

Capture and Sequestration of Carbon dioxide Using Animal Bones or the Determination of Amount of Calcium Carbonate Deposit

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ABSTRACT: Recently, the rate of Carbon Dioxide (CO₂) emission into the atmosphere has increased beyond an acceptable limit in the world. This has led to much adverse or severe negative effect on humanity such as global warming etc. Carbon capture and sequestration is one of the best ways of fighting this global problem. Most of the methods of CO₂ capture and sequestration mentioned in the chapter 2 of this work were faced with much limitations and disadvantages. These limitations made it necessary to carry out further research on CO₂ capture and sequestration using animal bones which are very cheap and available in abundance in billions of kilograms. In this research work animal bones were crushed and the calcium ion extracted using an acetic acid and the solution reacted with carbon dioxide gas in a reactor using the K Timiyan CO₂ capture and sequestration unit. Results show that the animal bones were able to capture and sequester the carbon dioxide gas in the form of CaCO₃ and also indicated that at average temperatures of 650C, 750C, 850C, and 950C, depositing 40.4g, 44.7g, 46.5g, 46.0g of CaCO₃ and 140.0ft³, 199.0ft³, 231.5ft³ and 232.2ft³ of Carbon Dioxide gas was captured respectively and stored by the calcium ion extracted from the bones respectively. By this research work carbon dioxide producing companies such as the oil and gas companies, cement industries, automobile industries etc. could capture and sequester carbon dioxide in the gas pipelines and industry plants cheaper and faster. This carbon dioxide capture and sequestration method is economical since the bones are readily available and the acid is also regenerated. The carbon dioxide captured and sequestered can be recovered by treating the CaCO₃ appropriately with a concentrated acid at given temperature and can be used for energy production, enhanced oil recovery, and other various applications. This multi-disciplinary research work can indeed save the world from the various dangers of emitting excess carbon dioxide into the atmosphere.

KEYWORDS: Capture, carbon dioxide, extraction, temperature, global warming, storage

I. INTRODUCTION

Continuous combustion of fossil fuels such as crude oil, petrol, diesel and gas causes rapid emission of carbon dioxide into the atmosphere leading to increase in global atmospheric temperature, increase in acidity of the sea, as well as melting of ice block in the polar regions. There is therefore need to find an easier and cheaper alternative of carbon dioxide capture and sequestration method to provide a lasting solution to the globally concerned problem.

Greenhouse gas, such as carbon dioxide (CO₂) is an emission from fossil fuel combustion which makes significant contribution to global warming as the temperature of the atmosphere increases beyond normal. Although greenhouse gas effect may occur in nature an increased greenhouse effect is obviously experienced when there is increase in the concentrations of the greenhouse gas. Figure 1.1 represents GHG emissions into the atmosphere while figure 1.1b, illustrates the greenhouse effect (Sparks, 2005). See appendix IV

In 2006, Ohio became the state having the highest air pollution as the burning of fossil fuel increases. Ohio was also among the top five states for CO₂ emission. In 1995, the emissions in the United States hit nearly 6 gigatons/year of CO₂ (Sparks, 2005). This was recorded as the highest in the world. However, there are recent estimates which reveal that China's CO₂ emissions might soon exceed the US CO₂ emissions. Results show that the current concentration of the world's CO₂ in the atmosphere is about 380ppm and rises at about 2ppm yearly. As stated earlier, the increase in levels of GHGs results in increased greenhouse effect which is termed global warming. In 2007, it was also estimated by the IPCC that even though the levels in 2000 may have been kept constant there would still be an occurrence of 0.1°C per decade increase of the world's atmospheric temperature. Currently, mitigation scheme of CO₂ emission are CO₂ separation, transportation, and sequestration. It is worthy of note that CO₂ separation cost performs a dominant role in the management of CO₂ emissions.

One of the methods for CO₂ capture is the use of calcium ions. Alternative to calcium-based sorbent CO₂ separation, includes membrane and cryogenic separation, adsorption, absorption etc. However, most of these methods require very high increase in the total cost of energy production due to their high energy consumption nature. Most of them also need high pressure and low temperature for increase in CO₂ solubility. By analysis, with a reaction-based system, these separation truly occurs at high temperature and low pressures, which drastically reduce the cost intensive cooling and compression process (Sparks, 2005) which is storing CO₂ beneath the earth's surface in deep reservoir. CO₂ sequestration is the next stage of CO₂ management after transportation since carbon dioxide capture and storage involves the capture and compression of CO₂ from major sources to be stored in some designated areas. There are different types of carbon dioxide sequestration which are: Geological sequestration which is considered of CO₂ storage the best due to low environmental risks, large storage potential, long storage retention times and maturity of the technology in comparison with other storage options. Another technique is Mineral sequestration which involves the chemical reaction of CO₂ and metal oxides permanently binding the carbon dioxide upon them. The injection of carbon dioxide into the bed of a very deep ocean is another method of storing CO₂. Reusing the CO₂ in other industrial processes is another method CO₂ management. Figure 1.3 represents possible CO₂ sequestration techniques. Refer to appendix iv.

Recently IPCC says, "Warming of the climate system is clearly unavoidable and undeniable, since the continuous observation of increase in ocean temperature and global average air as well as continuous rise of the global mean sea level and increased melting of snow and ice."

Figure 1.4 shows IPCC presentation, 2007 of three graphs: one representing the rise of global temperature, the rise of global sea level, and the last representing the declining nature of snow cover in the Northern Hemisphere. See appendix iv. Apart from the problems illustrated in Figure 1.4, there are many effects that could face the world in future, and is already seeing in some cases. Some of these effects are stated below:

i) There is clear increase in amount of precipitation deposited eastern parts of the Northern and Southern America, northern parts of Europe and northern and central parts of Asia,

ii) Significant dehydration of the Sahel, Mediterranean, southern Africa, Lake Chad and parts of southern Asia.

iii) Long time droughts observed since in the 1970s, especially in the tropics and subtropics areas of the world (IPCC, 2007).

Carbon Capture and Storage (CCS) is the process of capturing or collecting waste carbon dioxide (CO₂

) from large waste sources, such as fossil fuel power plants, transportation of the waste gas to a storage site, and depositing it properly preventing its escape into the atmosphere, where an underground geological formation is considered the best. The aim of this carbon capture and storage process is to deliberately avoid the release or escape of huge amount of CO₂ into the atmosphere either from fossil fuel during power generation or other industrial activities of engines. It is to ultimately have control over the contribution of fossil fuel emissions into the atmosphere in terms of global warming and ocean acidification. CO₂ injection into geological formations for has existed for several years and for several purposes including enhanced oil recovery method though long term CO₂ storage could absolutely be a new wide in the world.

The aim of this research work is to ensure and obtain the possibility of using animal bones which are rich in calcium to capture and sequester Carbon Dioxide and to quantify the calcium carbonate deposit having extracted the calcium ions from the bones in a reaction with an acid under certain conditions.

