



# Carbon Dioxide Capture: A Comprehensive Review

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## Abstract

*Rapid urbanization and industrialization in the last few decades have seen an increase in carbon dioxide levels in the atmosphere. Due to this, humanity has to deal with climate change and global warming. Carbon Capture and storage (CCS) is seen as the most effective technology to mitigate the CO<sub>2</sub> levels and meet the carbon emission goals. In this paper, different techniques of carbon capture and storage are reviewed and discussed. The selection of carbon capture technique is crucial depending on the source of carbon dioxide emission. Membrane separation technique is considered to be the future for CCS, while methods like absorption and adsorption are currently implemented on large scale. The carbon storage techniques like bio char and oceanic storage are practiced all over the world, but yet to be developed on large scale due to economic hurdle.*

**Keywords:** Carbon Capture, Sequestration, Membrane Separation, Absorption, Adsorption.

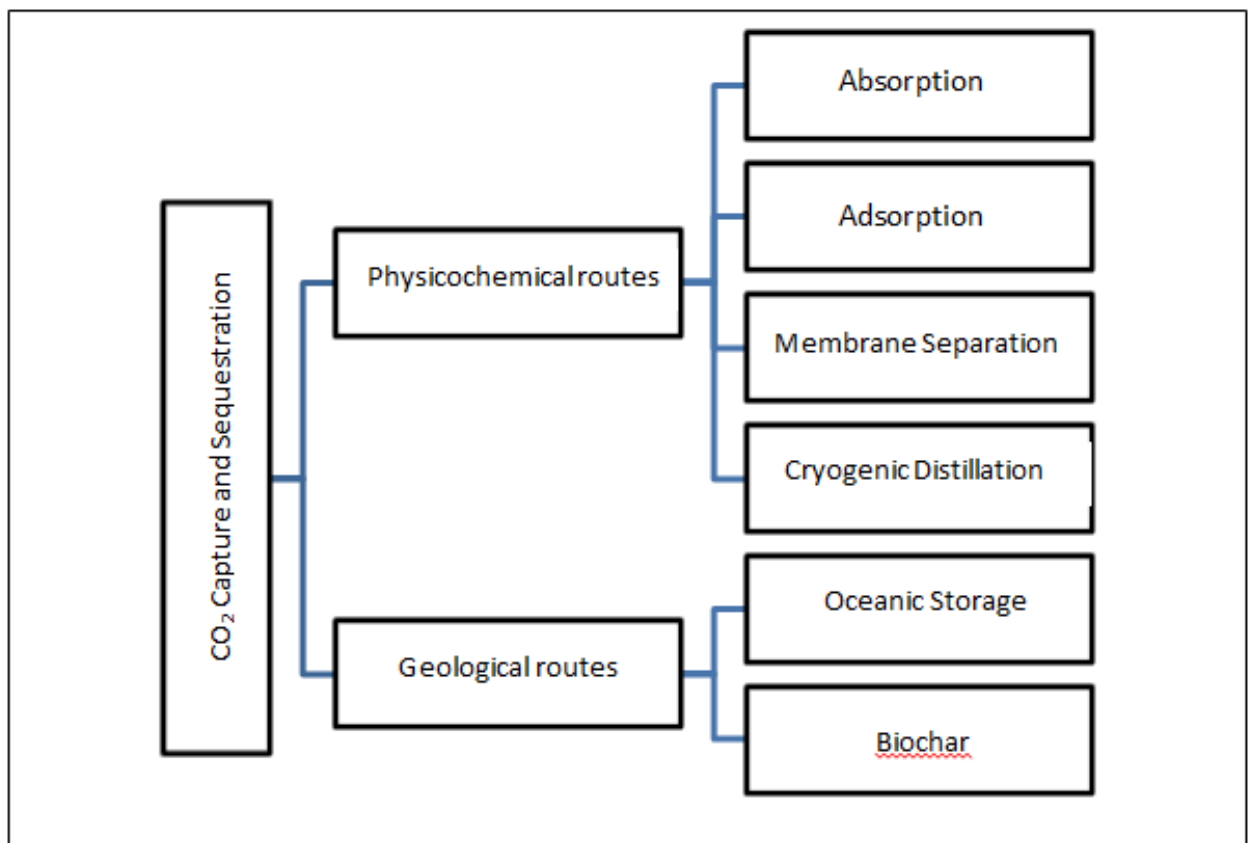
## 1. Introduction

Today, global warming and climate change have reached unprecedented levels leading to extreme weather change, affecting human population, rising sea levels and changing the wildlife habitat around the globe. The major cause of these changes is driven by the greenhouse gases which are continuously on a rise. The greenhouse gases in the earth's atmosphere include carbon dioxide, methane, nitrous oxide, and sulfur hexafluoride, hydro-fluorocarbon & per-fluorocarbon group of gases. Carbon dioxide (CO<sub>2</sub>) is a major constituent that affects climate change since it is present in abundance in the atmosphere compare to other GHGs. The heat radiated from the earth surface and oceans is continuously absorbed by these gases thereby maintaining an optimum average temperature. However, accumulation of these gases in higher concentration leads to increase in earth's average temperature, leading to global warming. At the dawn of the industrial revolution, the earth's atmosphere contained 278 parts of CO<sub>2</sub> per million. Each year large amount of carbon dioxide is added to the atmosphere compared to carbon dioxide removed by natural processes, which leads to increase in net global amount of carbon dioxide. The more we overshoot what natural processes remove, the faster the annual growth rate. The annual rate of increase in atmospheric carbon dioxide over the past 60 years is about 100 times faster than previous natural increase.

