

# POST COMBUSTION CARBON DIOXIDE CAPTURE

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**Abstract** - The industrial revolution was caused to develop the world with technological advancements and it affects badly to the environment. These reasons cause the development of different systems to control the emission of different gasses to the environment. At present CO<sub>2</sub> concentration in air is considerably high and it needs to be reduced before it release to the environment. For that purpose, CO<sub>2</sub> capturing methods have introduced for industries and power plants. There are several methods to capture CO<sub>2</sub> and only post combustion capturing methods will discuss in this article. Post-combustion capturing methods like Chemical absorption, Physical absorption, Membrane separation, Cryogenic separation, and Adsorption methods are discussed in this article. These systems will describe in detail with advantages and disadvantages.

**Index term** – Absorption, Adsorption, Cryogenic separation, Membrane separation, Post combustion

## 1 INTRODUCTION

Industrialization and many other factors are caused to emit CO<sub>2</sub> to the environment. CO<sub>2</sub> is one of the greenhouse gas that can absorb and emit thermal radiation. After the period of industrialization, the greenhouse gas that considerably emits to the environment is CO<sub>2</sub> gas [1]. The main reasons to emit CO<sub>2</sub> gas are fossil fuel combustion and cement production. The fossil fuel combustion and cement production lead to release the 321 billion tons of CO<sub>2</sub> [2, 3]. Fossil fuels usage can be seen in power plants and even in industries which used as a fuel for the combustion. These CO<sub>2</sub> emissions affect the environment in several ways, such as global warming, low visibility, etc. Its impact is not only for the environment but also for humans. For example, the people exposed to those gasses very frequently affect bronchitis, lung cancer, cough, etc. [4]. And it is estimated that fossil fuels are increased by 90% because of the demand in 2030 [3]. So it is essential to introduce the CO<sub>2</sub> capturing technologies in every power plant and industry to minimize the CO<sub>2</sub> emission.

When considering the current CO<sub>2</sub> capturing technologies, cost and equipment is need to be considered. From the whole system, 70%-80% cost is estimated to capture the CO<sub>2</sub> [3]. So the capturing technologies can be categorized into three types as post-combustion, pre-combustion, and oxy-fuel combustion [3]. They can be described as follows.

**Pre combustion capturing** – This process is done through oxygen- blown gasification. Integrated gasification combined cycle technology can be taken as an example of this process.

**Oxy-fuel combustion capturing** – In here nitrogen is removed before the combustion. Oxy-fuel gas turbine Technology can be taken as an example.

**Post-combustion capturing** – In this technology CO<sub>2</sub> is captured from flue gas and one of the examples is solvent processes.

Only post-combustion capturing technology is discussed in this article.

**1.1 Post combustion capture**

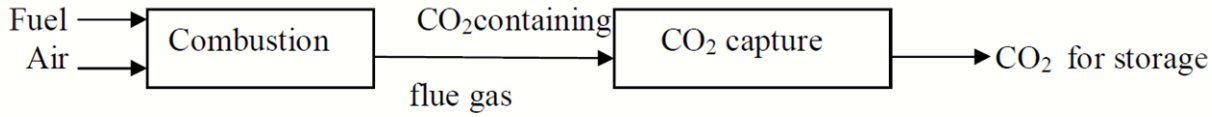


Fig.1.Post combustion capturing [3]

In this technology, CO<sub>2</sub> is separated from the flue gas and send to CO<sub>2</sub> storage as in Fig 1. When considering a boiler system, there is a flue gas stack to emit all the gasses, including the CO<sub>2</sub>, to the atmosphere. At present, solvent scrubbing is the most leading technology [3]. A chemical solvent is used for solvent scrubbing to react with CO<sub>2</sub>. Mainly, several types of post-combustion capture technology, as mentioned in Fig.2, will describe in the next topics.