1.1 Modern Technical Options For Carbon Dioxide Gas Separation

The capture of CO₂ contributes about 75 percent to the total CCS cost. Main while CCS causes increase in the cost of electricity production of about 50 percent (Feron & Hendriks, 2005). Even though the cost may be different from other CCS schemes, significant reduction of the CO₂ capture cost is considered the most crucial issue for the CCS process to be universally agreed and acceptable to any of the energy industries. Therefore, the focus of this article is on the progress made in technologies of separation of carbon dioxide and capture from a gas mixture in consideration of the chemical conversion point. Options of CO₂ separation and capture include adsorption, absorption, membrane as well as biotechnology. The most advantageous scheme of CO₂ capture could be determined by making analysis of the costs in terms of generation of power. The use of amine solution such as MEA in absorption/stripping process is a commercialized technology which has been in use in the gas industry for over 60 years and is still the most mature process in the industry. The CO₂ recovery rate for MEA is 98% (Yamasaki, 2003). There is larger room to further improve the stability of the amine as well as the energy consumption of the carbon dioxide stripping process. The same principle is also involved in the adsorption process but it involves the use of porous solid adsorbents such as activated carbon, zeolites and chemical reactions between the adsorbent where by carbon dioxide may or may not occur in these separation process.

1.1.1 Amine Absorption Process

The amine absorption process, MEA seem to be the most widely studied CO₂ absorption system worldwide. Several areas of MEA absorption were studied rec

ently, such as improve the process design, making partial changes of the absorbents, and/or making great improvement of the process operation (Aboudheir et al., 2006; Al-Juaied & Rochelle, 2006; Bello & Idem, 2006; Jassim & Rochelle, 2006). In this paper summaries made concern only the representative studies. Natural gas industry uses MEA for the absorption of carbon dioxide from natural gases. Few commercial MEA absorption processes are available by which CO₂ is almost completely removed from combustion flue gas stream in association with a natural gas fluid. In such processes the MEA solution is allowed to have proper contact with the flue gas inside an absorber in which CO₂ is absorbed by the MEA solution in the absorber. Reaction between the MEA solution and the CO₂ in the gas stream occurs resulting in MEA carbamate. The MEA solution which is rich with CO₂ is then passed through a conduit to a stripper where the stripper reheats it in order to release almost pure CO₂. The MEA solution can still be returned to the absorber to capture CO₂ again (Stewart & Hessami, 2005). One of the disadvantages of this process is that it is generally known to be uneconomical because it needs very large intensive energy input and equipment size to operate. It has been widely acknowledged that the heat duty for the regeneration of solvent contains almost 70% of the total operating costs in CO₂ capture plant (Idem et al., 2006). Some disadvantages of the MEA process are: low CO₂ loading capacity, high equipment corrosion rate, amine degradation by SO₂, NO₂, HCl, HF, and oxygen in flue gas, and high energy consumption rate (Fauth et al., 2005; Resnik et al., 2004; Yeh et al., 2005). Diethanolamine (DEA) and methyldiethanolamine (MDEA) are most at times used as absorbents apart from MEA.

1.1.2 Ammonium Absorption Process

According to Yeh et al. the Aqua Ammonia Process avoids the limitations of the MEA processes (Resnik et al., 2004; Yeh et al., 2005). In this process aqueous ammonia was used as CO₂ sorbent having the capability of multi-component control. The flue gas is pretreated by oxidizing SO₂ and NO to SO₃ and NO₂, respectively. The flue gas then reacts with aqueous ammonia in a wet scrubber as the gas flows through the bottom to the top of the scrubber. There is requirement of heat input to thermally decompose ammonium bicarbonate and ammonium carbonate during the regeneration of ammonium and that according to their estimate this process can clearly save up to 60 percent of energy compared to MEA process. The by-products obtained from this process are ammonium sulfate, ammonium nitrate and ammonium bicarbonate. Ammonium sulfate and ammonium nitrate are fertilizers perfectly known all over the world. The market for ammonium bicarbonate is uncertain but can be thermally decomposed to recycle ammonium. This process enhances the burning of cheap and abundant high-sulfur coals. Dual-

alkali absorption approach is also one of the CO₂ separation methods.

1.1.3 Molecular Sieve Adsorbent

Molecular sieves are made for the separation of molecules depending on their molecular size or molecular weight. This seems to be a cost-effective technology which can be applied several other carbon sequestration schemes or method (Stewart & Hessami, 2005). Many research activities were in place with the focus to effect improvement in the CO₂ adsorption by treating the surface of the molecular sieve chemically. Amines are adsorbents depend on based on high surface area inorganic supports that consist of basic organic groups are of great interest. The reaction between the acidic CO₂ molecules and basic surface is believed to have resulted in the production of surface ammonium carbamate in an anhydrous condition and in the form of ammonium bicarbonate and carbonate species in water. The CO₂ adsorption capacity is 0.5 mol CO₂/mol surface-bound amine group in the absence of water, 1.0 mol CO₂/mol surface-bound amine in the absence of water in this case.

1.1.4 Adsorption by Activated Carbon

Anthracites are materials known for the production of high surface area activated carbon. Maroto-Valer et al. studied the CO₂ capture behavior and capacity of steam-activated anthracite (Maroto-Valer et al., 2005). They discovered that CO₂ captured does not give a linear relationship with the surface area of the anthracites. CO₂ adsorption capacity at the highest level was 65.7 mg CO₂/g adsorbent for the anthracite temperature of 800°C for 2 hours while surface area was 540 m²/g while anthracite possessing the highest surface area of 1,071 m²/g only had a CO₂ adsorption capacity of 40 mg CO₂/g adsorbent. This phenomenon could be attributed to certain size pores sufficiently effective for CO₂ adsorption.

II. CHAPTER 2

MATERIALS AND METHODS

2.0 Materials

2.1 Apparatus and Reagents:

The apparatus and reagents for this experiment are Reactor, CO₂ filled gas cylinder, receiver empty gas cylinder, hose, bowl, 2.5 liter of acetic acid and grinded animal bones.

2.2 Methods

2.2.1 Experimental Procedure

This experiment was conducted in the petroleum/chemical Engineering laboratory in the Department of Petroleum Engineering of the Rivers State University. Below is a diagram describing in detail how the experiment was conducted which includes a reactor whose volume is about 636 cm³,

the two gas bottles of which one is filled with a CO₂ gas while the other is empty to receive unreacted CO₂ gas. The system also contains a thermometer to measure the temperature of the

fluids sent into it which are calcium acetate solution and CO₂ gas. A stirrer is also in the reactor to ensure uniform mixture between the two different fluids.