## 2. Sources of CO<sub>2</sub>

A major proportion of the GHGs in the atmosphere are due to anthropogenic reasons. The increased GHGs and also in the depletion of ozone layer is due to the increased consumption of fossil fuels, use of chlorofluorocarbons in refrigerants, solvents, foam blowing agents and spray propellants. The industrial practices such as processing of minerals, chemicals, solvents with the production and utilization of halocarbons, and SF<sub>6</sub> also contribute to this phenomenon. The natural events such as volcanic eruptions, forest fires and hydrothermal vents also contribute in releasing significant amount of GHGs into the atmosphere. The CO<sub>2</sub> released from volcanoes can be from the erupting magma and degassing of unerupted magma. The amounts of CO<sub>2</sub> generation and addition in environment are very large. Typically, a coal-fired power plant with a capacity of 1000 MWe generates approximately 30,000 tons of CO<sub>2</sub> per day.

## 3. Routes for Carbon Capture & Sequestration



*Figure-1: Routes for Carbon capture and Sequestration*



## 4. Physiochemical Routes

### 4.1 Absorption

Absorption is a gas-liquid operation where the gas components are absorbed into the new liquid phase. The solute is recovered from the solution by other mass-transfer operation. The capturing of CO<sub>2</sub> molecules from the exhaust gases can be achieved by physical or chemical method. In the physical process, i.e., dissolution processes the high concentrations of flue gases at high pressures to capture CO<sub>2</sub> are done by selecting a suitable solvent. The gas molecules dissolve into the chosen solvent at the given operating conditions to capture harmful gas effluents including CO<sub>2</sub>, NO<sub>x</sub>, SO<sub>x</sub>, and H<sub>2</sub>S. An additional advantage of physical absorption process is that the solvents are capable of absorbing H<sub>2</sub>S, carbonyl sulfide (COS) and hydrocarbons along with CO<sub>2</sub>. Selexol process is one of the physical absorption processes in which CO<sub>2</sub> is absorbed by the solvent mixture of dimethyl ethers and polyethylene glycol solution.