1. Chemical absorption
2. Physical absorption
3. Membrane separation
4. Cryogenic separation
5. Adsorption

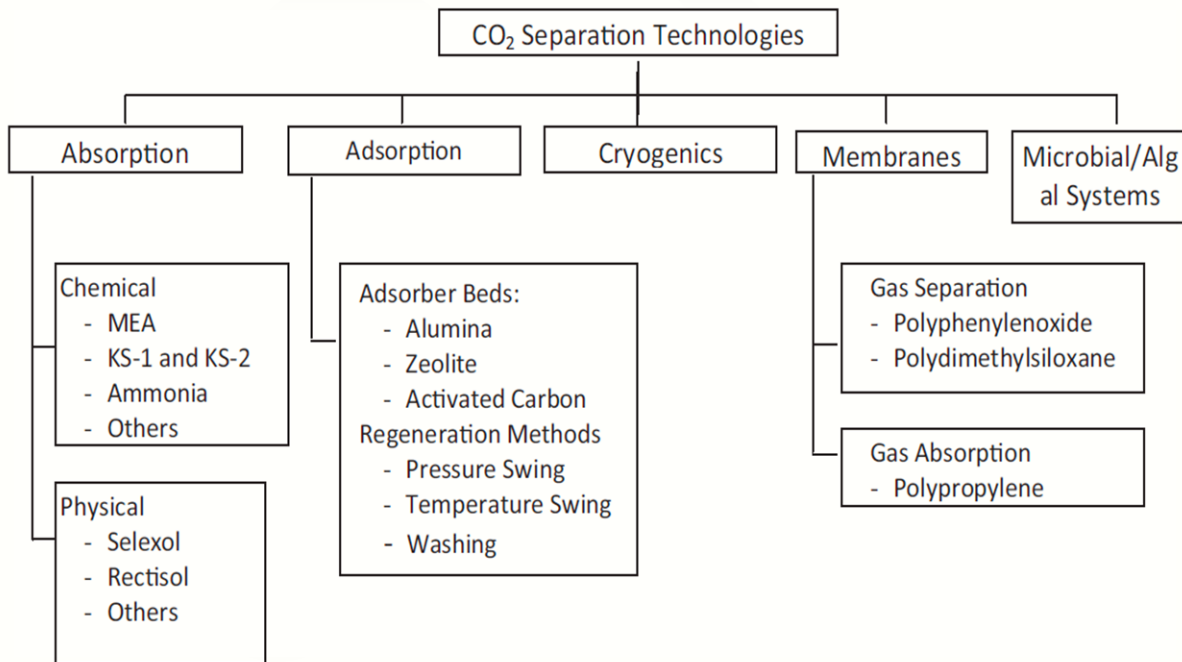


Fig.2. CO<sub>2</sub> separation technologies [5]

## 2 CHEMICAL ABSORPTION

### 2.1 Introduction

There are two types of absorption methods to capture CO<sub>2</sub>. They are the chemical absorption and physical absorption, as in Fig.3. The widely used process is the chemical absorption method. Chemical absorption has different processes like amine based-absorption, carbonate-based absorption, aqueous ammonia-based absorption, and sodium hydroxide based absorption. Here a chemical reaction happens between CO<sub>2</sub> and a chemical solvent. Then it causes to form an intermediate compound that is weakly bonded [4].

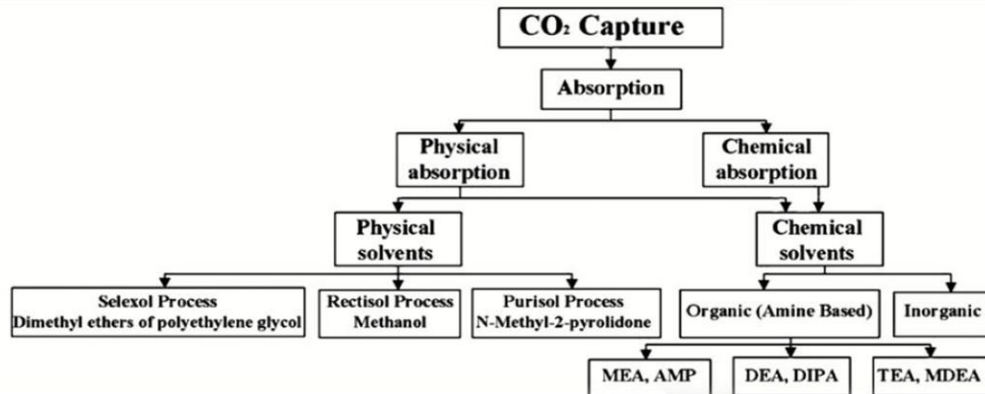


Fig.3. Absorption categories [5]