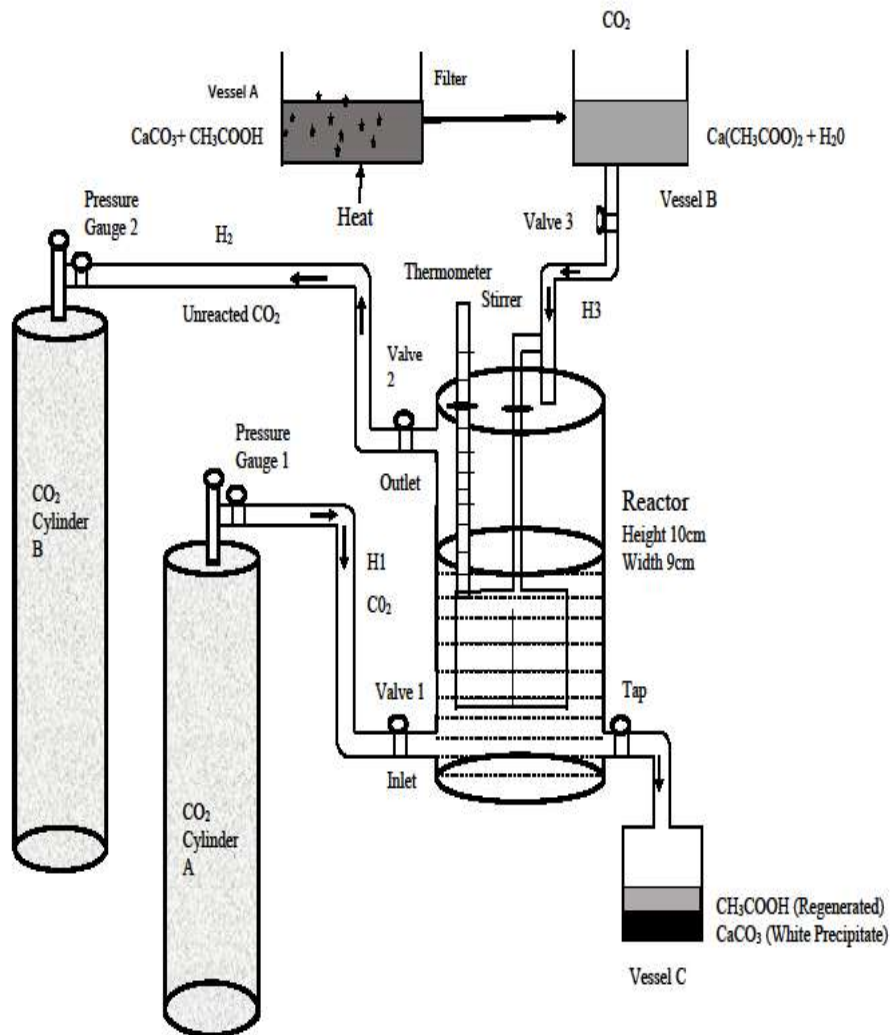


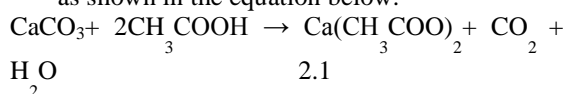
Figure 2.1 KTimiyan CO₂ capture and sequestration unit

The experiment according to the figure 2.1 above is based on the followings:

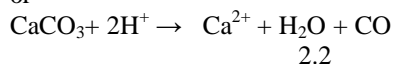
i) Animal bones were acquired and grinded to powder form.

ii) Extraction of the calcium ions from the bones was achieved by allowing the powdered bones to react with an acetic acid to form calcium acetate, carbon dioxide and water while the

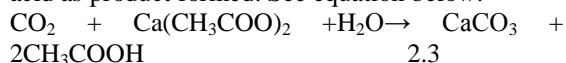
carbon dioxide is allowed to escape to the atmosphere since we are only interested in the calcium ions from the calcium acetate solution as shown in the equation below.



or



iii) The calcium acetate solution was then introduced into the reactor through the cap of the reactor after which a pressurized carbon dioxide gas in a cylinder at a given pressure was passed through valve 1 then enters from the bottom into the reactor to allow maximum reaction with the calcium acetate solution where the calcium ions captured and sequestered the carbon dioxide thereby producing calcium carbonate and acetic acid as product formed. See equation below.



iv) The acetic acid and the calcium carbonate formed is then received by a vessel through a tap at the bottom of the reactor.

v) The calcium carbonate is allowed to settle down at the bottom of the receiving vessel while the acetic acid is recovered and can be continuously re-used again.

vi) The insoluble carbon dioxide gas then passes through valve 2 to be stored in an empty gas cylinder and the entry pressure recorded by pressure gauges.

vii) During this process, pressure differences between the two gas cylinders as recorded by the gauges indicated that CO₂ was captured and sequestered.

viii) Different rates of gas solubility which indicates the amount or volume of CO₂ captured and sequestered was observed as temperature and pressure changes.

ix) A thermometer inserted on the reactor recorded the temperature as heat was applied at the bottom to obtain the best temperature or temperature range of solubility.

x) A stirrer was also included in the reactor to help obtain uniform temperature of the solution.

xi) The difference in pressure between the inlet CO₂ gas and the outlet un-reacted CO₂ gas was recorded as

$$\Delta P_g = P_{gA} - P_{gB}$$

3.1

Where ΔP_{gAB} = Change in pressure between the two gas cylinders.

P_{gA} = pressure of cylinder A

P_{gB} = pressure of cylinder B

2.3 Acetic Acid Solution Preparation

The acetic acid solution was prepared using a quantity of acetic acid solution, and then mixed with appropriate amounts of distilled water to obtain the desired concentration.

2.4 Sample Preparation and Characterization:

This involves the selection, washing, crushing and measurement of the bone in grams.

Animal bones samples were procured from appropriate sellers and some obtained from dump sites. The bones were crushed and pre-treated in an acetic acid solution in an external vessel to extract the calcium ions which was then introduced into the reactor to be mixed with the pressurized CO₂. The result will show the amount of CO₂ captured and stored for a particular quantity of bones as well as the required temperature and pressure. The bones were also sieved with a sieve size of 150 micron.

2.5 Preparation of Reagent

Different concentrations of an acetic acid were used to conduct this experiment.

Molecular formula is CH₃COOH

Where the molecular weight is obtained as follows:

$$12 + 1(3) + 12 + 16(2) + 1 = 60.05\text{g/mol}$$

$$\text{Density} = 1.05\text{g/cm}^3$$

$$\text{IM} = 60\text{ml dissolved in IL of H}_2\text{O}$$

$$\text{IL of H}_2\text{O} = 1000\text{ml}$$

$$\therefore 1\text{M Concentration of acid} = 940\text{ml of H}_2\text{O in 60ml of Acid}$$

Reaction of Acid With Bone Powder

Stage 1

- 100g of bone powder measured into a two litre reaction vessel.
- Acid concentration of 2.5M was introduced into the reaction vessel, vessel A.
- The mixture of the acid and bone was heated to a temperature of 65⁰C for the formation of Ca(CH₃COO)₂, i.e calcium acetate solution.
- Mixture was filtered to separate Ca(CH₃COO)₂ from the bone chaff.