Chemical absorption is one of the techniques in which CO<sub>2</sub> from flue gases reacts with the solvent in an absorption column. The exhaust gas from power plants is obtained at high temperatures and cooled to temperatures below 50°C before feeding it to an absorption column. The cooled gas stream is allowed to pass through the absorption column in which nearly 85–90 volume % of CO<sub>2</sub> is absorbed. The solvents react with CO<sub>2</sub> present in the effluent gas and form a stable product in the absorber. Then it is further passed to a stripping tower where the solvent can be regenerated by altering the temperature and pressure. The CO<sub>2</sub> lean stream solvent is recycled back to the absorption unit, and the energy intensity for recovering the solvent is high.

### 4.2 Adsorption

Adsorption is both a pre- and post-combustion CO<sub>2</sub> capture technology that involves a fluid-solid interface for effective capturing of CO<sub>2</sub>. The drawbacks of absorption process such as lower liquid-gas contact area and absorbent losses have focused the attention toward adsorption. Adsorption is a gas-liquid operation, in which the molecules from the gas stream are adsorbed on the surface of the solid adsorbent. Since adsorption is a surface phenomenon, determining an ideal adsorbent to capture CO<sub>2</sub> from flue gases is very important, the properties of solid adsorbents such as surface area, polarity, and porosity along with surface-reactive species are considered to select the most suitable adsorbent.

Physical adsorption is the method which is based on the interactions between the molecules of CO<sub>2</sub> and the solid adsorbent surface. The gas solute molecules of CO<sub>2</sub> prefer to interact and stick to the adsorbent surface if intermolecular forces between the gas molecules and adsorbent dominate the existing intermolecular forces between the gas molecules. Few of the potential adsorbents which are



found are carbonaceous materials, micro porous and mesoporous zeolites, chemically surface-modified polymeric materials along with metal-organic frameworks.

Chemisorption is the reaction of CO<sub>2</sub> with the reactive groups on the surface of adsorbent. Chemisorbents are classified into two categories, primarily amine-based adsorbents and other is alkali metal-based adsorbents. The methods used to synthesize the amine - based adsorbents are grafting and impregnation. In case of alkali metal-based adsorbents, calcium carbonates, potassium carbonates, sodium carbonates and lithium carbonates have proved to give better performance for capturing carbon dioxide. Lithium is considered to be metal having great potential for future, however lithium-based adsorbents are not used in commercial applications due to high adsorption capacities and high diffusional resistance.

### **4.3 Membrane Separation**

Membrane separation is an efficient technique for carbon capture and it is preferred over conventional systems such as adsorption and absorption for low carbon emission technologies. In membrane separation, the membrane used rejects the unwanted components and selectively permeates the desired product. This technique is usually preferred for separating CO<sub>2</sub> from the flue gas stream while carrying out the post combustion process.

#### **Advantages of membrane separation:**

- i. Low capital and operating cost:

The membrane is the only component required for separation of stream and no additional pretreatment equipment's are required. Replacement of membrane is the major operating cost involved in this technique

- ii. Membrane longevity and reliability

The membrane does not decay fast in performance and can be used in service for longer periods.

The feed stream passing through the membrane does not react with membrane, thus frequent shutdown can be avoided.

- iii. Adaptability

The membrane selection is done in a way to operate at removing required carbon dioxide concentration. Thus, variation in feed CO<sub>2</sub> concentration can be adjusted by changing the space velocity to get the desired quality.

- iv. Efficient Design



Membrane system selectively separates the components of the feed. Therefore, different separation processes can be integrated into this system (i.e., removal of H<sub>2</sub>S, Hg etc.). Conventional CO<sub>2</sub> separation techniques have to operate this process in different units, thereby increasing the cost.