### 2.2 Process description

In this section, amine-based chemical absorption with MEA is discussed in a detailed manner. First of all, the flue gas must be subjected to remove the other gasses before entering the CO<sub>2</sub> removal. For that, the flue gas flows through a dust removal, NO<sub>x</sub> removal, and SO<sub>x</sub> removal; otherwise, it causes acidification [6, 7].

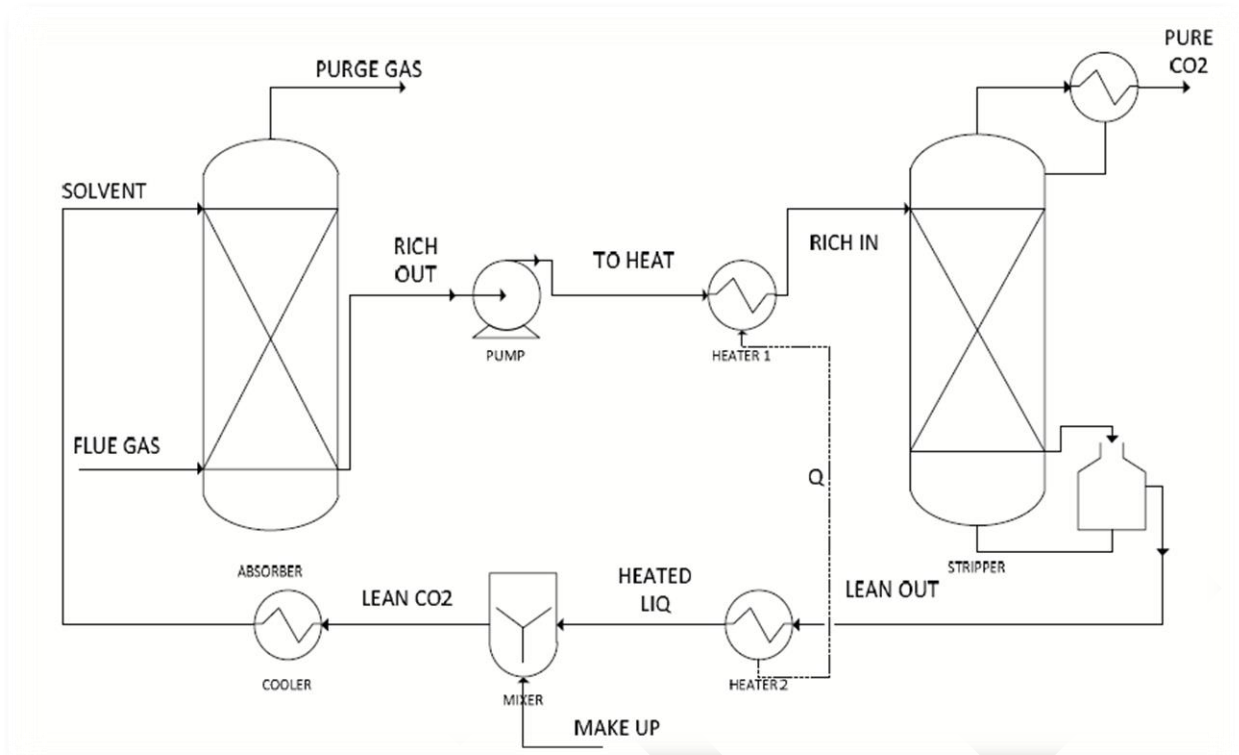


Fig.4. Process flow diagram [8]

A CO<sub>2</sub> capturing system can be seen in Fig.4. The cooled flue gas is supplied to the bottom, while the chemical solvent is provided to the absorber's top at 40°C. Then MEA and CO<sub>2</sub> flow through the packed bed, and they start to react with each other. After it, the rich solvent with CO<sub>2</sub> is discharged from the bottom, and at the same time, pure gas is left from the top of the column. Next, the temperature of the rich solvent is increased to 115°C by passing through a heat exchanger. Then the heated rich solvent passed to the top of the stripper section. In that section, the regeneration process happens with the introduction of the steam. Finally, the separated pure CO<sub>2</sub> allows us to leave the stripper from the top, and the lean MEA has left the stripper from the bottom. That lean out will enable us to pass through a heat exchanger. Before recycling the lean MEA to the absorber unit, it is balanced by water and MEA (makeup). The main reactions happened in this system are mentioned in below [8, 9, 10, 11].

