

Post Combustion Carbon Dioxide Capture

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Abstract— Capturing CO₂ from flue gas is one of the critical options to reduce greenhouse gas emission to the atmosphere for that post-combustion CO₂ capturing technology is widely used in most industries. Although various CO₂ capture technologies are available, chemical absorption and adsorption are currently believed to be the most applicable ones for post-combustion power plants and industries. As post-combustion CO₂ capturing techniques, the operation of chemical absorption, physical absorption, membrane separation, cryogenic separation, and adsorption are studied in this paper. In the past decade, several studies have been involved in developing post-combustion CO₂ capture from flue gas with high capturing capacity and desired economics. This post-combustion CO₂ capture technology's significant concerns include CO₂ capture efficiency, absorption rate, the energy required in regeneration, and capacity of the absorber. A variety of promising sorbents such as activated carbonaceous materials, zeolites, carbonates, and polymeric resins loaded with or without nitrogen functionality to remove CO₂ from the flue gas streams have been reviewed. The primary concerns for selecting adsorbent, including cost, adsorption rate, CO₂ adsorption capacity, and thermal stability, are evaluated in this paper.

Index Terms— Absorption, Adsorption, CO₂ capture, Post-combustion CO₂ capturing technologies.

1 INTRODUCTION

Carbon dioxide (CO₂) is considered a significant greenhouse gas, and fossil fuel-fired power plants are the primary emitting sources [1]. The ever-increasing concentrations of Carbon dioxide (CO₂) in the atmosphere require humankind to consider ways of managing emissions of this greenhouse gas to the atmosphere. Since most of this Carbon dioxide (CO₂) is produced by the combustion of fossil fuels and, simultaneously, the global energy demand produces more Carbon dioxide (CO₂). It is essential to find ways to sequester it. There are three main Carbon dioxide (CO₂) capture technologies available. They are pre-combustion, post-combustion, and Oxy-fuel combustion. Pre combustion is, capturing the Carbon dioxide (CO₂) before the combustion process. This is a costly process. Oxy-fuel combustion is, from the air, taking only Oxygen (O₂), and then Oxygen (O₂) react with the fuel and less amount of flue gas emitting. Post-combustion is, without caring about the fuel and the air, do the combustion and After the combustion process, remove the Carbon dioxide (CO₂) from the flue gas. There are also several options for post-combustion carbon capture from flue gas. They are Chemical absorption, Physical absorption, Membrane separation, Cryogenic separation, and Adsorption.

2 CARBON CAPTURE

2.1 Chemical absorption

chemical absorption is suitable for CO₂ capture for industrial flue gases. This process involves a reaction between CO₂ and a chemical solvent which forms a weak intermediate compound. This compound can be regenerated by applying heat producing the original solvent and a CO₂ stream. Here relatively pure CO₂ can be produced. Furthermore, the selectivity of this separation is high. monoethanolamine (MEA) is the most commonly used solvent for chemical absorption.

Acidic gases such as SO₂ and NO₂ can affect the performance of the system by forming heat stable salts with the solvent. Therefore, these gases should be removed before absorption. Also, a SO₂ concentration less than 110ppm is acceptable [2]. SO₂ removal takes place in a Flue Gas Desulphurization (FGD) unit. NO is removed using following methods,

- Selective Catalytic Reduction (SCR),
- Selective Non-catalytic Reduction (SCNR) or
- low NO_x burners.

Absorption process is done in towers called scrubbers. The turbulent flow of the solvents promotes rapid CO₂ extraction from gas to the solvent. The density difference help in the liquid gas separation. The CO₂ mixed solvent is pumped to the stripper and exposed to steam [3]. The CO₂ recovering process takes place in the stripper by heating the solvent to de-absorb the purified CO₂. After stripping, the solvent is recirculated back into the scrubbers. Although water has the capability to absorb CO₂ than N₂, it cannot meet with the large-scale CO₂ absorption. A large quantity of water is required to fulfil the particular requirement [4]. CO₂ has a higher solubility in organic solvents than in water even at high pressures. Therefore, organic solvents are better for use at large scale CO₂ absorption [4, 5].

Organic solvents combine with CO₂ in the scrubber and release it at the higher temperatures in the stripper. Amines are water-soluble organic chemicals. Amines contain reactive nitrogen atoms. Monoethanolamine (MEA) is the workhorse amine in the CO₂ separation process. Rapid reaction, non-volatility and the cost effectiveness are properties of amines which are advantageous for this process. But it can cost higher construction expenses due to its corrosion abilities [6, 7].

