convert CO into CO₂. In water gas shift reaction, the addition of steam and reduction of temperature actually promote the conversion of CO into CO₂ and increase the yield of H₂ [8]. From CO₂ and H₂ bearing stream, CO₂ is separated and sent to the compression unit and pure H₂ is further used as an input to a combined cycle to produce electricity (Fig. 1). Another option currently being developed is to use the hydrogen to power fuel cells with the intent of significant rising of overall plant efficiency. In future H₂ could also be used as transportation fuel [10].

The separation process typically uses a physical solvent such as rectisol and sellexol available at low cost. CO₂ is dissolved at higher pressure and then released as the pressure is reduced. No heat is required to regenerate the solvent and CO₂ can be released at above atmospheric pressure. The energy requirement for CO₂ separation and compression in pre-combustion capture can be in the order of half of that required for post combustion capture [8]. This process has a good advantage i.e. utilization of physical solvent which are available at low cost and require low energy for regeneration [6]. The main disadvantage of pre-combustion capture is that it requires a chemical plant in front of the turbine. Complicated chemical processes normally cause extra shut-downs of the plant, which can result to a lower power output. Other disadvantages are non-gaseous feed stocks, requirement of the cleaned gas stream and possible expensive scrubbing for high NOx emission control.

Presence of CO₂ at much higher concentrations in syngas makes CO₂ capture less expensive for pre-combustion capture in comparison with post-combustion capture. Currently, there are few gasification plants in full-scale operation and capital costs are higher than pulverized coal-fired power plants [10].

2.2. Post combustion capture

Post combustion capture involves removal of CO₂ from flue gas, which comes from the thermal power plant combustion chamber as shown in Fig. 2. Existing power plants use air for combustion and generate a flue gas at atmospheric pressure and typically have a CO₂ concentration of less than 15%. Thus the thermodynamic driving force for low CO₂ capture from flue gas is low creating a technical challenge for the development of cost effective advanced capture processes [6]. The low concentration of CO₂ in power-plant flue gas (13–15% for coal fired power plant, 7–8% gas fired power plant, etc. (Table 1)) needs a large volume of gas to be handled, which results in large equipment sizes and high capital costs. Technologies based on chemical absorption appear to be best adapted to this separation. Other technologies, adsorption, membranes and cryogenic, are less suitable for post-combustion capture than pre-combustion capture, mainly for the following reasons:

- A much lower partial pressure of CO₂ in post-combustion exhaust gases than in syngas originating from a gasifier or a reformer.
- The presence of larger quantities of dusts, impurities such as SOx and NOx, and non-condensable gases particularly oxygen.

Post combustion capture technology has a higher thermal efficiency for conversion to electricity than pre combustion Integrated Gasifier Combined Cycle (IGCC). It appears likely to give lower total electricity costs than pre combustion capture for natural gas plants [4,8]. Separation of CO₂ from flue gas stream of post combustion system is challenging for several reasons. The relatively high temperature of the flue gases offers a design challenge. Another challenge is that powerful chemical solvents have to be used for low concentration of CO₂ capture and regeneration of the solvents to release CO₂ will require a large amount of energy.

2.3. Oxy-fuel combustion

Oxy-fuel combustion is a promising technology for capturing of CO₂ from fuel gas or to modify the combustion process so that the flue gas has a high concentration of CO₂ for easy separation. In this process fuel is burned in combustion chamber in the environment of pure O₂ (>95%) mixed with recycled flue gas (RFG) as pictured in Fig. 3. In the most frequently proposed version of this concept, a cryogenic air separation unit is used to supply high purity oxygen. This high purity oxygen is mixed with RFG prior to combustion or in the boiler to maintain combustion conditions similar to an air fired configuration. This is necessary because currently available materials of construction cannot withstand at high temperatures resulting from coal combustion in pure oxygen. Flue gas stream from this system contains mainly CO₂ and water vapor. The water is easily removed by condensation, and the remaining CO₂ can be purified relatively at low cost. The CO₂ content of the dry flue gas varies in the range of 70–95% depending upon the fuel, the process used, the air in leakage, the O₂ purity and the excess O₂.

### Table 1

Typical CO₂ compositions in process streams [1,11].

| Process                        | CO₂ concentration (vol.%)
<table>
<thead>
<tr>
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<th></th>
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<tbody>
<tr>
<td>Power plant flue gas</td>
<td></td>
</tr>
<tr>
<td>Coal fired boiler</td>
<td>14</td>
</tr>
<tr>
<td>Natural gas fired boiler</td>
<td>8</td>
</tr>
<tr>
<td>Natural gas combined cycle</td>
<td>4</td>
</tr>
<tr>
<td>Coal—oxygen combustion</td>
<td>&gt;80</td>
</tr>
<tr>
<td>Natural gas partial oxidation</td>
<td>40</td>
</tr>
<tr>
<td>Blast furnace gas</td>
<td></td>
</tr>
<tr>
<td>Before combustion</td>
<td>20</td>
</tr>
<tr>
<td>After combustion</td>
<td>27</td>
</tr>
<tr>
<td>Cement kiln off-gas</td>
<td>14–33</td>
</tr>
<tr>
<td>Oil refineries and petrochemical plant fired heater</td>
<td>8</td>
</tr>
</tbody>
</table>

Fig. 1. Principle of pre-combustion CO₂ capture [6,9,10].

Fig. 2. Principle of post-combustion CO₂ capture [6,9,10].
3. Existing capture technologies

Several technologies are available to capture CO₂ from fossil fuel power plants. These include mainly physical and chemical absorption, adsorption, cryogenic and membrane processes.