1. Hydrolysis reaction
2. Dissolved carbon dioxide dissociation
3. Bicarbonate dissociation
4. Protonated MEA dissociation
5. Water ionization

These chemical absorption combustion processes can be used in coal and gas-fired power plants.

### 2.3 Advantages and disadvantages of chemical absorption

There are both advantages and disadvantages as shown in Table 1 [6].

Table 1. Advantages and disadvantages of chemical absorption

Advantages	Disadvantages
CO <sub>2</sub> with low concentrations can be used to separate.	Loading capacity of carbon dioxide is low.
Most of the facilities have implemented this method so well understood one.	Presence of SO <sub>2</sub> and O <sub>2</sub> in flue gas cause to solvent degradation.
95% of recovery rates	Energy consumption is high.
About 99% of product purity can be taken	High corrosion rate in equipment.
95% of recovery rates	Solvents emissions cause to impact environment

### 2.4 Challenges and breakthroughs in these systems

#### 1. Process intensification.

A huge cost saving can be done by using process intensification in carbon capture.

#### 2. Energy consumption reduction in CO<sub>2</sub> capture.

This target can be achieved by developing new solvents and by integrating power generation plants with CO<sub>2</sub> capturing plants.

#### 3. Simultaneous removal of CO<sub>2</sub> and SO<sub>2</sub>.

SO<sub>2</sub>, NO<sub>x</sub>, and CO<sub>2</sub> can be simultaneously removed by ammonia solvent. So total cost is reduced as a single process can be used to reduce all the gasses [5].

## 3 PHYSICAL ABSORPTION

Physical absorption is the process which use solvents to absorb CO<sub>2</sub> at low temperature and high pressure and desorbed at high temperature and low pressure. Absorption is occurring at high temperatures due to the solubility of the solvent. Simply the process is CO<sub>2</sub> is in the mixed gas dissolved in the solvent. The existing processes are Selexol Process, Rectisol Process, Purisol Process, Morphysorb Process, and Fluor process. The absorbents or solvents are used in Selexol Process are dimethyl ether or propylene glycol, methanol used in Rectisol Process, propylene carbonate for Fluor Process, Nmethylpyrrolidone is used in Purisol Process, and for Morphysorb Process morpholine is used [8].

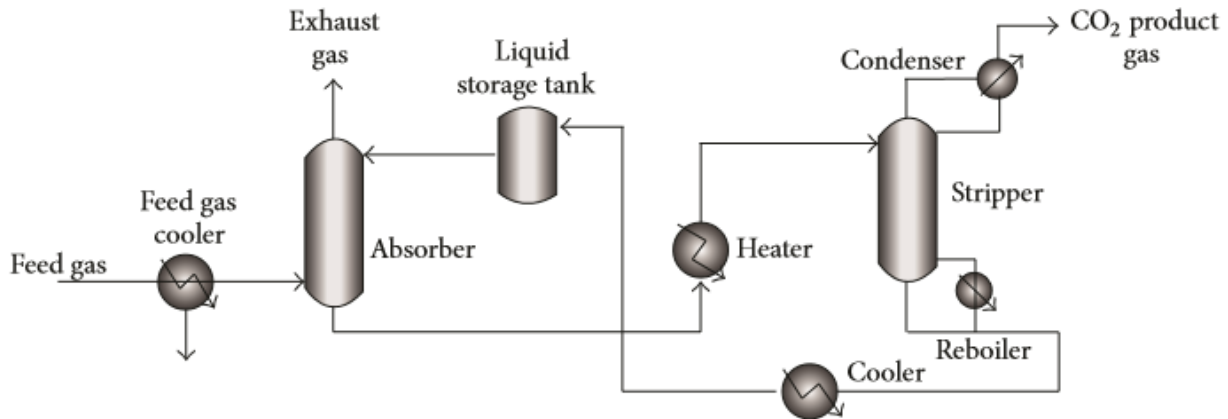


Fig.5. CO<sub>2</sub> absorption pilot project diagram [12].