Stage 2

- Ca(CH₃COO)₂ + H₂O was introduced into the reactor
- CO₂ gas was also introduced into the reactor to react with the Ca(CH₃COO)₂ at a given pressure. The inlet and outlet pressures of the CO₂ gas were noted
- A reaction time of about 2 min was allowed for each concentration of acid.
- The mixture was totally drained into vessel C through the tap

5. A retention time of about one hour was allowed
6. An impure white precipitate was found at the base of the vessel
7. The acetic acid was regenerated in the vessel

Reaction temperature of 65°C with 2.5M acetic acid

- 1 P₁ = 12.5 psi
- 2 P₂ = 11.1psi
- 3 Weight of dry bone powder = 100g
- 4 Conc. of acid = 2.5M
- 5 Volume of acid = 300ml
- 6 Temperature of (CaCO₃) + CH₃COOH = 65°C
- 7 Reaction time = 2min
- 8 Retention time = 1 hour
- 9 Reaction temperature = 65°C
- 10 Base temperature 26 °C

Reaction temperature of 75°C with 2.5M acetic acid

- 1 P₁ = 12.5psi
- 2 P₂ = 13.1psi
- 3 Weight of dry bone powder = 100g
- 4 Conc. of acid = 2.5M
- 5 Volume of acid = 300ml
- 6 Temperature of (CaCO₃) + CH₃COOH = 75°C
- 7 Reaction time = 2 min
- 8 Retention time = 1 hour

- 9 Reaction temperature = 75°C

- 10 Base temperature 26°C

Reaction temperature of 85°C with 2.5M acetic acid

- 1 P₁ = 12.5psi
- 2 P₂ = 15.0 psi
- 3 Weight of dry bone powder = 100g
- 4 Conc. of acid = 2.5M
- 5 Volume of acid = 300ml
- 6 Temperature of (CaCO₃) + CH₃COOH = 85°C
- 7 Reaction time = 2min
- 8 Retention time = 1 hour
- 9 Reactor temperature = 85°C
- 10 Base temperature 26 °C

Reaction temperature of 65°C with 2.5M acetic acid

- 1 P₁ = 12.5 psi
- 2 P₂ = 16.9 psi
- 3 Weight of dry bone powder = 100g
- 4 Conc. of acid = 2.5M
- 5 Volume of acid = 300ml
- 6 Temperature of (CaCO₃) + CH₃COOH = 95°C
- 7 Reaction time = 2min
- 8 Retention time = 1 hour
- 9 Reactor temperature = 95°C
- 10 Base temperature 26 °C

III. CHAPTER 3

3.0 RESULTS AND DISCUSSIONS

Table 3.1a Results of CaCO₃ Deposits at 65°C and Pressures between 12.5psi and 20.5psi

| Temp. (°C) | Conc. (M) | Press. (psi) Cylinder A | Press. (psi) Cylinder B | Time (min) | CaCO ₃ deposit (g) |
|----------------|------------|-------------------------|-------------------------|------------|-------------------------------|
| 65 | 2.5 | 12.5 | 12.1 | 2 | 37.2 |
| 65 | 2.5 | 14.5 | 13.1 | 2 | 38.0 |
| 65 | 2.5 | 16.5 | 15.0 | 2 | 41.5 |
| 65 | 2.5 | 18.5 | 16.9 | 2 | 42.3 |
| 65 | 2.5 | 20.5 | 18.8 | 2 | 42.8 |
| Average | 2.5 | 18.8 | 15.95 | 2 | 40.4 |

The results according to table 3.1a at a reaction temperature of 65°C reveals that at a constant temperature of 65°C, with a constant concentration of the acetic acid which is 2.5M at pressure of 12.5psi and 14.5psi recorded that 37.2g and 38.0g of CaCO₃ was deposited respectively as a result of the CO₂ captured by the bones. Similarly, at this isothermal condition of 65°C and at the same 2.5M acetic acid concentration at a pressure of 16.5psi it was recorded that 41.5g of CaCO₃ was deposited after the reaction of the acid and the bones. Also at a pressure of 18.5psi at the same constant temperature and concentration the amount of CaCO₃ deposit after the CO₂ capture reaction

builds up to 42.3g by the bones. Finally, at the same 65°C and 2.5M concentration and at an elevated pressure of 20.5psi, 42.8g of CaCO₃ was deposited by the bones. Average recording was calculated from the results at the same constant temperature of 65°C and 2.5M acid concentration which reveals that the average CaCO₃ deposition results 41.1g. The results indicate that there is gradual increase in CO₂ capture as the pressure increases though the increment looks minimal. In this experiment only pressure varies while temperature, concentration and time were kept constant.

Table 3.1b Results of CaCO₃ Deposits at 75^oC and Pressures between 12.5psi and 20.5psi

| Temp. (°C) | Conc.(M) | Press.(Psi) Cylinder A | Press.(psi) Cylinder B | Time (min) | CaCO ₃ deposit (g) | |
|----------------|--------------|------------------------|------------------------|------------|-------------------------------|---------|
| 7 | 5 | 2 . 5 | 1 2 . 5 | 1 1 . 1 | 2 | 4 3 . 5 |
| 7 | 5 | 2 . 5 | 1 4 . 5 | 1 3 . 1 | 2 | 4 4 . 0 |
| 7 | 5 | 2 . 5 | 1 6 . 5 | 1 5 . 1 | 2 | 4 4 . 6 |
| 7 | 5 | 2 . 5 | 1 8 . 5 | 1 7 . 2 | 2 | 4 5 . 7 |
| 7 | 5 | 2 . 5 | 2 0 . 5 | 1 9 . 3 | 2 | 4 5 . 8 |
| Average | 2 . 5 | 1 7 . 5 | 1 6 . 1 8 | 2 | 4 4 . 7 | |

The experiment at a temperature of 75^oC in table 3.1b is also similar to that of the 65^oC meaning that though reaction temperature is increased to 75^oC the concentration of the acid and reaction time were kept constant with pressure ranging from 12.5psi to 20.5psi. The results of the experiment at 75^oC indicate that there is increase in the CO₂ capture capacity of the bones at this higher reaction temperature though kept constant at this

condition while the pressure increases gradually from 12.5psi to 20.5psi. For instance, 43.5g and 44.0g of CaCO₃ was deposited after the reaction of the acid and the bones at a pressure of 12.5 and 14.5psi respectively while there is increase in the deposits up to 44.6g as the pressure increases to 16.5psi. Also, at a pressure of 18.5psi the CaCO₃ deposit builds up to 45.7g and up to 45.8g at 20.5psi.

Table 3.1c Results of CaCO₃ Deposits at 85^oC and Pressures between 12.5psi and 20.5psi

| Temp. (°C) | Conc.(M) | Press.(Psi) Cylinder A | Press.(psi) Cylinder B | Time (min) | CaCO ₃ deposit (g) | |
|----------------|--------------|------------------------|------------------------|------------|-------------------------------|---------|
| 8 | 5 | 2 . 5 | 1 2 . 5 | 1 1 . 1 | 2 | 4 5 . 7 |
| 8 | 5 | 2 . 5 | 1 4 . 5 | 1 3 . 1 | 2 | 4 6 . 2 |
| 8 | 5 | 2 . 5 | 1 6 . 5 | 1 5 . 1 | 2 | 4 6 . 8 |
| 8 | 5 | 2 . 5 | 1 8 . 5 | 1 7 . 2 | 2 | 4 6 . 9 |
| 8 | 5 | 2 . 5 | 2 0 . 5 | 1 9 . 2 | 2 | 4 6 . 9 |
| Average | 2 . 5 | 1 7 . 5 | 1 6 . 1 5 | 2 | 4 6 . 5 | |

Table 3.1c shows results of the experiment at temperature of 85^oC and follows similar pattern as in the case of results at 65^oC and 75^oC in table 4.1a and 4.1b. At the constant temperature of 85^oC it is clearly observed that as pressure increases from 12.5psi to 20.5psi there is higher deposition of CaCO₃ indicating that there is increase in CO₂ capture capacity as pressure increases at the elevated temperature which was kept constant. According to the results, 45.7g and 46.2g of CaCO₃ was deposited when CO₂ gas at pressures of

12.5psi and 14.5psi respectively was sent into the reactor to react with the calcium acetate from the bones. Similarly, at a pressure of 16.5psi, 46.8g of CaCO₃ was deposited while 46.9g of CaCO₃ was deposited at a pressure of 18.5psi and finally 46.9g of CaCO₃ was deposited when pressure was increased to 20.5psi at the same constant temperature of 85^oC. The results also show that equal amount of CaCO₃ was deposited as pressure increases to 20.5psi at 85^oC.