#### ➤ **Membranes for Pre-Combustion Capture**

In pre-combustion process, the carbon dioxide gas is separated from other fuel compounds before the combustion is carried out. The solid, liquid or gaseous fuel is initially converted into mixture of syngas and carbon dioxide by steam reforming or gasification. The water gas shift reaction proceeds after this, to reduce content of carbon monoxide and increase the generation of hydrogen and carbon dioxide. Once the necessary pre-processing is done, membrane separation unit is set up for separation of H<sub>2</sub> and CO<sub>2</sub>. Two types of membranes are used in this process, hydrogen selective membrane and carbon dioxide selective membrane. The latter permeates CO<sub>2</sub> while retains H<sub>2</sub> on the feed side. The CO<sub>2</sub> stream is transported for storage while the H<sub>2</sub> stream enters the combustion chamber. The carbon dioxide obtained from this process is at high temperature between 300-700 °C and high pressure up to 80 atm, this is due to pre-processing reactions such as steam reforming, gasification and water gas shift reaction. The membrane separation for pre-combustion is not implemented on industrial scale with membrane separation system. Few pilot scale membrane systems have been developed but not been applied to large scale due to high cost and reliability issues.

#### ➤ **Membranes for Post-Combustion Capture**

The post combustion process involves separation of carbon dioxide from flue gases which mainly contains carbon dioxide, nitrogen, water vapor etc. Water vapor is generally taken out by condensation. Carbon dioxide and nitrogen separation is done by using membrane separation technique. This separation is done at moderate temperatures, thus have fewer operating difficulties than pre-combustion process, where it is carried out at high temperature and pressure. However, the flue gases contain low carbon dioxide volume fraction which makes it difficult for separation due to low driving force of CO<sub>2</sub> permeation. To overcome this challenge, the membrane to be used should have high CO<sub>2</sub> permeability, high thermal and chemical stability & high CO<sub>2</sub>/N<sub>2</sub> selectivity ratio. In recent technological advancement, polymer-based membranes are a viable option for commercial purpose. The membrane used is poly sulfone, polycarbonates, and polyamides.

#### ➤ **Membranes for Oxy-Fuel Combustion**

In oxy-fuel combustion process, combustion is carried out by supplying oxygen instead of air; this eliminates the presence of nitrogen in flue gases. Thus, efforts on separating carbon dioxide and nitrogen are reduced, as carbon dioxide is major gas component (80-98% volume) which can be



compressed and stored. The process is currently in development stage. The oxygen needed for the combustion is sourced from the energy intensive separation of air.

The air separation is carried out by ion transport mechanism and O<sub>2</sub> selective membranes are generally preferred. Fluorite-based and perovskite-based membranes are used to separate oxygen and nitrogen through this mechanism.

#### **4.4 Cryogenic Distillation**

In this technique, carbon dioxide is separated from flue gases based on the principle, where the flue gas mixture is cooled below desublimation point of CO<sub>2</sub> (i.e., 173 to 238K), to separate the less volatile gas than carbon dioxide and liquefied CO<sub>2</sub> stream is obtained at high pressure. This technology cools the flue gas stream to the point where the CO<sub>2</sub> gas desublimates, separates the solids from the light gases, then pressurizes the CO<sub>2</sub> stream, and warms both the gas streams back to their initial temperature through heat recovery, delivering liquid CO<sub>2</sub> and light gases, both at ambient temperature. In this process the sensible energy required for this process comes from the heat integration units. Whereas, the refrigeration units provide only the heat needed for phase change and separation of gases. The cryogenic distillation is currently developed and used for post combustion process. The cryogenic distillation can be carried out in two ways:

- a) The CO<sub>2</sub> is desublimated into solid CO<sub>2</sub> and then it further heated and pressurized to yield liquid CO<sub>2</sub>.
- b) The desublimated CO<sub>2</sub> is recovered from the packing materials of the packed bed column.

Advantages of this process:

- 1) The energy requirement is low and has lower cost involved than other carbon capture techniques.
- 2) Non condensable gases that are heavier than carbon dioxide can also be captured and stored if needed
- 3) It requires only electrical power and a gas source for operation; thus, it is retrofit technology that can be installed in the existing plants.