Fig.5. shows a process flow diagram of the CO<sub>2</sub> absorption. The flue gas, which contains CO<sub>2</sub>, is cooled using a feed gas cooler between 318K and 323K. Then it fed into the absorption column allowing solvents to absorb the CO<sub>2</sub>. After that, a CO<sub>2</sub> rich solution is sent to the heater to increase the solution's temperature. Finally, the solution is fed into the stripper column to release the absorbed CO<sub>2</sub>. CO<sub>2</sub>, which released, is compressed, and the absorbent solution is cooled and reused in the absorber column [12].

This CO<sub>2</sub> absorption process is widely used in natural gas production, hydrogen and synthesis gas production with CO<sub>2</sub> content resources. The advantages of the physical absorption process are low capital and operation cost, low vapor pressure, low corrosive, and less toxicity solvent. Due to less corrosive of the solvent, pipe and other equipment do not need to make from alloy steel. Solvent regeneration can easily be carried out with the inert gas trapping, thermal regeneration, or pressure reduction. For inert trapping and also pressure reduction needs less amount of energy than thermal regeneration. But energy used for thermal regeneration is less when compared with chemical absorption [8]. The disadvantage is the consumption of a high amount of energy to compress the feed air high pressure.

#### 4 MEMBRANE SEPARATION

Another method of CO<sub>2</sub> capture is Membrane separation. Simply membrane is acting as a filter that allows some molecules to enter and some molecules do not. This technology is already used for liquid separation, Reverse Osmosis, Desalination, Micro-filtration, and Ultra-filtration. But for the gas separation, membrane technology is still a developing technology. According to the pour size, membrane classified into three as Micropore, Mesopore, and Macropore [13].

##### 4.1 Membrane separation mechanism

CO<sub>2</sub> separation from gas mixture through membrane is occurring due to the different permeability of different gases. For the separation, there has to be a greater difference in permeability between gases. The membrane separation mechanisms are Size sieving, Surface diffusion, Solution diffusion, Facilitated transport, and ion transport.

#### 4.1.1 Size sieving

Size sieving is the separation mechanism according to the size of a gas molecule. Here the membrane pore size is between small gas molecules it allows to pass small molecules while large molecule traps the other side of the membrane. This separation used to separate which has very different molecule sizes such as CO<sub>2</sub>, Hydrocarbons, and H<sub>2</sub>.

#### 4.1.2 Surface diffusion

Surface diffusion, the membrane material has a higher affinity for a particular component than other components. The component which has affinity is absorbed into the surface of the membrane and move thorough pores to another side. This membrane process mainly used to separate the absorbing gas with non-absorbing gas. Examples are CO<sub>2</sub> with H<sub>2</sub> and CO<sub>2</sub> with He [13].

### 4.2 Membrane

Specification of CO<sub>2</sub> capture membrane should have is high carbon dioxide permeability, cost-effective, the selectivity of CO<sub>2</sub> from the flue gas, and less production for the different modules. The membranes used for Post-combustion membrane separation are polymeric, inorganic, mixed matrix membranes, Hollow fiber membrane, and facilitated transport membranes [8].

#### 4.2.1 Polymeric Membranes

The Polymeric membrane transport gases through the membrane by solution diffusion mechanism. Examples for polymeric membranes used for CO<sub>2</sub> separation are polyarylates, polycarbonates, polyetherimides, polyethylene oxide, polyimides, polyphenylene oxides, polypyrroles, Polyacetylenes, polyaniline, polyaryleneethers, polysulfones, and amino groups such as polyethyleneimine blends, polymethacrylates. Advantages of Polymeric membrane are high performance in CO<sub>2</sub> separation, cost of production is less, has high permeability, and also selectivity in CO<sub>2</sub> separation. The disadvantages are thermal stability of membrane is low and flue gas must cool down for 313K-333K for the process [8].

