

## COMPARISON OF METHODS OF CARBON DIOXIDE CAPTURE WITH EMPHASIS ON USAGE OF CARBONIC ANHYDRASE

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### ABSTRACT

Global warming and climate change are the main causes that have prompted global efforts to reduce the concentration of atmospheric carbon dioxide (CO<sub>2</sub>). Carbon dioxide capture and storage (CCS) is considered to be a crucial strategy for meeting CO<sub>2</sub> emission reduction targets. Some of the CO<sub>2</sub> capture techniques are absorption with novel solvents, adsorption, conversion of CO<sub>2</sub> into chemical products, calcium looping and membrane technology etc. Carbonic anhydrase (CA) is a powerful biocatalyst that accelerates the transformation of carbon dioxide to bicarbonate ion. Experimental results show that carbonic anhydrase significantly enhances the absorption of carbon dioxide in aqueous N-Methyl diethanolamine (MDEA) solution. This paper focuses on finding an efficient method of carbon dioxide gas capture by analyzing the major sources of the CO<sub>2</sub> emissions and studying current remedial methods. The possible application of carbonic anhydrase to store the captured CO<sub>2</sub> is discussed in the final section.

**KEY WORDS :** Carbon dioxide, Remedial methods, Capture, Carbonic anhydrase (CA)

### INTRODUCTION

Carbon dioxide (CO<sub>2</sub>) is given out into Earth's atmosphere mainly by the burning of carbon-containing fuels and the decay of wood and other plant matter. Industrially, carbon dioxide is principally an irreformable waste product, produced by several methods which may be put at various scales (Pierantozzi, Ronald, 2001).

#### Natural and Anthropogenic sources of Carbon dioxide emissions

Fig.1 shows the distribution of natural carbon dioxide emissions. It can be seen clearly that the ocean atmospheric exchange is almost double of the emissions by decomposition or respiration. 70% of the earth is oceanic bodies therefore it can be said that the biggest carbon dioxide source considering both natural and anthropogenic are the oceans (Olivier *et al.*, 2017).

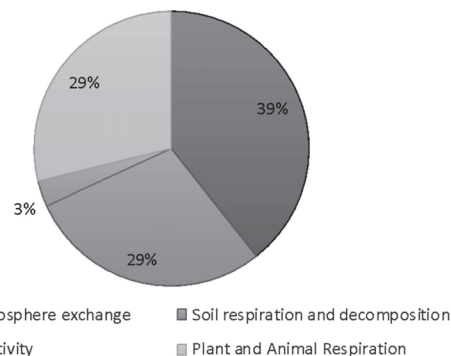


Fig. 1. Natural Sources of CO<sub>2</sub>

### ANTHROPOGENIC CO<sub>2</sub> EMISSION SOURCES

#### Stationary Point Sources

Any source of CO<sub>2</sub> that acts as an immobilized emitter can be termed as a stationary source of carbon dioxide (Koerner *et al.*, 2002). Examples include power plants fueled by fossil fuels, oil

refineries, process plants in the industry and other industrial sources. Mobile sources and stationary sources can be easily differentiated. Some examples of mobile sources include automobiles, aircraft and ships etc.

### Industrial Processes

Several industrial methods engender  $\text{CO}_2$  as a waste gas. Cement is engendered by heating calcium carbonates ( $\text{CaCO}_3$ ), such as chalk or limestone, decomposing them into lime ( $\text{CaO}$ ) and  $\text{CO}_2$ . Proximately 900 kg of  $\text{CO}_2$  is abandoned for every 1000 kg of cement produced (Ali Naqi *et al.*, 2019). Refineries are a big contribution for carbon dioxide emissions in the industry sector. In the steel industry melted iron ore ( $\text{Fe}_2\text{O}_3$ ) is reduced to Fe by reacting with carbon monoxide gas. This produces pure iron and  $\text{CO}_2$ . Carbon dioxide emitted from steel production primarily comes from energy consumption of fossil fuel as well as the use of limestone to purify iron oxides (Chang-qing *et al.*, 2006).