### **5. Geological Routes:**

#### **5.1 Biochar**

The carbon capture & sequestration involves capturing of carbon dioxide from the atmosphere and storing it in the environmental surroundings, to reduce the greenhouse effect. Biochar is an efficient method to be a carbon sink for storing the unwanted CO<sub>2</sub>. It is a carbon negative approach.



Biochar can be termed as one of the by-products obtained by pyrolysis or gasification of biomass. The biomass includes tree branches, woods, barks, plant wastes, residues from pulp & paper industries, agricultural sector etc. All these biomasses include the carbon captured from atmosphere by natural photosynthesis. When this biomass is burned the carbon dioxide is released back to the atmosphere which is not beneficial. However, with the production of biochar which mainly comprises of aromatic form of carbon and it cannot be easily oxidized to release CO<sub>2</sub> in atmosphere. One ton of biochar has a capacity of storing 3 net tons of CO<sub>2</sub> removed from atmosphere by photosynthesis.

Applications of biochar:

- 1) For stimulating industrial biological processes such as anaerobic digestion.
- 2) Deposition in soil to cultivate any type of plant
- 3) Deposition in urban lands to fix pollutants and enhance microbial activities.

Carbon capture systems are still under development stage and not fully commercialized to separate carbon dioxide from atmosphere. In this condition we could see biochar as a great potential as it a low technology process and easy for large scale operations. In Canada, AIREX ENERGY have a fully operational biochar production plant is in operation from 2016. Four large-scale production biochar projects are currently in development to serve the markets of Canada, the United States, Europe, and Asia.

## **5.2 Oceanic storage**

70 % of the total earth area is covered with oceans, which become a suitable and widely available carbon pit for sequestration of carbon dioxide. In recent years, annual average carbon dioxide emission throughout the world is 34 billion tons per year. Emission at this rate would increase the load on the atmosphere, hence finding an alternative for emission and storage of carbon dioxide is necessary. Different techniques are involved for carbon dioxide sequestration.

### **Direct injection of carbon dioxide in the deep sea:**

The carbon dioxide is captured, separated, liquefied and then transported through pipelines in the deep sea. The carbon dioxide can be isolated and stored at great depths due to high pressure and low temperatures which makes it denser than water. This prevents it from rising to the surface, minimizing the chance of CO<sub>2</sub> leakage.



However, with climate change and rise in temperatures, it limits the storage of carbon dioxide in ocean. The sequestration is highly dependent on oceanic circulation and behavior of marine ecosystem to the climatic changes (i.e., high temperatures and increased CO<sub>2</sub> levels).

#### **Drawbacks:**

- 1) The carbon dioxide stored in deep sea, tend to increase the pH and acidification of water in the stored area. This adversely affects the marine life organisms.
- 2) It can alter chemical and biological cycling of many elements and compounds.
- 3) Ocean knowledge is still an unknown parameter, and further research is required to analyze and assess the operating and costing of such future projects.

Recently, Northern Sea Transition Authority has identified 13 areas off the Teesside Coast, UK where mixture of depleted oil and gas fields and porous rock formations filled with salt water is available for carbon dioxide storage. Offshore Energies UK aims to store 50 million tons of CO<sub>2</sub> a year by 2035.

#### **6. Conclusion**

As we know that most of the energy requirements for industrial applications and transportation activities are fulfilled from fossil fuels and results into release of CO<sub>2</sub> in the environment. CO<sub>2</sub> capture and storage is considered feasible and could play a significant role in reducing greenhouse gas emissions over the course of this century. The currently available technologies for carbon capture and sequestration can be classified under physicochemical and geological routes. The physicochemical route includes techniques for the separation of CO<sub>2</sub> from flue gas with the use of absorbents, adsorbents, gas separation membranes and cryogenic distillation. Many issues still need to be resolved before it can be deployed on a large scale. The CO<sub>2</sub> capture techniques, such as membrane separation process can separate about 90% of CO<sub>2</sub>. Geological and oceanic injection techniques are having good potential for CO<sub>2</sub> sequestration and worldwide capacity of about 2200 GtC.

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