Table 3.1d Results of CaCO₃ Deposits at 95^oC and Pressures between 12.5psi and 20.5psi

| Temp. (°C) | Conc.(M) | Press.(Psi) Cylinder A | Press. (psi) Cylinder B | Time (min) | CaCO ₃ deposit (g) |
|------------|----------|------------------------|-------------------------|------------|-------------------------------|
|------------|----------|------------------------|-------------------------|------------|-------------------------------|

| | | | | | | | | | | | | | | | | | |
|----------------|---|----------|---|----------|----------|----------|---|----------|----------|----------|---|----------|----------|----------|---|---|----------|
| 9 | 5 | 2 | . | 5 | 1 | 2 | . | 5 | 1 | 1 | . | 1 | 2 | 4 | 5 | . | 7 |
| 9 | 5 | 2 | . | 5 | 1 | 4 | . | 5 | 1 | 3 | . | 1 | 2 | 4 | 5 | . | 8 |
| 9 | 5 | 2 | . | 5 | 1 | 6 | . | 5 | 1 | 5 | . | 1 | 2 | 4 | 6 | . | 0 |
| 9 | 5 | 2 | . | 5 | 1 | 8 | . | 5 | 1 | 7 | . | 1 | 2 | 4 | 6 | . | 1 |
| 9 | 5 | 2 | . | 5 | 2 | 0 | . | 5 | 1 | 9 | . | 1 | 2 | 4 | 6 | . | 2 |
| Average | | 2 | . | 5 | 1 | 7 | . | 5 | 1 | 6 | . | 1 | 2 | 4 | | | 6 |

Table 3.1d shows results of the experiment at temperature of 95°C and follows similar pattern as in the case of results in table 4.1a, 4.1b, and 4.1c. At the constant temperature of 95°C it is clearly observed that as pressure increases from 12.5psi to 20.5psi deposits of CaCO₃ remain almost constant, increasing very slowly as pressure increases at the elevated temperature in its isothermal state. According to the results, 45.7g and 45.8g of CaCO₃ was deposited respectively when reaction took place between CO₂ gas and the calcium acetate from the bones at 12.5psi and 14.5psi. Similarly, at a pressure of 16.5psi 46.0g of CaCO₃ was deposited

while 46.1g of CaCO₃ was deposited at a pressure of 18.5psi and finally 46.2g of CaCO₃ was deposited when pressure was increased to 20.5psi at the same constant temperature of 95°C. This almost constant CaCO₃ deposit could be ascribed to the fact that excessively high temperature could lead to reduction of the strength of the acetic acid or the present amount of the calcium acetate solution from the bones may have reached its maximum capacity of CO₂ capture at the current conditions. Therefore, it will be better to perform CO₂ capture with animal bones using acetic acid at a temperature not exceeding 85°C.

Table 3.2 Average values of CaCO₃ deposit.

| Temperature (°C) | CaCO ₃ deposit (g) |
|------------------|-------------------------------|
| 6 | 5 |
| 7 | 5 |
| 8 | 5 |
| 9 | 5 |

Table 3.2 above clearly shows the average values of CaCO₃ deposit according to the specified temperatures ranging from 65°C to 95°C. This table indicates that the average amount of CaCO₃ deposited increases greatly from 40.4g at a temperature of 65°C to 44.7g at a temperature of 75°C and increased to 46.5g at 85°C and almost

remains constant 95°C having a result of 46.0g of CaCO₃ deposited during the CO₂ capture process. This obviously shows that the CO₂ capture process using acetic acid at temperature above 85°C may not produce a favourable result. Plots describing the CO₂ capture and CaCO₃ deposited are presented below.

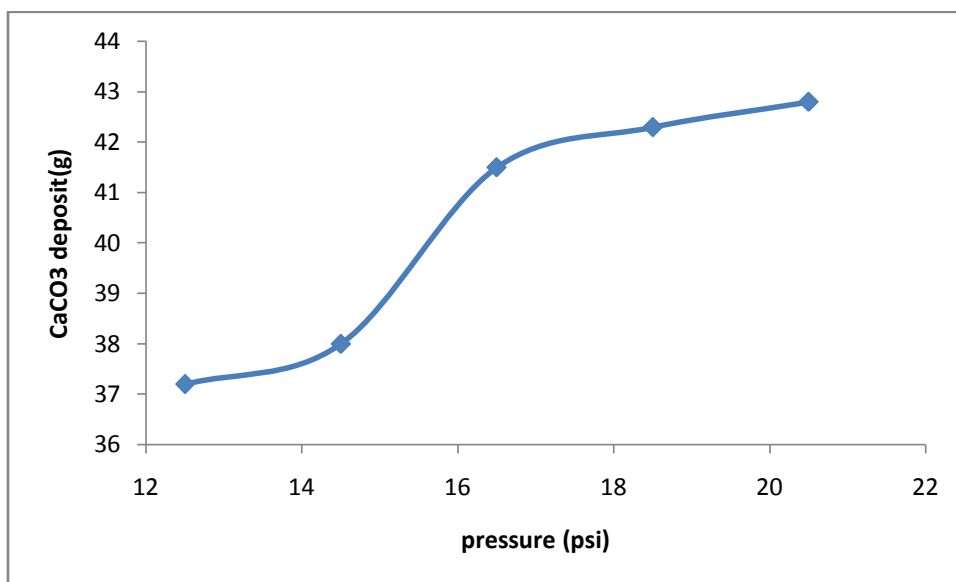


Figure 3.1a CaCO₃ deposited and pressure at 65⁰C

The figure above describes the amount of CaCO₃ deposits at the specified pressures from 12.5psi to 20.5psi at a constant temperature of

65⁰C. The graph indicates that the amount of CaCO₃ deposit initially was low but increases gradually with increase in pressure.