#### 4.1.1 Inorganic

Inorganic membrane classified into two according to the structure [12]. They are porous and dense. Aluminum, zeolites, carbon, and silica are the material which includes in the inorganic membrane. The inorganic membrane has a resistance to high temperature and pressure when compared to the polymeric membrane [14]. The permeability and selectivity of the inorganic membrane are very low [12].

#### 4.1.2 Mixed matrix membranes

The materials which consist in mixed matrix membrane are Carbonmolecular sieves, Zeolites, and many polymeric materials. These materials add transportation properties for CO<sub>2</sub> separation [12].

#### 4.1.3 Hollow fiber membrane

The most favorable and industrial important gas separation is a Hollow fiber membrane. Asymmetric hollow fiber membranes are suitable for CO<sub>2</sub> separation and absorption in the gas-liquid membrane using high permeability and low resistance of mass transfer. This membrane has high efficiency because of the large surface area [12].

#### 4.1.4 Facilitated transport membranes

The mechanism of the Facilitated transport membrane is a selective reversible reaction between the carrier agents and the gas component [14]. Facilitated transport membrane has high selectivity and also high fluxes. The high selectivity of FTM is obtained through the existence of carriers in the membrane. The main disadvantage is stability problems due to the evaporation of the carrier medium. To reduce that problem in FTM, chemically bonded the carrier consist of carbonates or secondary amines to the backbone of the membrane. An example of that membrane is the Fixed carrier membrane [15].

#### 4.1 Membrane separation process

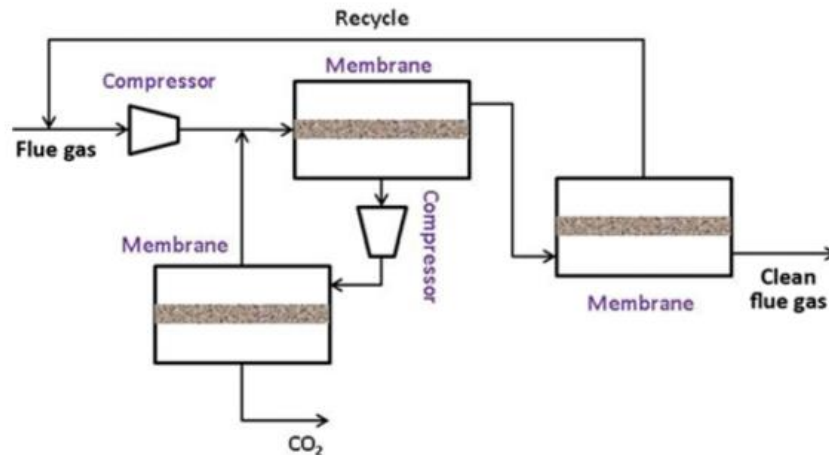


Fig.6. Membrane separation process [16]

The pressure difference is the driving force for the membrane; it can generate pressurizing the gas or creating a vacuum on one side. The efficiency of a membrane is determined by the Permeability and selectivity of the membrane. As shown in Fig.6. Membrane separation can be done with multistage and also the single stage. But the disadvantage is with multistage are high capital cost, the complexity of the membrane process, and the energy [16].

#### 4.1 Advantages and Disadvantages of the Membrane separation process

Advantages of the membrane separation are it has high separation energy efficiency when compared with the absorption and adsorption processes, there is no regeneration process need for membrane process, the capital cost is relatively low also the operational cost is low, and last it is the environmentally friendly process. On the other hand, the disadvantages of the membrane process are the gas need to compress, CO<sub>2</sub> permeation is reduced due to the presence of water inflow and the limitation of operating temperature [6].