3.1. Absorption process

Chemical or physical absorption processes are widely used in the petroleum, natural gas and coal fired power plants as well as chemical industries for separation of CO₂. It is based on the reaction between the CO₂ and chemical solvent such as aqueous solution of mono-, di- and tri-amino, di-isopropanol amine, etc. [5,9]. In this method absorber and regenerator are working continuously. Flue gas stream containing CO₂ is introduced at the bottom of the absorber and regenerator, where desorption of CO₂ occurs and regenerated solvent is recycled for further use, desorbed CO₂ is compressed and sent to storage. Available literature reveals that the chemical absorption holds good result in terms of removal efficiency and can be used for low concentration flue gases [12]. Chemical absorbents such as monoethanol amine (MEA), diethanol amine (DEA), N-methyl diethanolamine (MDEA), and di-2-propanolamine (DIPA) are commonly used [13,14]. Other absorbents such as, diglycolamine (DGA), 2-(2-aminoethylethanol) ethanol (AEE), 2-amino-2-methyl 1-propanol (AMP), N-2-aminoethoxy 1,3-propanediamine (AEPDNH₂), triethanol amine (TEA), triethylene tetra amine (TETA), piperazine (PZ), glucosamine (GA), NaOH, NH₃, K₂CO₃, KOH, Na₂CO₃, etc. were also tested for CO₂ removal, however their individual limitations make them less suitable for large scale industrial CO₂ removal. For the concept of blending, in which a solution of two or more solvents in varying concentrations are mixed to produce absorbents with excellent absorption characteristics as well as savings in energy requirements [15–19].

3.1.1. Absorption of CO₂

Recently blends of alkanolamines are mostly preferred for absorption of CO₂. This process involves passing of gaseous CO₂ through an amine solution until equilibrium is reached. The reaction of CO₂ with aqueous amine can theoretically be represented in three individual steps as shown in Fig. 4 [5,20].

3.1.1.1. Dissolution of the gaseous CO₂. Initially, diffusion of CO₂ occurs from gas to liquid phase. This step is a purely physical process and must occur prior to further reaction of CO₂ in the liquid phase. Very small quantity of CO₂ remains in the form of aqueous CO₂, and this step is followed by bicarbonate and carbamate formation.

3.1.1.2. Formation of bicarbonate and carbamate. In this step, the amine behaves simply as a base and reacts with carbonic acid formed in the previous step with a CO₂ to amine ratio of unity. Obviously, the bicarbonate also exists in equilibrium with carbonate and carbonic acid. The position of this equilibrium is governed by pH and CO₂ to amine ratio. The bicarbonate predominates under absorber condition and this pathway is referred to as the acid pathway [20]. Carbamate formation occurs at a CO₂ to amine ratio of 0.5 which means one molecule of CO₂ is absorbed by every two molecules of amine. One amine molecule is required to form carbamate, while the second molecule acts as a base to react with the proton released. This low CO₂ to amine ratio results in a lower efficiency and lower CO₂ capacity than that for the acid pathway. In addition, carbamate formation is associated with a high enthalpy of reaction. Reversing this reaction in the stripper consequently requires the addition of large amount of energy, making the entire process relatively energy intensive.

3.1.2. Reaction mechanism

An overview on the reaction mechanisms between CO₂ and alkanolamines in both aqueous and non aqueous solutions was available in literature [21]. Danckwerts and McNeil proposed the mechanism of reaction between CO₂ and primary and secondary alkanolamines in two-steps as given below [22]:

**Step 1: Carbamate formation (Rate determining step)**

\[
\text{CO}_2 + R_1R_2NH \rightarrow R_1R_2N \text{CO}^- + \text{H}^+ \quad (1)
\]

**Step 2: Protonated alkanolamine formation (Instantaneous reaction)**

\[
R_1R_2NH + \text{H}^+ \rightarrow R_1R_2N\text{H}_2^+ \quad (2)
\]

A second-order overall reaction is as follows:

\[
\text{CO}_2 + 2R_1R_2NH \leftrightarrow R_1R_2N\text{COO}^- + R_1R_2\text{NH}_2^+ \quad (3)
\]
A lot of work has been carried out on the reaction between CO₂ and alkanolamines in aqueous solutions [23–28]. However, only for MEA, as a primary amine, the overall reaction order and the value of the kinetic constant are in accordance with the mechanism of Rxn. (3). For other primary and secondary alkanolamines, the overall reaction orders were found to be varying between 2 and 3, for both aqueous and non-aqueous solutions. For example, the overall reaction order for DEA, as a secondary alkanolamine, was found to be 3 and some authors reported between 2 and 3. Therefore, the reaction mechanism between CO₂ and alkanolamines needs to be modified.

### 3.1.2.1. Zwitterion mechanism

This reaction mechanism was first proposed by Caplow [29] and reintroduced by Danckwerts [30] in which the reaction between CO₂ and alkanolamines results in the formation of a zwitterion intermediate followed by the removal of a proton by a base B:

\[
\text{CO}_2 + R_1 R_2 \text{NH} \rightarrow R_1 R_2 \text{NH}^+ \text{COO}^- \quad (4)
\]

\[
R_1 R_2 \text{NH}^+ \text{COO}^- + B \rightarrow R_1 R_2 \text{NCOO}^- + BH^- \quad (5)
\]

This mechanism comprises of formation of the CO₂-amine zwitterion (Rxn. (4)) followed by base-catalyzed deprotonation of this zwitterion (Rxn. (5)). Any base present in solution will contribute to the deprotonation of the zwitterion. Hence, in an aqueous solution of a single primary or secondary amine, the zwitterion deprotonation depends on free amines, H₂O, and OH⁻ concentrations. By using the pseudo-steady-state assumption for the zwitterions concentration, the overall forward reaction rate can be written as:

\[
r_{\text{CO}_2} = \frac{k_2^f [\text{CO}_2] [R_1 R_2 \text{NH}]}{1 + \sum k_{b_i}[B]} \quad (6)
\]

where \( k_2^f \) and \( k_{b_i} \) are the forward and reverse rate constants where superscript \( f \) denotes zwitterion and \( b_i \) [B] is the contribution to the zwitterion deprotonation by all bases present in the solution.