The trace impurities in the flue gas can reduce solvent's performance. Amine solvents like MEA degrade on contact with certain impurities such as excess oxygen, Sulphur dioxide or nitrous oxides to form substances including heat stable salts. Part of the bottoms product from the stripper is sent to a re-claimer unit where the solvent is evaporated and returned leaving the nonvolatile solvent wastes. The temperature inside the absorber is between 40°C and 60°C. The rich solvent is heated in a cross-heat exchanger by regenerated lean solvent from the Stripper. It is then pumped to the top of the Stripper where it is regenerated at high temperatures (100°C-120°C) and at a pressure (1.5 – 2 atm). Heat is supplied by the re-boiler [6]. The regenerated solvent is pumped back to the Absorber using the cross-heat exchanger to reduce the temperature (Figure 1).

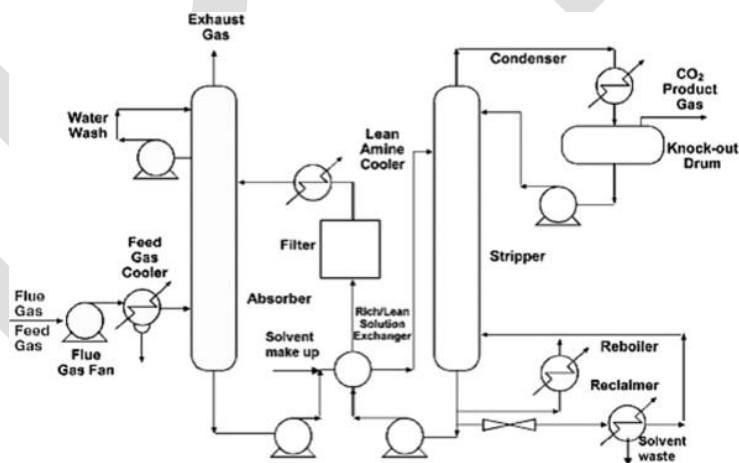


Figure 1: operational process structure of the absorption process [8]

2.2 Physical Absorption

Growing environmental issues after neutralization for global warming and climate change have motivated research activities to develop new models and processors for carbon dioxide capture (CO₂) from significant emitting sources. The Intergovernmental Panel on Climate Change (IPCC) 4th assessment report and some studies have stated that, as a result of anthropogenic CO₂ emission, global atmospheric concentration has

increased from a preindustrial value of 280 ppm to 400 ppm in 2019 [9, 10]. Therefore, it is necessary for taking useful action regarding uncontrolled CO₂ emission to the atmosphere.

Among various technologies, some industries use the physical absorption method for CO₂ post-combustion capture. So, we have discussed further physical sorbent absorption in this section. Within the last few decades, researchers have involved in developing many physical sorbents to capture CO₂ from flue gas because it is essential to develop new technologies that will allow us to utilize the fossil fuels while controlling the emissions of greenhouse gases since it has become world's problem.

Physical absorption is a method Can be introduced as a physically dissolving gas in a physical solvent. It is generally considered to be based on Henry's law, which states that a dissolved gas loading in a physical solvent is proportional to the partial pressure of the gas. As shown in the gas-liquid equilibrium diagram (Figure 2), the physical solvent absorbs a given gas under conditions of high partial pressure in the gas phase and desorbs it under the condition of lower partial pressure [11]. Since a given gas is separated from the solvent using a driving force of a pressure difference, it is possible to remove and recover the gas with less energy.

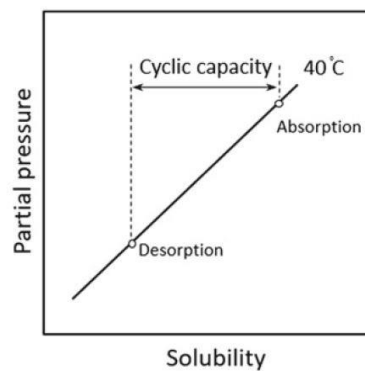


Figure 2: physical absorption[9]

As there many physical sorbents available in the market, we discuss only activated carbon base sorbents, Polymer-Based Sorbents, Zeolite-Based Sorbents, and Silica-Based Sorbents in this section for the removal of CO₂ from the flue gas stream [12].