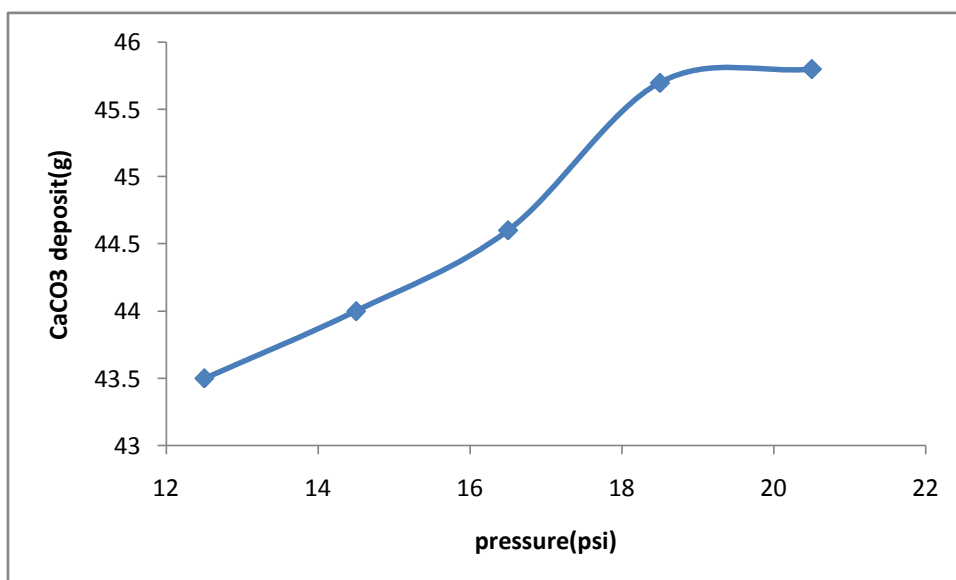


Figure 3.1b CaCO₃ deposited and pressure at 75⁰C

Then pressure versus CaCO₃ deposit graph above describes the amount of CaCO₃ deposits at the specified pressures from 12.5psi to 20.5psi at a constant temperature of 75⁰C. The graph indicates that the amount of CaCO₃ deposit initially was higher than that of the 65⁰C then after

increases slightly and almost became constant at higher pressures. This means that the increase in the temperature of the reaction has contributed to the increase in the amount of CaCO₃ deposit due to CO₂ gas captured.

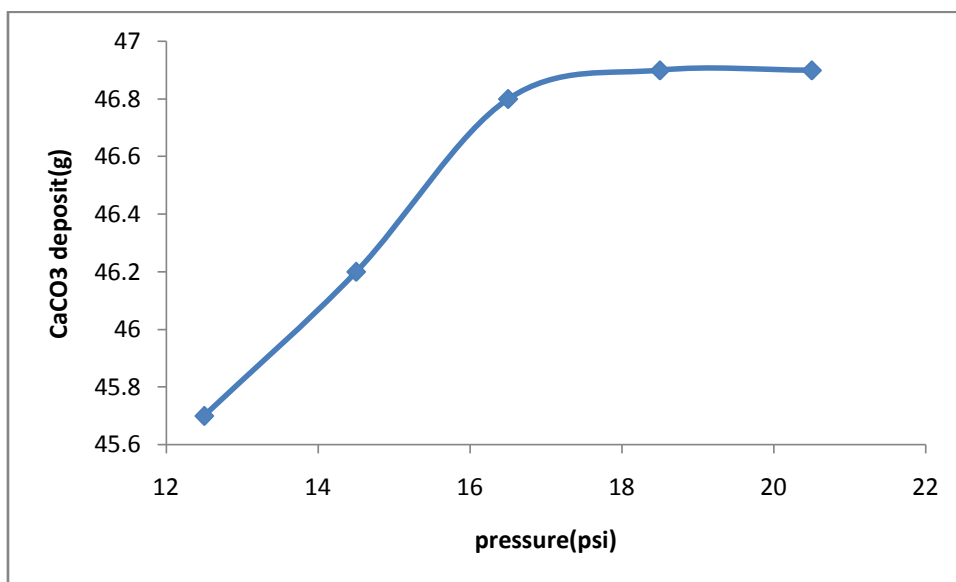


Figure 3.1c CaCO₃ deposited and pressure at 85⁰C

Then pressure versus CaCO₃ deposit graph above describes the amount of CaCO₃ deposits at the specified pressures from 12.5psi to 20.5psi at a constant temperature of 85⁰C. The graph indicates that the amount of CaCO₃ deposit initially was higher than that of the 65⁰C then after

increases slightly and almost became constant too at the higher pressures. This means that the increase in the temperature of the reaction has contributed to the increase in the amount of CaCO₃ deposit due to CO₂ gas captured.

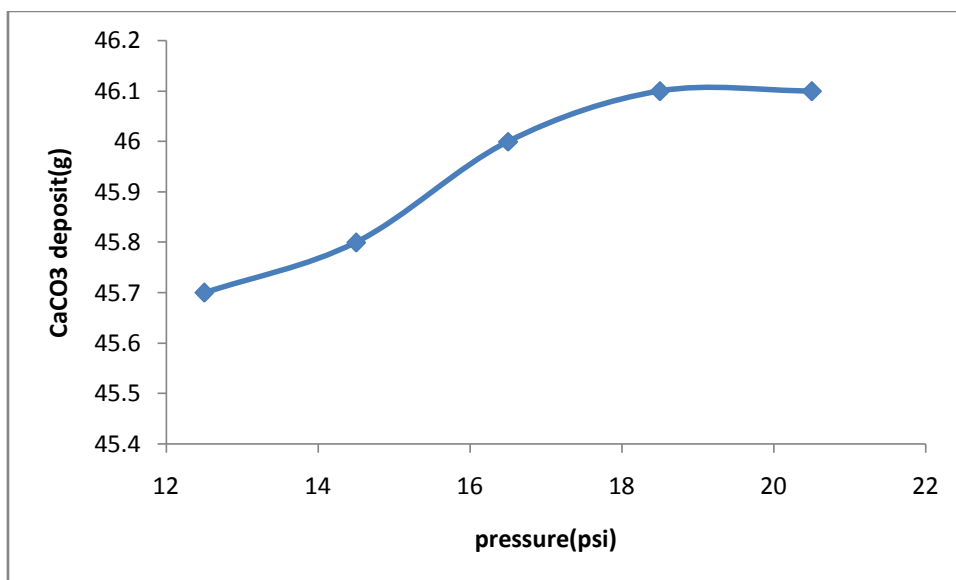


Figure 3.1d CaCO₃ deposited and pressure at 95⁰C

Then pressure versus CaCO₃ deposit graph above describes the amount of CaCO₃ deposits at the specified pressures from 12.5psi to 20.5psi at a constant temperature of 95⁰C. The graph indicates that the amount of CaCO₃ deposit initially was high as that of the 85⁰C but remains almost constant even as pressure increases. This

means that operating this system above 85⁰C could lead to waste of energy.

3.1 Carbon Dioxide Capture/Sequestration Indicators

The presence of the followings indicated that CO₂ was captured and stored

1. Pressure differences between cylinder A and cylinder B
2. Presence of white precipitate collected in vessel C. The white precipitate is CaCO_3 meaning that the calcium ions Ca^{2+} have captured and stored CO_2
3. Change in mass of the calcium acetate before reaction and after reaction.

The CO_2 gas can thereafter be regenerated through calcinations processes with heat or treatment of the CaCO_3 with a high concentration of an appropriate acid such as concentrated acetic acid or hydrochloric acid. The CO_2 can then be used for enhanced oil recovery, for energy production and other uses.

A certain proportion of the acetic acid for this experiment was regenerated making the experiment more economical as it applies to industrial process of CO_2 capture by this method. The amount of CaCO_3 formed depends on the amount of Ca^{2+} present in the calcium acetate solution, the concentration of the acid, the inlet pressure and the temperature applied. The CaCO_3 precipitated is impure as it is yet to undergo a purification process which is above the scope of this work.