## 5 ADSORPTION PROCESS

The adsorption process is adsorbed one or more components of a mixture from gas, liquid, or dissolved solid with the help of a solid adsorbent surface. In this process, an adsorbate film is created on the surface of the adsorbent. A material that capable of being adsorbed is called adsorbate and the adsorbent is the substance that adsorbed the adsorbate. Adsorption operations required lower energy requirements and reduce the cost of capture and separation of CO<sub>2</sub> in post-combustion capture. To develop an appropriate CO<sub>2</sub> capture, it is



important to find adsorbent with suitable properties such as low heat capacity, fast kinetics, high CO<sub>2</sub> adsorption capacity, and possess good thermal, chemical and mechanical stabilities. Also, adsorbent should be a low-cost material. According to the adsorbent use for CO<sub>2</sub> capture, it has two categories named as physical adsorption and chemical adsorption [8].

Table 2. List of chemical and physical adsorbent [17].

Adsorption	
Chemical adsorbents	Physical adsorbent
Amine-based adsorbents (Amine grafted, Amine-impregnated)	Carbon-based materials
Metal oxides	Mesoporous silica
Metal salts	Zeolites
Double salts	Metal-Organic Frameworks (MOFs)
Hydrotalcites	Zeolitic Imidazolate Frameworks (ZIFs)
	Blended adsorbent

### 5.1 Physical adsorption

Carbonaceous material such as activated carbon and inorganic porous materials such as zeolites are the major physical adsorbent. Carbon-based materials such as activated carbon, charcoal, and coal are widely used in CO<sub>2</sub> capturing process. Because they are widely available, low cost, sensitivity to moisture is less and thermal stability is high. Also, the adsorption capacity is high and less energy requirement for CO<sub>2</sub> regeneration due to the formation of a new bond between the sorbate and sorbent is not occurred [8].

However, activated carbon application is limited to only high-pressure CO<sub>2</sub> capturing applications. Their high surface area causes greater adsorption capacities at high pressure. At high temperature, sensitivity is high and has low CO<sub>2</sub>/N<sub>2</sub> selectivities in operation. But CO<sub>2</sub>/N<sub>2</sub> selectivities in zeolitic materials offer 5-10 times greater than carbon-based material. Also, it has heat adsorption capacity higher than activated carbon. The adsorption capacity and selectivity depend on the size, pores diameter and charge density of zeolites materials [9]. Zeolite is used at high pressures above 2 bars. The adsorption capacity will be reduced because of moisture in the gas and it causes to increase the temperature requires for regeneration.

Metal-Organic Frameworks (MOF) adsorbent also use because of their properties and advantages. The most prominent property is a high surface area. Pore's structure of MOF is controllable. It has tunable pore surface properties. The pore surface can be tuned by using organic building blocks and metal ions. MOFs have a flexible design and great potentials for CO<sub>2</sub> capture. As well as, MOFs are excellent material for carbon capture as carbon dioxide adsorption is reversible. The adsorption of CO<sub>2</sub> depends on the pore size and nature of the pore surface. They have greater adsorption capacity compare to Zeolite and activated carbon [14]. Meso-pores silica also uses as physical adsorbent as they have high volume and surface area. Their pore size is tunable and has mechanical and thermal stability [18].

### 5.2 Chemical adsorption

In this process, CO<sub>2</sub> capture by a chemical reaction occurs at the exposed surface. This method consumes more power due to the regeneration procedure. In the chemical adsorption process, amine-based adsorbents are widely using. Amine based adsorption is more advantageous when compared to aqueous amines as it consists of low heat of regeneration. The commercialization of these methods is a bit complicated because of its high cost and low adsorption capacity of CO<sub>2</sub>. But this system can be improved by the following methods [19].

1. By preparing of high amine loading supports.
2. Using the amines that contain high nitrogen content.
3. Amine introduction with effective methods

By considering amine interaction with supports, there are two main types of adsorbents as amine- grafted materials and amine- impregnated. When comparing these two, amine-grafted materials have high adsorption rates and stability in the cyclic run. But the surface silanol groups effects on the amine grafted amount. In some cases, it leads to reduce the loading of amine. So a high amount of amine can be loaded by impregnation. In addition to that the coal power plants which emit the flue gas (55°C) with 3-5% water, 10-15% CO<sub>2</sub> need to evaluate the kinetic and heat effects by improving the operations [8].