### 3.1.2.2. Single-step-termolecular mechanism

Single-step-termolecular mechanism was proposed by Crooks and Donnellan [31] in which, amine bonding to CO₂ and proton-transfer takes place simultaneously, and was reviewed by da Silva and Svendsen [32]. The reaction uses the accepted mechanism proposed by Danckwerts [30] in which the zwitterion intermediate is formed by making the assumption that the reaction proceeds through a loosely bound encounter complex as the initial product. The forward reaction rate for this mechanism is

\[
r_{\text{CO}_2} = -k_{\text{obs}}[\text{CO}_2] \quad (7)
\]

where,

\[
k_{\text{obs}} = k_1^f [R_1 R_2 \text{NH}]
\]

\[
= k_{\text{amine}}[R_1 R_2 \text{NH}] + k_{\text{H}_2\text{O}}[\text{H}_2\text{O}] + k_{\text{OH}^-}[\text{OH}^-][R_1 R_2 \text{NH}] \quad (8)
\]

Chemical absorption is the most mature and reliable technology for post combustion CO₂ removal from thermal power plant. Among all types of amines, MEA has received much attention, mainly due to its high rate of reaction, low solvent cost, and easy regeneration [33–37]. MEA however has several drawbacks too, including low CO₂ loading capacity (0.5 mol CO₂/mol amine), high equipment corrosion rate, and amine degradation by SO₂, NO₂, HCl, HF, and oxygen in flue gas which includes a high absorbent makeup rate, high energy consumption during high temperature absorbent regeneration [38–41]. Primary and secondary amines react rapidly with CO₂ to form carbamate with stoichiometric loading of 0.5 mol CO₂/mol amine. For tertiary amine, MDEA, loading value approaches to 1.0 mol CO₂/mol amine as it does not form carba-

mure. However its absorption rate is low as compared to primary and secondary amines [42]. A commercially attractive alternative solvent, AMP, which is sterically hindered amine, forms unstable carbamate ions in its reaction with CO₂, leading to higher absorption capacity. It has good regeneration capability, degradation resistance, and higher absorption rate than MDEA [5] but its reaction rate is lower than MEA at 40 °C [43]. It is therefore used with other solvents to enhance the absorption performance. A comparative test performed by different authors [44,45] reveals that MEA is superior to AMP in the CO₂ removal efficiency but AMP is more suitable than MEA in CO₂ absorption amount. In absorption/ regeneration process, reaction rate constant of blended MEA/AMP solutions increases and CO₂ loading of rich amine decreases with an increase of MEA contents. On the other hand, with the increase of AMP contents, CO₂ loading has increased. The MEA/AMP blend showed more satisfactory removal than MDEA/MEA [46].

PZ is the solvent which is used as an activator for CO₂ removal solvents. It is a diamine that acts as a promoter for amine systems to improve kinetics, such as MDEA/PZ or MEA/PZ blends. The CO₂ absorption rate with aqueous PZ is more than double as that of MEA and volatility at 40 °C ranges from 10 to 19 ppm. Thermal degra-

dication is negligible in concentrated PZ solutions up to a tempera-
ture of 150 °C [47,48]. Various studies on PZ blend, viz., MDEA/PZ [49,50], glycine (GLY)/PZ [2], DEA/PZ [42], etc. revealed that CO₂ loadings at corresponding partial pressures were higher than individual solvent without PZ. Thus the blended solvent has shown good result as compared to single solvent. Literature on blended solvent is scarred and need to more research for understanding the mechanism of this process.

Amine based CO₂ absorption process has several limitations among these the main focused on regeneration cost of solvent (roughly 70–80% of total operating cost of the system). Implement-

tation on this, a new method pH swing has also been proposed. The principal feature of this process is adding the acid to process steam just before the regeneration step to lower the pH so that the regeneration will take place at low temperature and finally the overall cost of the process will be reduced. The addition of few weak acids (suberic, pathalic and oxalic acid) was reported for desorption rate of CO₂ and found that the CO₂ released much faster and in much larger quantity [40].

#### 3.2. Adsorption process

Adsorption is a process for removal of one or more components of a mixture with the help of a solid surface. The adsorption processes are based on significant intermolecular forces between gases (including CO₂) and the surfaces of certain solid materials (such as molecular sieves and activated carbon). Depending on the temperature, partial pressure, surface force and adsorbent pore sizes, single or multiple layers of gases can be adsorbed [51].

In CO₂ capture by adsorption technology, a packed column is mainly filled by spherical adsorbent and CO₂ bearing stream is passed through the column. CO₂ is attracted towards the adsorbent and adheres on the surface of adsorbent. After achieving the equilibrium, desorption takes place to get CO₂ in pure form and regenerated adsorbent can be utilized for further cycle. This process can be carried out in different manners as discussed in the preceding section.