Activated carbon-based sorbents

Activated carbon has been widely used for CO₂ capture due to its full availability, low cost, high thermal stability and low sensitivity to moisture are few reasons. But their applications are limited to treat high-pressure flue gas. Activated carbon-based sorbents can be categorized into weak CO₂ absorption material and high co₂ absorption materials [13]. The absorption capacity of these materials can be enhanced by improving the surface area and pore structure. However, the main issue with activated carbon base sorbent is CO₂ absorption capacity decreases as the temperature increases.

Polymer-Based Sorbents

Polymeric based sorbents have been used for capture CO₂ in closed environments, such as aircraft, submarine, and space shuttles, under the concentration of CO₂<1 % [14]. However, the cost of these sorbents is too high for large-scale applications in the industry. Table 1 shows the CO₂ adsorption capacity of polymer-based solid sorbents.

Table 1. CO₂ adsorption capacity of polymer-based solid sorbents [12]

Sorbent	Pore size (nm)	Pore volume (cm ³ /g)	BET surface area (m ² /g)	Temperature T (K)	Pressure p (atm)	Capacity (mol/g)
HSC*				313	1	0.91
TEPA-impregnated PMMA				343	0.15	14.03 (humid)
DBU-impregnated PMMA	20.3	0.58	94	298,338	0.1	3.0 (humid) 2.34 (humid)
PEI-impregnated PMMA				318	0.1	2.40 3.53 (humid)
PEI cross-linked with EP-coated fiber				303	1	6.30 (humid)
PEI cross-linked with ECH-coated fiber				303	1	4.12
Allylamine-grafted PAN fiber	3.08	0.0051	6.57	295	0.15	6.22

Zeolite-Based Sorbents

Natural and synthetic sorbents are widely used in industries gas separation and flue gas purification processes. The porous of Zeolite-based silicate frameworks has a negative charge within their pore structure, which helps to separate CO₂ molecules via the molecular sieving effect. Table 2 shows the CO₂ absorption capacities of various Zeolite-based sorbents.

Table 2: Absorption capacities of various zeolite-based sorbents [15]

Schemes	Material	CO ₂ uptake
Structure and composition adjustment	CU-SSZ-13 H-SSZ-13	3.8 mmol g ⁻¹ at 25°C. 1 bar 4.0 mmol g ⁻¹ at 25°C. 1 bar 1.2 mmol g ⁻¹ at 30°C. 1 bar

Cation exchange	Li-Rho Li-ZK-s Ca-A Zeolite Ca Sr ²⁺ -SAPO 34 CHA and 13X	3.4 mmol g ⁻¹ at 25°C. 0.1 4.7 mmol g ⁻¹ at 25°C. 0.1 3.7mmol g ⁻¹ at 40°C. 15 bar 1.6 mmol g ⁻¹ at atroom temperature, 1bar 3.0mmol g ⁻¹ at 25°C. 1 bar 1.4 mmol g ⁻¹ at 200°C. 20
Amine modification	TEPA modified zeolite Y TEPA modified zeolite A G- SBA-15-NNN- (10)	2.6mmol g ⁻¹ at 60°C. 1 bar 3.8mmol g ⁻¹ at 25°C. 1 bar 2.2mmol g ⁻¹ at 40°C. 1 bar
Hybrid materials	SBA- 3/cotton fiber	2.4mmol g ⁻¹ at 75°C. 1 bar

Silica-Based Sorbents

These sorbents have a high surface area, large pore volume, narrow pore size distribution, and excellent regeneration stability. According to literature, silica is mainly used as support, on which amines are added for capturing CO₂ [15]. Therefore, the research activities on silica-based CO₂ adsorbents are mostly focused on making different types of silica's-based sorbents with a high capacity of CO₂ absorption from flue gas. As there many silica-based sorbents, few of them are only used industrially by considering cost-effective and commercially availability. Table 3 shows silica-based CO₂ sorbents and their performance in CO₂ capture.

Table 3: Silica-based CO₂ sorbents and their performance in CO₂ capture [12]

Silica types	Surface Modifications	CO ₂ uptakes
Conventional silica	PAA modified PEI modified	3.8mmol g ⁻¹ at 40°C. 1 bar 2.4mmol g ⁻¹ at 25°C. 1 bar
Silica hollow sphere	TEPA modified APTES & BTME modified MCFs PEI modified	4.4mmol g ⁻¹ at 110°C. 1 bar 1.7mmol g ⁻¹ at 0°C. 1 bar 6.0mmol g ⁻¹ at 85°C. 1 bar
Silica nanotube	Tertiaryamines modified	1.3mmol g ⁻¹ at 30°C. 1 bar
Chemical grafting	APS Grafted APMS grafted APTMS and Poly-L-alamine co- grafted	0.7mmol g ⁻¹ at 27°C. 1 bar 2.0mmol g ⁻¹ at 60°C. 1 bar 3.9mmol g ⁻¹ at 50°C. 1 bar

3. Membrane Separation

Membrane processes have been initially seldom considered within a post-combustion carbon dioxide capture framework. More traditional processes, particularly gas-liquid absorption in chemical solvents, are often considered as the most appropriate solution for the first generation of technologies [16]. Membrane separation might be a promising way with operating parameters beyond current technologies as they often have low energy consumption, low operational cost, small footprint and easy scale up and incorporation into existing technologies [17].