### Agriculture and Land Use

The Intergovernmental Panel on Climate Change (IPCC) reported that the Agriculture, Forestry, and Land Use (AFOLU) sector was responsible for about a quarter of global greenhouse gas emissions (Makino Yamanoshita, 2019). There are two main contributors to incrementing emissions. A rapidly growing global population requires an overall higher food production. This incremented requisite for food has led to both expansion of agricultural land and an amplification of farming practices. Agricultural land often expands into forested areas and this process of deforestation releases  $\text{CO}_2$  stored in trees and soils (Sarah Derouin, 2019). It is estimated that up to 80 percent of deforestation is the result of agricultural expansion.

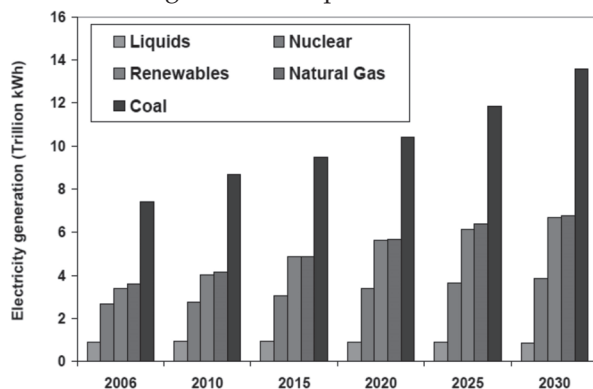


Fig. 2. World electricity generation by fuel (2006 – 2030)

### Power Sector

Studies show that the power and industry sectors cumulated dominate current global  $\text{CO}_2$  emissions, accounting for about 60% of total  $\text{CO}_2$  emissions (Hannah Ritchie and Max Roser, 2019). In theory, all point sources of  $\text{CO}_2$  may be taken and stockpiled. Coal is now the dominant fuel in the power sector, accounting for 38% of electricity generated in 2000, with hydro power accounting for 17.5%, natural gas for 17.3%, nuclear for 16.8%, oil for 9.8% and other renewables for 1.6%. Coal is anticipated to still be dominant fuel for power generation in 2020, while natural gas generation will beat hydro to be the second largest. As shown in Fig. 2, Coal is predicted to be the most used fuel source for power even in 2030 (Morena, 2011).

### Mobile Sources-Transport Industry

The sectors of the economy, such as the residential and transport sectors contribute around 30% of global  $\text{CO}_2$  emissions and produce many point source emissions. However, the emission capacities from the individual sources in these sectors incline to be very small in comparison to those from the power and industry sectors and are much more widely distributed, or even mobile rather than stationary. In the near future, the consumption of low-carbon energy carriers, such as electricity or hydrogen engendered from fossil fuels, may consent  $\text{CO}_2$  emissions to be caught from the residential and transport sectors.

As shown in Fig. 3 (Rosswen, 2019) there is an overall increase in the total anthropogenic sources over the past two decades. Fuel combustion and fugitive emissions from fuels (without transportation) have slightly reduced from 62% to 55%. This could potentially be due to the raised awareness of climate change and the improved technology for  $\text{CO}_2$  capture. The conventional methods of  $\text{CO}_2$  capture are adsorption, absorption and conversion of the  $\text{CO}_2$  into other chemical products. Membrane technologies have now emerged and are more commonly used in industries.

### Current Remedial Methods

#### Post-combustion capture

Post-combustion capture is a downstream process that is like flue gas desulfurization. It is the removal of  $\text{CO}_2$  from the flue gas produced after the combustion of the fuel. The oxidant used for