#### 3.2.1. Pressure swing adsorption (PSA)

In PSA, the gas mixture flows through bed at elevated pressure and low temperature until the adsorption of CO₂ approaches to
equilibrium conditions at the exit of bed [51]. The beds are then regenerated by stopping the flow of the feed mixture, reducing the pressure and elutriating the adsorbed constituents with a gas having low adsorptivity. Once regenerated, the beds are ready for another adsorption cycle.

3.2.2. Temperature swing adsorption (TSA)

Alternative procedure is temperature swing adsorption in which flue gas is passed over bed. Selective adsorption takes places on the adsorbent until to reach equilibrium. The desorption of gas can be done at elevated temperature by supplying the additional heat. Additional requirement of heat in TSA makes it costlier than PSA [51].

3.2.3. Electrical swing adsorption (ESA)

In this method low voltage electric current is passed through the adsorbent [52]. The ESA has the potential to reduce the cost of CO₂ capture compared with other conventional adsorption technologies as reported in literature [53,54]. Therefore, ESA can be believed to be able to make the process of CO₂ capture more cost-effective than TSA and PSA.

3.3. Cryogenic process

Cryogenic separation method is widely used commercially for separation of CO₂ from streams having high CO₂ concentrations (typically more than 50%). It is not normally used for dilute CO₂ streams such as flue gas from coal/natural gas fired boilers as the amount of energy required for refrigeration is uneconomical for the plant [55].

This process involves compression and cooling of the gas mixtures in several stages to induce phase changes of CO₂ in flue gases and invariably other components present in the mixture. Depending on the operating conditions the CO₂ can arise as a solid or liquid together with other components from which it can be distilled. Water vapor in the CO₂ feed mixture leads to the potential formation of solid CO₂ clathrates and ice, and can result in major plugging problems [51]. The main advantage of cryogenic CO₂ capture is that no chemical absorbent is required and the process can operate at atmospheric pressure. Moreover it directly produces liquid CO₂, which is needed for economical transport, such as transport in ship and pipeline [55].

The main disadvantage of this system is that the water content in the feed stream to the cooling units should be minimal in order to prevent the plugging by ice or unacceptably high rise in pressure drop during operation. Therefore, several costly steps are required to remove all water traces from the flue gas. In addition the increasing layer of solid CO₂ onto heat exchanger surfaces during the capture cycle will adversely affect the heat transfer which in turn reduces the process efficiency [56]. The most promising application for cryogenic is expected to remove CO₂ from high pressure gases, such as in pre-combustion capture processes or oxyfuel combustion in which input gas contains high concentration of CO₂ [55].

3.4. 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 (oxyfuel combustion system). Membranes are semi-permeable barriers able to separate substances by various mechanisms (solution/diffusion, adsorption/diffusion, molecular sieve and ionic transport). These are available in different material types, which can be either organic (polymeric) or inorganic (carbon, zeolite, ceramic or metallic) and can be either porous or non-porous. With regards to CO₂ capture, the membrane processes are classified into two types:

- Gas separation membrane
- Gas absorption membrane

3.4.1. Gas separation membrane

Fig. 5 shows gas separation membranes which operate on the principle of preferential permeation of mixture constituents through the pores of the membrane causing one component diffuses through the membrane faster than the others. The main design and operational parameter of membrane are selectivity and permeability. In this process, the gas stream containing CO₂ is introduced at elevated pressure into the membrane separator consisting typically a large number of hollow cylindrical membranes arranged in parallel. CO₂ selectively permeates through membrane and is recovered at reduced pressure on the shell side of the separator [51,58].

Various types of gas separation membranes including ceramic, polymeric and combination of both materials or mixed matrix membranes are available [55]. The separation of the gases is relied on solubility or diffusivity of gas molecules in the membrane and difference in partial pressure is driving force for gas separation.

3.4.2. Gas absorption membrane

Gas absorption membrane consists of micro porous solid membrane which is used as contacting device between the gas and liquid flow as shown in Fig. 6. From Fig. 6, it is evident that CO₂ to be separated from flue gas is diffused through membrane, and then is recovered by liquid absorbent by absorption. This process gives higher removal rate than gas separation membrane due to high driving force at any instant. The advent of independent control of gas and liquid flow results minimum entrainment, flooding, channeling and foaming. The equipment used also tends to be more compact than conventional membrane separator [51].

Membrane processes are highly capable of maintaining product purity even though the capacity is reduced down to 10% of the initial design value. It can be done by either reducing feed pressure, increasing permeate pressure, or by isolating modules from the system. Moreover it is a low cost process for separating gases and extremely reliable with respect to the on-stream factor. The membrane separation process is continuous and has few control

![Fig. 5. Principle of gas separation membrane](image-url)
components which can cause a shutdown. The response time of membrane systems is essentially instantaneous, and corrective action has immediate results. The start-up time required by the process is extremely short. There are number of losses associated with the CO₂ capture from flue gases, which limit the use of membrane. The membrane systems can be considered highly flexible only when the CO₂ concentration is higher than 20%. For CO₂ concentration lower than 20% the membrane system offer a very low flexibility [58]. A further reduction in CO₂ concentration, in fact, produces a reduction of the driving force with a consequent decrease in CO₂ recovery and in product purity. However, the main problem related to limited use of membrane technology is lower concentration of CO₂ in flue gases. For high temperature application, membrane technology needs additional pre-treatment (cooling for reduced temperature) [52,58].