Membrane performs as a filter. It allows certain molecules to permeate through, while blocks other specific molecules from entering the membrane. Gas permeation flux across unit membrane area under unit pressure difference through unit membrane thickness is called permeability ($\text{mol s}^{-1} \text{m}^{-2} \text{Pa}^{-1}$) and the ratio of permeabilities of different gases through the same membrane is defined as selectivity. The gas separation mechanism varies from membrane to membrane. The selectivity of different gases may result from the difference in molecular size, affinity to membrane material, molecular weight, etc., depending on the gas and membrane of interest [18].

In order to recommend a membrane system for a specific gas separation process it should be proven that it can perform better separation or has better economics than other competing separation processes. Absorption, adsorption, and cryogenic distillation are widely adopted processes for large scale production when high purity and high recovery are required. Nevertheless, these processes are high energy consuming giving room for membrane systems to compete with these processes on an economical basis [19].

The flue gas mainly contains CO_2 , H_2O and N_2 . In here we discussed the CO_2 capturing using membrane arrangement. Post-combustion capture separates CO_2 at moderate temperatures and ambient atmosphere pressure. As a result, post-combustion capture has encountered much less difficulties and is therefore rather closer to practical application. The major challenge for post-combustion capture is the low CO_2 volumetric fraction in flue gas, that is, about 15%, which results in a low driving force of CO_2 permeation. The separation of CO_2 mainly relies on surface diffusion and solution diffusion, which is driven by the difference in adsorbability and solubility between the gases [18].

Schematically, the analysis of gas separation membrane processes for CO_2 capture depends on two different types of factors, which will be detailed in the next sections:

- a materials science aspect which addresses the evaluation of the intrinsic separation performances of the membrane. This topic typically requires the structure and/or the mass transfer mechanisms taking place in the membrane to be determined [16].
- a process engineering science aspect, which aims at the determination of the best design and operating conditions for a given membrane material. Classical tools of chemical engineering and separation science are used for this purpose [16].

Combining materials and process engineering considerations, the energy requirement and the size of the installation, the two-key data of technico-economical studies, can be finally obtained [16].

CO_2 is more likely to be favored by majority of the membrane materials via adsorption or absorption. Therefore, for post-combustion capture, CO_2 selective membranes are generally used. To capture CO_2 from flue gas, a membrane should satisfy a few requirements such as high CO_2 permeability, high CO_2 selectivity, high thermal and chemical stability and acceptable costs. So far, polymer-based membranes are the only commercially viable

type for CO₂ removal from flue gas. The membrane materials include cellulose acetate, polyimides, polysulfone and polycarbonates. Table 4 shows the performance of several such membranes[18].

Table 4: CO₂/N₂ separation performance by polymer-based membranes.[18]

Membrane	Permeance ^a or Permeability ^b (mol s ⁻¹ m ⁻² Pa ⁻¹)	CO ₂ /NO ₂ selectivity	Temperature (°C)
Cellulose acetate	$2.48 \times 10^{-7}a$	40.17	Not reported
Polymides-TMeCat	$6.30 \times 10^{-10}b$	25	30
Polymides-TMMPD	$1.89 \times 10^{-9}b$	17.1	Not reported
Polymides-IMDDM	$6.17 \times 10^{-10}b$	18.1	Not reported
Polysulfone-HFPSF-oHBTMS	$3.31 \times 10^{-10}b$	18.6	35
Polysulfone-HFPSFTMS	$3.47 \times 10^{-10}b$	18	35
PolysulfoneTMPSFHBTMS	$2.27 \times 10^{-10}b$	21.4	35
PolycarbonatesTMHFPC	$3.50 \times 10^{-10}b$	15	35
Polycarbonates-FBPC	$4.76 \times 10^{-10}b$	25.5	35
a Permeance			
b Permeability			