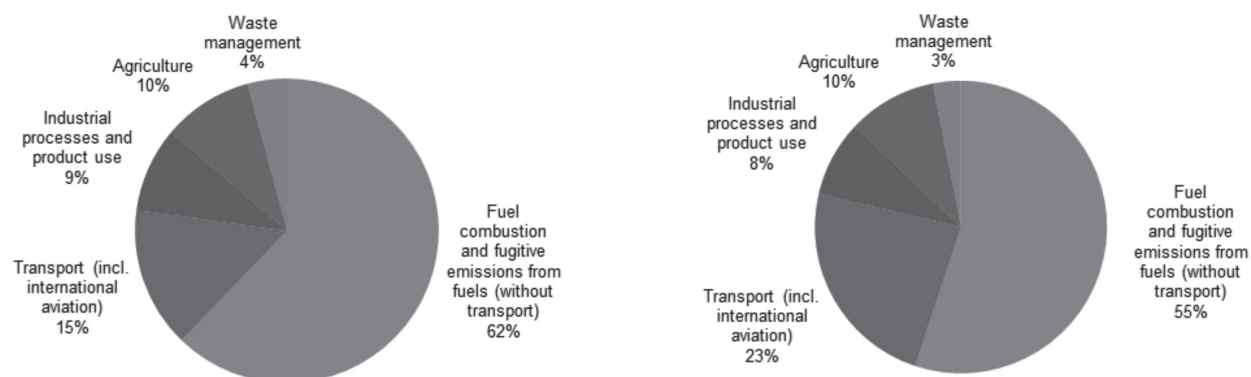


Fig. 3. Comparison of anthropogenic sources between 1990 and 2018

combustion is usually air and therefore, the flue gases are diluted significantly with nitrogen (Kothandaraman *et al.*, 2009). The main problem is the low partial pressure of  $\text{CO}_2$  in the flue gas, which also contains other gases such as oxygen, water vapour and nitrogen.

### Chemical Absorption

Chemical absorption systems at present are the most common solution for post-combustion capture of  $\text{CO}_2$ . In the MEA (Monoethanolamine) process  $\text{CO}_2$  from the cooled power plant exhaust gas reacts with aqueous solution of MEA in an absorption tower at pressures remotely above the ambient pressure (Dennis *et al.*, 2014). The first step requires compression to about 1.3 bar to overcome pressure drops within the system; the temperature is then reduced to about  $50^\circ\text{C}$ . The gases move on to the absorption column where the solvent molecules chemically bind to the  $\text{CO}_2$  gas. The solution containing the absorbed  $\text{CO}_2$  flows to a heat exchanger. The solvent is then decomposed thermally due to the solvent regeneration by heat. The  $\text{CO}_2$  and water vapor leaving the desorber is next cooled and essentially pristine  $\text{CO}_2$  leaves the plant for further treatment. The size of the absorption chamber as well as the concentration of  $\text{CO}_2$  contained in the exhaust determines the possible amount of  $\text{CO}_2$  that can be abstracted.

### Adsorption

The most effective adsorbents currently used are beds of alumina, zeolite and activated carbon (Younas *et al.*, 2016). Though this technology seems promising it requires massive amount of energy to meet cost and efficiency requirements. The main types of adsorption processes are as follows:

- Temperature swing adsorption (TSA)
- Pressure swing adsorption (PSA)

In PSA, the gas mixture flows through packed beds of spherical materials at high pressures and low temperatures until the adsorption of the desired component approaches equilibrium conditions in the end of the bed and then the adsorbent is regenerated by reducing the pressure.

In TSA, heat is utilized to regenerate adsorbents by raising their temperature. PSA and TSA are commercially utilized for gas disengagement and in the abstraction of  $\text{CO}_2$  from natural gas, though TSA requires more energy, time for regeneration and large adsorbent beds.

### Membrane Separation

Membranes are specially manufactured materials that let selective passage of a gas through them: a process that depends on the nature of the materials and the pressure difference across the membrane itself which favours high-pressure streams (Guozhao Ji and Ming Zhao, 2017). The permeability and selectivity of membranes have a large range, making this a powerful technique. The applicability of this technology to  $\text{CO}_2$  capture is thus ideal for a concentrated  $\text{CO}_2$  source stream with few contaminant gases.

### Calcium Looping Technology

Capture of  $\text{CO}_2$  from flue gas through calcium looping may be an attractive opportunity because of reasonable price and availability of sorbent limestone. Calcium looping does not require as much power as other capture techniques and therefore also reduces the electricity costs. In looping technology, calcium oxide reacts with  $\text{CO}_2$  to form calcium carbonate in a fluidized reactor

(carbonator) at a temperature around 650 °C, in an exothermic reaction (Chameera K. Jayarathna *et al.*, 2015). The calciner, CaCO<sub>3</sub> decomposes into CaO and CO<sub>2</sub> at a temperature close to 900 °C. A heavy flow of thermal energy is required to be supplied to the calciner to generate a response since this is an endothermic system. The regenerated CaO is separated from the CO<sub>2</sub> in a fuel/solid separator and is sent back to the carbonator. Here is where the carbonation of the CO<sub>2</sub> in the flue gas occurs where the CO<sub>2</sub> reacts with CaO to form CaCO<sub>3</sub> and heat as products. The heat supplied for the calcination reaction in the calciner is recovered through the exothermic carbonation reaction in the carbonator. CO<sub>2</sub> loaded sorbent is then transferred to the calciner.