4. Limitations and implementation on existing technologies

4.1. Absorption process

Chemical absorption capture technologies are best suitable for post combustion. Various solvents are available which have the tendency to absorb CO₂ such as MEA, DEA, and MDEA, K₂CO₃, Na₂CO₃, NaOH, NH₃, AMP, etc. Among these MEA provides a good absorption capacity, but regeneration is lower than AMP. Recently blended solvents provide an enhancement in overall efficiency than individual solvent [5]. However, several limitations to absorption process such as, solvent degradation, corrosion, solvent regeneration efficiency, etc affect the efficiency of CO₂ removal. So much research is needed in the direction of:

- Improvement of solvents.
- Modification in gas—liquid contacting devices.
- Development of degradation and corrosion inhibitors.
- Development of alternative solvents such as ionic liquids, blended solvents, etc.

4.2. Adsorption process

Solid adsorbents such as activated carbons, zeolites, mesoporous silicates, alumina, and metal oxide have been extensively used for gas separation [59]. Adsorption of CO₂ from a gas stream is a dry process and hence it has no by-product such as wastewater in conventional absorption process. Moreover it requires low energy as compared to that of cryogenic and absorption processes. But there are some limitations that make this process less effective such as:

- Low selectivity and capacity of available adsorbent for CO₂.
- Lower removal efficiency as compared to other technologies such as absorption and cryogenic [5,58].
- Regeneration and reusability of adsorbent.

In view of the above, much attention is required for developing the new adsorbents or modification on surface chemistry of existing adsorbents so that the adsorbents can operate at higher temperatures in the presence of steam with increased capacity and improved selectivity. Recently, gas adsorption by activated carbon fibers and carbon fiber composites has been identified as a promising alternative. Lately, structured porous monolith material made from carbon fibers has the ability to selectively absorb gases due to their molecular sieving characteristics [59]. Combination of PSA and TSA such as PTSA (pressure and temperature swing adsorption), or ESA can be used for CO₂ removal. PTSA reduces power consumption required for separation as compared to PSA system by 11% [55].

4.3. Cryogenic process

Cryogenic process is inherently difficult to apply for CO₂ capture, because mostly CO₂ occurs in conjunction with other gases (SOₓ, NOₓ, H₂O) which severely interfere with cooling and cause corrosion, fouling and plugging [51]. There is a need to remove all trace water from feed which leads to increase the CO₂ capture cost. Furthermore the phase behavior of CO₂ is complex and it easily leads to the formation of solids which plug equipment and severely reduce heat transfer rates resulting in the reduction of process efficiency [51,56]. In light of these limitations and high cost of refrigeration, this process can be used only for special circumstances as an adjunct to other processes.

4.4. Membrane process

In membrane technology for CO₂ separation, the required energy per unit mass of CO₂ captured is least in the range of 0.5—6 MJ/kg of CO₂ as compared to other existing technologies [58]. But low removal efficiency and low purity of CO₂ make this process ineffective. Also its feasibility is decreased when concentration of CO₂ in feed stream is below 20% [52,58]. Since, the membrane cannot usually achieve high degree of separation it can’t be optimized for large volume of gas separation. So, multiple stages and/or recycle of one of the streams are necessary and also membranes are sensitive to sulfur compounds and other traces [52,55]. Thus much attention is needed in the direction for improving the transport properties of membrane:

- Development of some alternative membranes.
- Combination of two membrane materials to produce composite membrane for enhanced removal of gases.

Facilitated transport membrane, mixed matrix membrane etc. are good enhancement in membrane technology. Also the membrane process in combination with other existing processes may increase the overall efficiency of the process, e.g. membrane with cryogenic [60] and membrane with absorption process [52].
5. Progress in CO2 capture

5.1. Chemical looping combustion (CLC)

A promising technology for fossil fuel combustion uses the concept of preventing CO2 dilution with flue gases by avoiding the direct contact between flue and combustion air [61–63]. In this process oxygen required for combustion of fuel is supplied in the form of metal oxide as in solid phase. Transition metal oxides such as nickel, copper, cobalt, iron and manganese are good oxygen carriers. In CLC process, two interconnected fluidized beds are used as air reactor and fuel reactor, respectively. A gaseous fuel is fed into the fuel reactor, where it is oxidized by lattice oxygen of metal oxide, which is circulating between the reactors. Complete combustion in fuel reactor produces condensable water vapor and CO2. Therefore, the CO2 formed can be readily recovered by condensing water vapor, eliminating the need of an additional energy intensive CO separation process [4,10,52]. The water free CO2 can be sequenestrated and used for other applications.

A generalized description of the overall reaction stoichiometry in the fuel reactor can be written as follows:

\[(2n + m)M_{\text{ox}} + C_{\text{arb}}H_{2n}m \rightarrow (2n + m)M_{\text{ox}} - 1 + mH_2O + nCO_2 \]  

Once fuel oxidation completed the reduced metal oxide \(M_{\text{ox}}-1\) (or metal) is transported to the air reactor where it is reoxidized according to the following reaction:

\[M_{\text{ox}} - 1 + \frac{1}{2}O_2(\text{air}) \rightarrow M_{\text{ox}} + N_2(\text{air}) \text{+ excess O}_2\]  

The outlet gas stream of the air reactor contains nitrogen and unreacted oxygen. These gases can be released to the atmosphere with minimum negative environmental impact. This process has several advantages in comparison with conventional combustion process. The CLC does not bring any enthalpy gain because the overall heat generation is equal to the heat of combustion. Its main advantage, however, resides in the inherent separation of both CO2 and H2O from the flue gases. In addition, CLC also minimizes NOx formation since the fuel burns in the fuel reactor in an air free environment and the reduced oxygen carrier is re-oxidized in the air reactor in the absence of a fuel at comparatively lower temperatures.