Selectivity larger than 20 was observed for all the polymer-based membranes with decent permeability. The high solubility of CO₂ in polymers ensures sufficient CO₂/N₂ selectivity. Furthermore, polymers with a high fractional free volume present excellent gas transport property.[18]

Mixed-matrix membrane is a new option to enhance the properties of polymeric membranes. The microstructure consists of an inorganic material in the form of micro- or nanoparticles in discrete phase incorporated into a continuous polymeric matrix. The addition of inorganic materials in a polymer matrix offers improved thermal and mechanical properties for aggressive environments and stabilizes the polymer membranes against the changes in chemical and physical environments. Carbon molecular sieves membranes also show interesting performance for CO₂ separation applications. Polyimide is the most used precursor for carbon membranes. Carbon membranes improved gas transport properties for light gases (molecular size smaller than 4.0–4.5 Å) with thermal and chemical stability. The major disadvantages of mixed-matrix and carbon membranes that hinder their commercialization include brittleness and the high cost that is 1–3 orders of magnitude greater than polymeric membranes [18].

4.Cryogenic Separation

Cryogenic separation is also one of the physical processes, which is the Cryogenic separation produces liquid Carbon dioxide with under the high pressure [20, 21, 22]. Normally, a series of compression, refrigeration, and separation steps are using when the component of gas mixtures separating during the Cryogenic separation process [23]. Cryogenic separation is still not an economical process due to its variable high refrigeration cost. The high operating cost for cold production is the main limitation of the cryogenic separation process [24]. The simple process of the Cryogenic separator shows bellow in the Figure 3 [25].

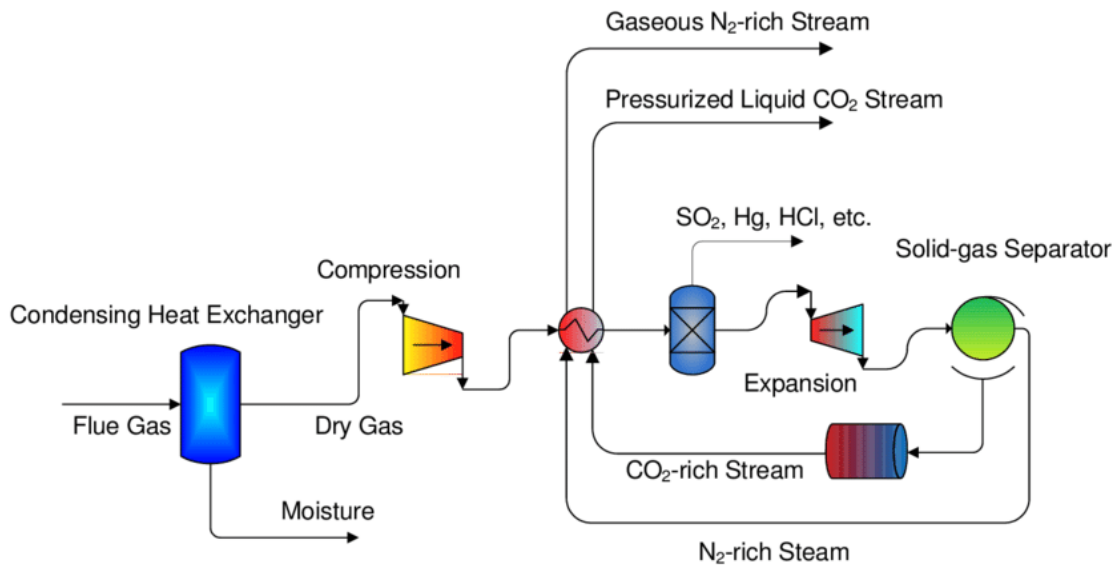


Figure 3: Simple schematic diagram of the cryogenic carbon capture process

Classification of cryogenic technologies: -

01. Conventional cryogenic methods: - liquid-vapor-based distillation and extractive distillation technologies
02. Nonconventional methods: - solid vapour desublimation-based separation, condensed contaminant centrifugal separation, successive release and recompression, and cryocoolers such as Stirling coolers
03. Hybrid technologies [26].

Advantages of cryogenic separation over chemical and adsorption-based processes: -

- Recurring consumable costs and secondary pollution of an industry can be avoided due to not use of chemicals and solvents. As well as solvent recovery plants are not required
- Makeup water supply and treatment are not required
- Process heating systems are not required
- Minimum corrosion potential
- There is no foaming potential
- Not need of winterization requirements for cold climates
- Pumping and storage of captured carbon dioxide are comfortable because of the cryogenic separation methods can capture carbon dioxide in a liquid form [26] [27].