#### **Incorporation and effect of Carbonic Anhydrase in different methods of CO<sub>2</sub> capture**

The transitional number one amine, Monoethanolamine (MEA) is currently the maximum used industrial approach to the capture CO<sub>2</sub> from flue gases. The benefit of MEA may be very practical for the capture of CO<sub>2</sub> as it has a very fast initial absorption rate. However, the reaction rate reduces as time passes and can lead to high power intake for the procedure (José I. Huertas *et al.*, 2015). Due to the increase in power intake requirement and the absorption temperature we tend to use secondary and tertiary amines. A few examples are inclusive of N-Methyl diethanolamine (MDEA), Dimethylethanolamine (DMEA) adopted for carbon capture. These are more energy green than primary and secondary amines. The absorption rate is slow in the above process and hence a more efficient absorber or desorber is needed to capture CO<sub>2</sub>. The slower reaction rate (absorption of CO<sub>2</sub>) is the major drawback of such solution. Since enzyme carbonic anhydrase (CA) is reported to catalyze CO<sub>2</sub> fixation in nature by hydrating CO<sub>2</sub> to bicarbonate, it is expected that use of the efficient biocatalyst can enhance the CO<sub>2</sub> absorption rate.

#### **Use of Biocatalyst Carbonic Anhydrase in the desorber**

The combination of an energetically favorable aqueous N-Methyl diethanolamine (MDEA) solution and the enzyme carbonic anhydrase is investigated in a packed column pilot plant (Leimbrink M. *et al.*, 2017). The simplest application is to dissolve the enzyme in the solvent. In this case,

the enzyme works in the boundary layer. However, due to the temperature sensitivity that may lead to the enzyme getting denatured, an additional enzyme recovery step proceeding to the desorber might be required if desorption is to occur at high temperatures. Second method is the use of membrane contacting technology, When passed via the membrane contactor CO<sub>2</sub> is absorbed and will be removed from the solution but then it will subsequently be desorbed at an external desorption unit to regenerate the solution. The solution may be the same as used for the absorption in column, however, the hydrophobic membrane defines the interfacial area between gas and liquid phase very precisely (Taek-Joong Kim *et al.*, 2016). In a membrane contactor the advantages of absorption technology and membrane technology are combined, as direct contact by mixing of the solution and gas feed stream is avoided. The major benefit of membrane contactors is the provision of large surface (interfacial) area per volume as accompanied by the prevention of dispersion of the two phases as well as solution losses. The carbonic anhydrase (CA) promotes bicarbonate formation towards equilibrium. It may be explained that the carbonic anhydrase does not accelerate the specific reaction between MEA with CO<sub>2</sub>. The faster the chemical reaction itself, the less acceleration can be obtained by the addition of carbonic anhydrase.

### **CONCLUSION**

At present the chemical absorption of CO<sub>2</sub> into a monoethanolamine solvent is the most widely accepted commercial approach to carbon dioxide capture. Operational problems that are observed in absorption columns such as foaming, channeling and entrainment are minimized by means of the well-defined contacting area in the membrane contactor. But the desorption of CO<sub>2</sub> from the solvents is extremely energy intensive. The slow reaction kinetics of CO<sub>2</sub> absorption step limits application. This obstacle can be overcome by the use of a carbonic anhydrase (CA) enzyme as a reaction promoter. There by the stability of the enzyme can be increased and its thermal denaturation can be prevented. Any research done must take into consideration the mass transfer of CO<sub>2</sub>, design of highly active, stable CA, the process economics of enzyme production in large scale and its long term performance under real flue gas conditions.

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