5.2. Integrated Gasification Combi Cycle (IGCC)

The IGCC is a very promising power generation technology for pre combustion process. The gasification system converts coal or other carbon based feedstock such as petroleum coke, heavy oils, biomass etc. into synthesis gas (syngas) which consists of hydrogen and CO [6,9,64]. The syngas with added steam is then sent to a shift converter where the water gas shift reaction converts CO to CO2 and additional H2. The CO2 is separated from the H2, which is mixed with steam or nitrogen from air separation unit and sent to a combustion turbine. The hot exhaust gas from the combustion turbine goes to a heat recovery steam generator system to produce steam for the steam turbine that generates additional power and increases the overall efficiency [6]. Gasifiers applied for IGCC fueled with bituminous coal are typically oxygen-blown entrained flow gasifiers operating at pressures between 30 and 70 bar and temperatures from 1000 to 1500 °C [9].

A major bottleneck for large scale commercial application is relatively high investment costs in comparison to post combustion. Moreover, IGCC is a technically more complex system than post combustion, leading to a relatively low availability and poor operational flexibility. In order to increase plant efficiency to a level of 85–90%, a spare gasifier might be required which will increase total investment costs [9].

5.3. Dual-alkali absorption approach

The Solvay process employs a dual alkali approach with ammonia as a catalyst to aid the reaction of CO2 with sodium chloride for the production of sodium carbonate [65]. The reaction was performed by saturating brine with ammonia, and then with CO2 [4,52]:

\[\text{CO}_2 + \text{NaCl} + \text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NaHCO}_3 \downarrow + \text{NH}_4\text{Cl} \]  

Product sodium carbonate is obtained by heating sodium bicarbonate:

\[2\text{NaHCO}_3 \rightarrow \text{Na}_2\text{CO}_3(s) + \text{H}_2\text{O} + \text{CO}_2(g) \]  

The ammonia is recovered by reacting ammonium chloride with lime:

\[2\text{NH}_4\text{Cl} + \text{Ca(OH)}_2 \rightarrow 2\text{NH}_3 + \text{CaCl}_2 + \text{H}_2\text{O} \]

However, this approach poses several drawbacks when applied to CO2 capture from flue gas. The use of limestone as source of lime for the regeneration of ammonia makes the process ineffective because of the consumption of limestone, production of CO2, and extensive energy requirement during calcination. In the Solvay process, for every 2 mol of CO2 captured, 1 mol of CO2 is released from calcination of limestone. This can be seen from the overall reactions:

\[\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \]  

\[2\text{NaCl} + 2\text{CO}_2 + \text{CaO} + \text{H}_2\text{O} \rightarrow 2\text{NaHCO}_3 + \text{CaCl}_2 \]

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

\[\text{CO}_2 + \text{NaCl}_2 + \text{HOCH}_2\text{CH}_2(\text{CH}_3)\text{NH} + \text{H}_2\text{O} \rightarrow \text{NaHCO}_3 \downarrow + \text{HOCH}_2\text{CH}_2(\text{CH}_3)\text{NH} - \text{HCl} \]  

The CO2 absorption capacity of methylaminoethanol (MAE) is greater than that of MEA. The maximum CO2 absorption capacity of an amine is 0.5 mol CO2/mol amine for carbamate and 1.0 mol CO2/ mol amine for bicarbonate formation. 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 used in place of limestone to regenerate ammonia at 25 °C, the primary alkali in the Solvay process according to the following reaction:

\[\text{NH}_4\text{Cl} + \text{AC} \rightarrow \text{NH}_3 + \text{AC} \text{HCl} \]  

The basicity of the AC is responsible for the adsorption of HCl molecules from NH4Cl solution with the liberation of ammonia. This group of research does not require any secondary alkali to regenerate the primary alkali like MAE [52].

6. Emerging technologies

6.1. Enzyme based separation

In this process, CO2 is removed from gas mixture based upon naturally occurring reactions of CO2 in living organism (enzyme). Enzyme mainly proteins catalyzes the chemical reaction. The process using carbonic anhydrase (CA) in a hollow fiber with liquid
membrane has demonstrated the potential for 90% CO2 capture followed by regeneration at ambient conditions in laboratory-scale operation. The CA process has been shown a very low heat of absorption that reduces the energy penalty typically associated with absorption processes.

The rate of CO2 dissolution in water is limited by aqueous CO2 hydration and CO2 carrying capacity is limited by buffering capacity. Addition of CA enzyme to solution enhances the CO2 dissolution and forms carbonic acid. CA has the ability to catalyze the hydration of 600,000 molecules of CO2 per molecule of CA per second compared to a theoretical maximum rate of 1,400,000. This fast turnover rate minimizes the amount of enzyme required [6]. Finally by pressure-swing desorption, solid carbonate precipitation, chemical treatment, or some other means, the process must incorporate a mechanism by which CO2 can be released from the system as a concentrated stream [66].

The idea behind this process is to use immobilized enzyme at the gas/liquid interface to increase the mass transfer and separation of CO2 from flue gas. Technical challenges of this technology include membrane boundary layers, pore wetting, surface fouling loss of enzyme activity, long-term operation, and scale-up of the process. Small amount of CA requirement and life of the CA around 6 months and high catalyzed activity indicate that it will be a great improvement in cost and performance of CO2 capture in large scale power plants [6,65]. So, this can be an alternative for existing technology for CO2 capture.