3.2 Characterization of the CaCO_3 Deposit

The CaCO_3 deposit was characterized by the following chemical and physical properties:

1. It was reacted with a concentrated HCL whereby generating CO_2 gas bubbling. The gas generated extinguished a candle flame of fire when exposed to it which indicates that it was a CaCO_3 deposit.

2. The deposit was whitish in colour indicating that it was a CaCO_3 compound.
3. The compound deposited was also found to be odourless which is a true characteristics of CaCO_3 .
4. The compound deposited was insoluble in water thereby sinking down to the bottom of the beaker.
5. The substance deposited was observed to be non-corrosive which is a true indication of a CaCO_3 compound.

The plots in previous pages obviously indicate that the formation of CaCO_3 which is due to the capture and sequestration of CO_2 is directly proportional to the temperature and pressure. From the results it is clear that CO_2 gas was captured by the calcium ions from the animal bones proven according to the following reasons.

White precipitates of various quantities were formed as observed at the base of the receiving vessel, vessel C. This white precipitate is an indication of the presence of CaCO_3 . There was pressure differences observed at the gauges of the gas cylinders where the CO_2 gas flows from cylinder A to the reactor and then the un-reacted gas to the cylinder B for storage.

1. The pressure change is an indication that a portion of the CO_2 gas was captured and sequestered by the bone calcium ions.
2. A certain proportion of the acetic acid was regenerated which indicates that CaCO_3 was formed with it as products of the reaction.

3.3 Atomic Absorption Spectrometry (AAS) Analysis of Bones

Table 3.3 AAS Results Showing Calcium Concentrations in Bones before Extraction

| Bone Label | Element | Concentrations |
|------------|------------------|----------------|
| A | Ca^{2+} | 2377.239 ppm |
| | Na^+ | 909.691ppm |
| | K^+ | 108.764ppm |

Analysis was made on the various classes of bones to obtain the concentrations of the metallic ions that constitute the bones. The ions include Ca^{2+} , Na^+ , K^+ and even phosphorus, a non metal. According to the results obtained Ca^{2+} concentration in the bones is 2377.239ppm and that

the concentration of the Ca^{2+} (2377.239ppm) was far higher than that of the Na^+ which has a concentration of 909.691ppm and K^+ with a concentration of 108.764ppm in the bones. Refer to appendix I AAS analysis for Ca^{2+} .

3.4 By-products Analysis

Table 3.4 AAS Results of By-Product Analysis

| Bone Label | Element | Concentrations |
|------------|------------------|----------------|
| A | Ca^{2+} | 92.235 ppm |

Further analysis was made on the by-product of the bones after the calcium ion

extraction process to ascertain the effectiveness of the extraction process. Results show that the

extraction process was almost 100% perfect as over 96.1 % of the calcium ions in the bones were extracted by the acetic acid at elevated temperatures. It was observed that after the extraction process there was a drastic reduction of the calcium ions from an initial concentration of 2377.239ppm to a final concentration of 92.24ppm. The result of the by-product analysis is shown above in table 4.4. From the results above the total amount of calcium ions extracted from the bones for the CO₂ capture is given as:

$$\text{Total Ca}^{2+} = 2377.239\text{ppm} - 92.235\text{ppm} = 2285.004\text{ppm}.$$

IV. CONCLUSION

Carbon dioxide capture and sequestration is not a new topic of discussion but the use of animal bones to capture and sequester CO₂ in this research work may be the first of its kind in the world. Our oil gas wells produce a lot of CO₂ gas dissolved in them. The flaring of gases and the combustion of gases and other sources of fuel releases excess amount of CO₂ into the atmosphere. The cement industries, electrical industries and many other large energy consuming industries release a lot of CO₂ into the atmosphere. The atmosphere is getting saturated with the excess CO₂ released into it.

This condition has depleted the ozone layer, causing global warming all over the world, ice blocks in the polar regions melts drastically causing rapid increase of sea water which could soon cover the earth surface, excess CO₂ released into the atmosphere has caused drought in many parts of the world as the atmospheric temperature caused by the excess CO₂ increases. Soon the world will never be a conducive environment for one to live due to excess CO₂ in the atmosphere. By this experiment animal bones which are produced in billion of kilogram in the world have been seen as a means of capturing and sequestering CO₂.

Having noticed the limitations facing the various methods of CO₂ capture and sequestration mentioned in chapter 2 such as processing difficulties/non-selectivity of gas molecules, exhibition of substantial changes in pore sizes in oxidizing environment, low CO₂ capture capability e.t.c as the cases of mixed-matrix/ hybrid membrane, carbon membrane and activated carbon method respectively, there was obvious need to obtain far cheaper method of CO₂ capture with low operating cost and readily available materials for CO₂ capture and sequestration.

This research work using animal bones to capture and sequester CO₂ as yielded a positive result owing to the fact that CO₂ was captured and stored by the bones at various conditions and amount of bones utilized. It is also observed that the materials for the work such as the bones are very cheap and readily available in billions of kilograms all over the world and that electricity consumption was also moderate. This has been able to tackle the challenges/limitations faced by various CO₂ capture and storage methods discussed in chapter 1

This experiment has revealed the formation of white precipitate deposited after the reaction of the animal bones with acetic acid after which CO₂ gas was passed through the solution. The CO₂ captured by the calcium ions to form CaCO₃ can be recovered and be converted when necessary to produces energy, for enhanced oil recovery and for many other uses as stated earlier in chapter two.

This experiment (if applied) could help the auto mobile industries, cement industries and the upstream and downstream companies to separate CO₂ from reservoir fluids such as natural gas in gas wells or pipe line capturing and storing the CO₂ gas in the form of CaCO₃ to avoid global warning and store the CO₂ for many more uses and for many years.

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ABBREVIATIONS

- CCS - Carbon Capture and Storage
- CO₂ - Carbon Dioxide (Carbon (IV) oxide)
- EGR - Enhanced Gas Recovery
- EOR - Enhanced Oil Discovery
- GHG - Greenhouse gases
- IGCC - Integrated Gasification Combined Cycle
- IPCC - Intergovernmental programme for Climate Change
- Mg/Kg - Milligram per kilogram
- PPM - **APPENDIX I**