5.Adsorption

Atmospheric CO₂ concentrations are rising due to anthropogenic emissions. Adsorption-Based CO₂ Capture Processes has motivated efforts to develop cost-effective and energy-efficient carbon capturing. Cyclic

adsorption-based CO₂ emission capture has emerged as a promising approach. There are mainly three adsorption methods. They are pressure swing adsorption (PSA), vacuum swing adsorption (VSA), temperature swing adsorption (TSA) and electric temperature swing adsorption (ESA)[28]. PSA operates above atmospheric pressure, VSA happens at atmospheric pressure while desorption takes place under low pressure. During TSA, a desorber is heated by an external heat source. ESA is a type of TSA where electricity is used for fast desorption. In the moving process, adsorption and desorption happen alternatively to acquire high purity CO₂. This cycle is intermittent, and therefore a second set of the adsorber and the desorber is required to achieve continuous operation. Also, various solid adsorbents, which are classified into physical and chemical adsorbents, can be selected for capturing CO₂ in different applications.

As the Physical sorbents, zeolite 5A, zeolite 13X, activated carbon (AC) and silica gel have been widely investigated for adsorption-based CO₂ capture which is inexpensive, insensitive to moisture and with a large surface area. Several novel physical adsorbents, e.g. metal-organic framework (MOF), have attracted attention due to their large adsorption capacity and high gas selectivity. Nevertheless, their costs are relatively high compared to those of conventional adsorbents. As for chemical sorbents, amine-based materials are more advantageous due to their lower generation heat. [29].

Adsorption-based carbon capture is a material enabled technology. Porous materials including activated carbon, zeolites, and metal-organic frameworks, have been actively examined for use in CO₂ capture processes. Although capable cycle configurations are essential, the performance of cyclic adsorption processes depends heavily on the selection of adsorbent materials. layered double hydroxides (LDH), Zeolites and zeolites coated LDH composites are mainly used as the adsorption materials. CO₂ capture technologies have been lately implemented in many industries. However, the commercially mature technology to capture CO₂ remains an amine-based scrubbing, but its high cost and hazardous by-products force humankind to find out alternative technologies. [30]

The development of new solid adsorbents has flourished in the last decade. depending on their working temperature range the sorbents can be classified into high-temperature (> 400°C), intermediate-temperature (200–400°C), low-temperature (< 200°C) CO₂ adsorbents. layered double hydroxides (LDH) known as hydrotalcite-like compounds, are a class of layered materials which comprise mono or di and trivalent cations. In recently several researches have been dealing with the high potential of LDHs derived CO₂ adsorbents, especially conventional Mg-Al LDHs, which demonstrated excellent performance at high temperatures. Likewise, zeolites have also been subjected to further research for the adsorption of CO₂ due to their high stability, high capture capacity, low regeneration temperatures and over several adsorption-desorption cycles. Regarding sorbents working at an intermediate temperature range, recent studies have shown great potential from LDH coated zeolites. A significant increase in the adsorption of CO₂ was observed after the coating of LDH over a zeolite core at temperatures ranging from 35 to 300°C[28].

Conclusion

Carbon dioxide (CO₂) is the primary emitting source during the combustion of fossil fuel and it is a major

greenhouse gas. Therefore it is needed to control the emission of flue gas to the environment to minimize the greenhouse effect. Out of the three methods of capturing CO₂ such as pre-combustion, post-combustion and Oxy-fuel combustion, post-combustion can be considered as a more effective method. Among the post-combustion methods (Chemical absorption, Physical absorption, Membrane separation, Cryogenic separation and Adsorption), chemical absorption and physical adsorption are the most applicable ones for post-combustion power plants and industries. In chemical absorption, amines are used as a cost effective, rapidly reactive and non-volatile solvent. Adsorption-Based CO₂ Capture Processes has motivated efforts to develop cost-effective and energy-efficient carbon capturing.

As the Physical sorbents, zeolite 5A, zeolite 13X, activated carbon (AC) and silica gel have been widely used for adsorption-based CO₂ capture which is inexpensive, insensitive to moisture and with a large surface area.

The membrane separation process is also effective as it has low energy consumption, low operational cost, small footprint and easy scale up and incorporation into existing technologies.

Although Cryogenic separation is having many advantages over chemical and adsorption based processes, it is not an economical process due to its variable high refrigeration cost. The high operating cost for cold production is the main limitation of the cryogenic separation process.

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