6.2. Facilitated transport membrane (FTM)

A facilitated transport membrane for CO2 separation was patented by Hagg [67]. It has received a lot of attention in gas separation because it offers higher selectivity and larger flux. Higher selectivity in FTM is achieved by incorporating a carrier agent into membrane such as cross linked polyvinylamine, which reacts reversibly with the penetrating species [4,58]. The permeating species dissolves in the up stream portion of the membrane and reacts with the carrier agent inside the membrane to form complex. This complex diffuses across and releases permeate on the downstream side of the membrane, while the carrier agent is simultaneously recovered and diffuses back to the feed side. In case of CO2 separation, a fixed carrier helps so that the CO2 molecules in combination with moisture to form HCO3-, which is then quickly and selectively transported through the membrane. This technology is effective and eco-friendly (as the membranes are based on nanostructure material) and can be used for practically all types of CO2 removal from other gases. Its effectiveness increases proportionally to the concentration of CO2 in the gas [58].

6.3. Hydrate based separation

Hydrate-based separation as a promising technology has attracted more attention. This process begins by forming the hydrate by exposing the exhaust gas stream containing CO2 to water under high pressure. As the hydrate forms, the CO2 is captured. The hydrate is then separated and dissociated by releasing CO2 in pure form. Gas hydrates are crystalline composed of water and gas under suitable condition of low temperature and high pressure. When gas hydrates are formed from mixture of gases, the concentration of the gases in the hydrate phase is different as that in the gas phase. Consequently, the component that forms hydrate more easily might be enriched in the hydrate phase. Because hydrates have the capacity to store large amount of gas [68], hydrate based technology can be attracted much attention as a potential means for capturing CO2.

The process of hydrate based CO2 capture was systematically studied with tetrahydrofuran (THF) as an additive [69,70]. The result shows that the addition of THF reduces the operating pressure and enhances the corresponding kinetic rate. It is verified that the hydrate-based gas separation process makes it possible to recover more than 99% of CO2 from flue gas. Although the result is promising, the separation process with THF as an additive has some problems:

- Very low temperature is required in the process (0.6 °C).
- THF is harmful to health/safety and well known contaminant to the environment.
- The hydrate formation rate is slow.

Recently, tetra-n-butyl ammonium salts such as tetra-n-butyl ammonium bromide (TBAB) and tetra-n-butyl ammonium fluoride (TBAF) have received much attention as attractive additive for CO2 capture [68].

6.4. Mixed matrix membrane

Mixed matrix membranes are a well-known route to enhance the properties of polymeric membranes. Their microstructure consists of an inorganic material in the form of micro- or nanoparticles incorporated into a polymeric matrix. The use of two materials with different flux and selectivity provides the possibility to design an efficient membrane for CO2 capture, allowing the synergistic combination of polymers for easy process ability and superior gas separation performance of inorganic materials. Furthermore the addition of inorganic materials in a polymer matrix offers enhanced physical, thermal and mechanical properties for aggressive environments and represents a way to stabilize the polymeric membrane against change in permeability with temperature [4,58].

Many researches direct at mixed-matrix membranes specially the polymer-zeolite pairs which include polydimethylsiloxane-silicalite [71], polyimide-carbon molecular sieve, polyimide-silica [72], nafion-zirconium oxide [73], HSSZ-13-polyetherimide, acrylonitrile butadiene styrene-activated carbon [74]. It is known that the permeability of a gas through a zeolite-filled polymeric membrane depends on the intrinsic properties of zeolite and the polymer [71]. However their performances are suffered from defects caused by poor contact at the molecular sieves/polymer interface. This can allow gases to flow non-selectively around the solid particles. Sonication and decantation techniques have been suggested to overcome this issue. The successful implementation of this membrane process depends on both, the selection of polymeric matrix and inorganic zeolite, and the elimination of interfacial defects [74]. Mixed matrix membranes offer very interesting properties, however, their cost, difficulty of commercial scale manufacturing and brittleness remain important challenges. Researchers proposed some criteria for material selection and preparation protocols in order to match the necessary transport characteristics of materials to prepare high performance mixed matrix membranes for CO2 capture [58,75,76].

6.5. Calcium looping CO2 capture

This technology utilizes the concept of reversible reaction between CaO and CO2 to form calcium carbonate in calcium looping cycle [4,77,78]. The use of CaO-based solids to capture CO2 at high temperature is the core of several CO2 capture and zero emission power plant concepts [79,80]. Similar to CLC, there are two reactors in this system. Primary fuel combustion takes place in the
Comparative analysis of different technologies.

<table>
<thead>
<tr>
<th>Sr no.</th>
<th>Parameter</th>
<th>Absorption</th>
<th>Adsorption</th>
<th>Membrane</th>
<th>Cryogenic</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Operating flexibility</td>
<td>Moderate</td>
<td>Moderate</td>
<td>High (CO₂ &gt; 20%)</td>
<td>Low [5,40,51]</td>
</tr>
<tr>
<td>2.</td>
<td>Response to variations</td>
<td>Rapid (5–15 min)</td>
<td>–</td>
<td>Instantaneous</td>
<td>Slow [40,51]</td>
</tr>
<tr>
<td>3.</td>
<td>Start-up after the variations</td>
<td>1 h</td>
<td>–</td>
<td>Extremely short (10 min)</td>
<td>8–24 h [40]</td>
</tr>
<tr>
<td>4.</td>
<td>Turndown</td>
<td>Down to 30%</td>
<td>Down to 10%</td>
<td>Down to 50% [40]</td>
<td></td>
</tr>
<tr>
<td>5.</td>
<td>Reliability</td>
<td>Moderate</td>
<td>Moderate</td>
<td>100%</td>
<td>Limited [13,51]</td>
</tr>
<tr>
<td>6.</td>
<td>Control requirement</td>
<td>High</td>
<td>High</td>
<td>Low</td>
<td>High [40,81]</td>
</tr>
<tr>
<td>7.</td>
<td>Ease of expansion</td>
<td>Moderate</td>
<td>Moderate</td>
<td>Very high</td>
<td>Very low [13,40,51]</td>
</tr>
<tr>
<td>8.</td>
<td>Energy requirement</td>
<td>4–6 MJ/kgCO₂</td>
<td>2–3 MJ/kgCO₂</td>
<td>0.5–6 MJ/kgCO₂</td>
<td>6–10 MJ/kgCO₂ [81–83]</td>
</tr>
<tr>
<td>9.</td>
<td>CO₂ recovery</td>
<td>90–98%</td>
<td>80–95%</td>
<td>80–90%</td>
<td>&gt;95% [13,51,52]</td>
</tr>
</tbody>
</table>