### 6 CRYOGENIC SEPERATION

In this method, the condensation, separation, and purification stages use low temperatures during the CO<sub>2</sub> separation. The compression, cooling and expansion steps have the ability to separate components in the cryogenic process. As a result of it, the liquid CO<sub>2</sub> is formed, and with the help of liquid pumping that liquid CO<sub>2</sub> is stored and sequestered in high pressures. The important thing is high-pressure feed gasses are more effective for these types of systems. Sometimes this is also well suited for oxy-fuel combustion. A Cryogenic liquefaction and separation system for CO<sub>2</sub> is shown in Fig.7. In this system, compression, refrigeration, and separation stages have used two-stage methods. As well as, cryogenic energy is recovered in this system. CO<sub>2</sub> recovery in this system is only used 0.395 MJ/kg of energy [9].

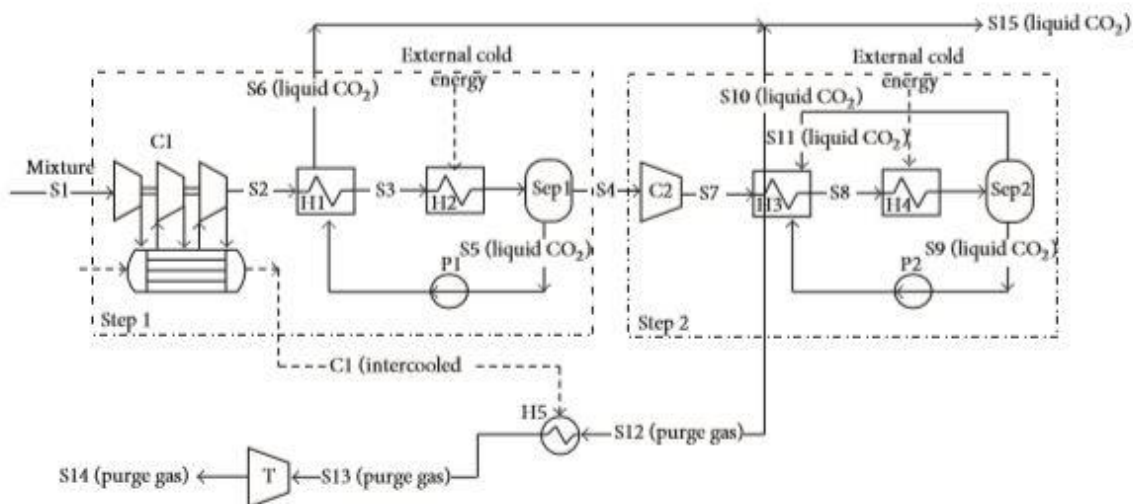


Fig.7. Cryogenic liquefaction and separation system [9].

#### 6.1 Advantages and Disadvantages

Solvents or other components are not involving in this process, cryogenic separation can be used for enhanced oil recovery because CO<sub>2</sub> is directly produced, no process makeup water supply and treatment is required, the chemical agent is not used in this process and it helps to avoid secondary pollution. No solvent recovery plants are required.

The major disadvantages of cryogenic separation of CO<sub>2</sub> are the large amount of energy required for the refrigeration and the CO<sub>2</sub> solidification under low temperature. Another challenge in this process is that removal of water is required before gas stream cooling to avoid freezing and blockage of process equipment. Also, SO<sub>x</sub>, NO<sub>x</sub>, and other trace components should be removed before distillation. Capital expenditure of cryogenic separation is high. Because of that, this method is suitable if the CO<sub>2</sub> percentage in the stream is high [20].

## 7 CONCLUSION

In an industry or a power plant, several CO<sub>2</sub> capturing systems can be implemented as pre-combustion capturing, post-combustion capturing and oxy-fuel combustion capturing systems. In post-combustion capturing systems, there are several methods to capture the CO<sub>2</sub>, and the most prominent one is chemical absorption technology. For adsorption, there are regeneration methods that can be used in terms of pressure and temperature. In membrane separation systems, different polymer-based membranes are used for gas separation. Considering all these methods, it can be concluded that there are several existing difficulties in implementing these systems. So improvements and developments need to be done to implement these systems in possible facilities.

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