| Table 2 |

Regarding to adsorption process, activated carbon and CaO reacts with CO₂ in the same reactor achieving in-situ CO₂ capture. The reaction is as follows:

\[
\text{CaO(s) + CO}_2(g) \rightarrow \text{CaCO}_3(s) \quad (18)
\]

Temperature is in the range of 650–700 °C depending on pressure of the system. CaCO₃ is heated to regenerate CaO in calciner as given by Rxn (11) and the heat is provided by burning a secondary fuel such as petroleum coke.

\[
\text{CaCO}_3(s) \rightarrow \text{CaO(s) + CO}_2(g) \quad (19)
\]

Depending on the partial pressure of CO₂ temperature can rise above 900 °C. The CO₂ thus regenerated in the calciner is delivered for storage. The overall thermal efficiency has been shown to be comparable to that of a current combustion system without CO₂ capture [4,78]. The carbonation can either occur at in-situ or ex-situ and heat released from exothermic carbonization can be used to run steam cycle.

There are intrinsic benefits to be gained from utilizing this carbonation—calcination cycle to separate CO₂. The most important fact is that, as it is a high-temperature CO₂ separation process, there will be modest efficiency penalties and opportunities for a high degree of integration in the combustion plant (for example, at atmospheric pressure the heat required for calcination at temperature over 900 °C is recovered in the carbonation step at 650 °C). Secondly, there are plentiful sources of cheap, widely available sorbent (limestone) and furthermore, there is an increasing background of knowledge for the reactions required in these separation processes [79,80]. Despite the known limits to the maximum carbonation conversion, the reaction rates are sufficiently high even at low temperatures, to allow compact reactor designs for the carbonator. Recently, this has been confirmed in post combustion tests reported using three different interconnected fluidized bed installations [78].

7. Discussion

The major improvements of various technologies to existing processes are highly novel approaches for CO₂ capture. Chemical looping, IGCC are great modification to the existing combustion based capture systems. FTM, mixed-matrix membrane are well routes for enhancing the properties of the membrane. Hydrate and enzyme based separations are two different alternative technology for CO₂ capture. Dual-alkali approach and blended solvents have resulted satisfactory performances of the absorption process. Regarding to adsorption process, activated carbon and carbon fiber composite have been identified as promising alternative adsorbents. The PTSA or ESA alone can be used for effective CO₂ removal. There is no unique solution for CO₂ capture. Same kind of approaches can be considered and can be implemented in the absorption process for improved overall removal efficiency of CO₂ such as:

- Development of new solvent or blended solvent.
- Modification on process system or integration with other conventional process (e.g. absorption + membrane).
- Development of suitable corrosion inhibitors.

A comparative analysis of different technologies is presented in Table 2. The CO₂ capture/separation depends on status, level of maturity, cost and limitations of various technologies available for sustainable power generation system [84,85]. If CO₂ composition in the flue gas streams, extent of CO₂ separation/capture and uses of separated CO₂ are well defined then from this analysis we can suggest a suitable technology for CO₂ capture.

8. Conclusions

A comprehensive overview of the current status of existing technologies for CO₂ capture has been discussed. Absorption is matured technology for post combustion capture but solvent losses, corrosion and high cost of separation are the main issues for this process. Low selectivity and low capacity of the available absorbents make adsorption process ineffective for large scale industrial applications. Membrane process has several advantages over conventional processes but high capacity and stability are still uncertain. Cryogenic process has produced liquid CO₂ and no separation media is required. Very high cost of separation and necessary control requirement make this process only suitable for special circumstances. All existing technologies have their own advantages and limitations but their reliability, stability and removal efficiency are main challenges. There is a great need for understanding the existing technology to improve the performance, and reduce the cost and energy required for CO₂ separation.

Acknowledgment

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Nomenclature

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Chemical Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC</td>
<td>activated carbon</td>
</tr>
<tr>
<td>AEE</td>
<td>2-(2-aminoethylamino) ethanol</td>
</tr>
<tr>
<td>AEPDNH₂</td>
<td>N-2-aminoethyl 1,3-propanediamine</td>
</tr>
<tr>
<td>AMP</td>
<td>2-amino 2-methyl 1-propanol</td>
</tr>
<tr>
<td>CA</td>
<td>carbonic anhydrase</td>
</tr>
<tr>
<td>CLC</td>
<td>chemical looping combustion</td>
</tr>
<tr>
<td>DEA</td>
<td>diethanol amine</td>
</tr>
<tr>
<td>DGA</td>
<td>diglycolamine</td>
</tr>
<tr>
<td>DIPA</td>
<td>di-2-propanolamine</td>
</tr>
</tbody>
</table>
References


[21] IPCC. Intergovernmental Panel on Climate Change. IPCC Intergovernmental Panel on Climate Change