Table 1: AAS Analysis on Ca²⁺, K⁺ and Na⁺ concentrations

| Date Time | Label | Element Label (nm) | Conc | %RSD | Unadjusted Conc | Intensity | %RSD |
|--------------------|--------------|--------------------|----------------|-------|-----------------|-------------|----------|
| 2/26/2019 09:52:33 | Blank | Ca (393.366 nm) | 0.000 (ppm) | N/A | 0.000 (ppm) | 0.000 | > 100.00 |
| 2/26/2019 09:52:33 | Blank | K (766.491 nm) | 0.000 (ppm) | N/A | 0.000 (ppm) | 0.000 | > 100.00 |
| 2/26/2019 09:52:33 | Blank | Na (588.995 nm) | 0.000 (ppm) | N/A | 0.000 (ppm) | 0.000 | > 100.00 |
| 2/26/2019 09:54:14 | Standard 1 | Ca (393.366 nm) | 1.000 (ppm) | N/A | 1.000 (ppm) | 838942.417 | 1.75 |
| 2/26/2019 09:54:14 | Standard 1 | K (766.491 nm) | 1.000 (ppm) | N/A | 1.000 (ppm) | 86366.486 | 1.55 |
| 2/26/2019 09:54:14 | Standard 1 | Na (588.995 nm) | 1.000 (ppm) | N/A | 1.000 (ppm) | 605354.222 | 0.59 |
| 2/26/2019 10:29:37 | Standard 2 | Ca (393.366 nm) | 3.000 (ppm) | N/A | 3.000 (ppm) | 1979778.191 | 1.52 |
| 2/26/2019 10:29:37 | Standard 2 | K (766.491 nm) | 3.000 (ppm) | N/A | 3.000 (ppm) | 247975.374 | 0.42 |
| 2/26/2019 10:29:37 | Standard 2 | Na (588.995 nm) | 3.000 (ppm) | N/A | 3.000 (ppm) | 1520422.966 | 0.98 |
| 2/26/2019 10:27:52 | Standard 3 | Ca (393.366 nm) | 5.000 (ppm) | N/A | 5.000 (ppm) | 3120096.599 | 1.31 |
| 2/26/2019 10:27:52 | Standard 3 | K (766.491 nm) | 5.000 (ppm) | N/A | 5.000 (ppm) | 368857.543 | 0.60 |
| 2/26/2019 10:27:52 | Standard 3 | Na (588.995 nm) | 5.000 (ppm) | N/A | 5.000 (ppm) | 2479356.639 | 1.02 |
| 2/26/2019 09:59:26 | Qc | Ca (393.366 nm) | 1.126 (ppm) | 1.72 | 1.126 (ppm) | 754080.501 | 1.72 |
| 2/26/2019 09:59:26 | Qc | K (766.491 nm) | 1.104 (ppm) | 1.93 | 1.104 (ppm) | 90334.949 | 1.93 |
| 2/26/2019 09:59:26 | Qc | Na (588.995 nm) | 1.155 (ppm) | 0.90 | 1.155 (ppm) | 638149.991 | 0.90 |
| 2/26/2019 10:26:18 | Blank | Ca (393.366 nm) | -0.005 (ppm) | 22.49 | -0.005 (ppm) | -3081.791 | 24.01 |
| 2/26/2019 10:26:18 | Blank | K (766.491 nm) | 0.002 (ppm) | 3.83 | 0.002 (ppm) | 126.755 | 3.83 |
| 2/26/2019 10:26:18 | Blank | Na (588.995 nm) | 0.001 (ppm) | 13.21 | 0.001 (ppm) | 399.798 | 13.08 |
| 2/26/2019 10:22:36 | Class A Bone | Ca (393.366 nm) | 2377.239 (ppm) | 0.94 | 4.754 (ppm) | 3184300.960 | 0.94 |
| 2/26/2019 10:22:36 | Class A Bone | K (766.491 nm) | 108.764 (ppm) | 2.31 | 0.218 (ppm) | 17805.413 | 2.31 |
| 2/26/2019 10:22:36 | Class A Bone | Na (588.995 nm) | 909.691 (ppm) | 0.54 | 1.819 (ppm) | 1004931.912 | 0.54 |
| 2/26/2019 10:24:41 | Blank | Ca (393.366 nm) | -0.014 (ppm) | 3.99 | -0.014 (ppm) | -9465.105 | 4.07 |
| 2/26/2019 10:24:41 | Blank | K (766.491 nm) | 0.001 (ppm) | 11.79 | 0.001 (ppm) | 44.451 | 11.79 |
| 2/26/2019 10:24:41 | Blank | Na (588.995 nm) | 0.004 (ppm) | 15.44 | 0.004 (ppm) | 1954.844 | 15.41 |

Table 3: AAS Analysis on K⁺ and Na⁺ concentrations on by products

| Bones.mpws | | Report Date: Tuesday, March 05, 2019 3:21 PM | | | | | |
|-------------------|-------|--|----------------|------|-----------------|--------------|------|
| Date Time | Label | Element Label (nm) | Conc | %RSD | Unadjusted Conc | Intensity | %RSD |
| 3/5/2019 14:44:55 | Bones | K (766.491 nm) | 4.573 l (ppm) | 5.34 | 0.152 l (ppm) | 11842.268 l | 5.53 |
| 3/5/2019 14:44:55 | Bones | Na (588.995 nm) | 19.195 l (ppm) | 3.36 | 0.640 l (ppm) | 166768.487 l | 2.08 |

Appendix II

Table 1: Phosphorus concentration in bone

| CERTIFICATE OF ANALYSIS | | | |
|-------------------------|--------------|-----------|------------------|
| S/N | Sample ID | Method | PHOSPHORUS mg/kg |
| 1 | CLASS A BONE | API-RP-45 | 121.63 |

Appendix III: Figures

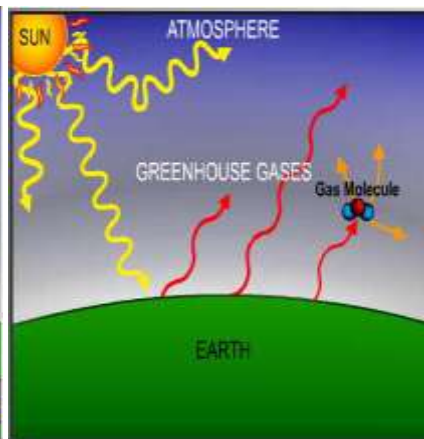


Figure 1.1a Schematic of Pollution Emissions into Atmosphere

Figure 1.1b Green House Effect

Source: Sparks, 2005



Figure 1.2 Pollution Emissions into Atmosphere

Source :(Hunts, 2006)

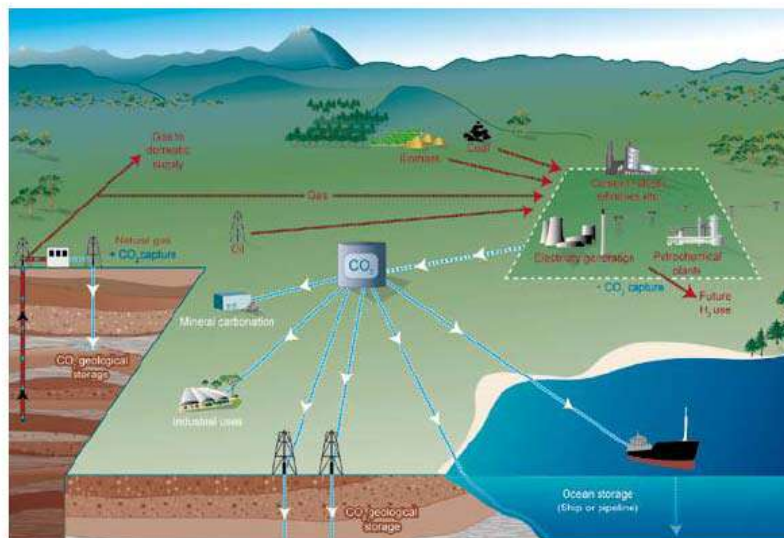


Figure 1.3 Possible CCS Systems showing sources for which CCS might be relevant, transportation and storage of CO₂.

Source: Sally Benson M. et al, 2008

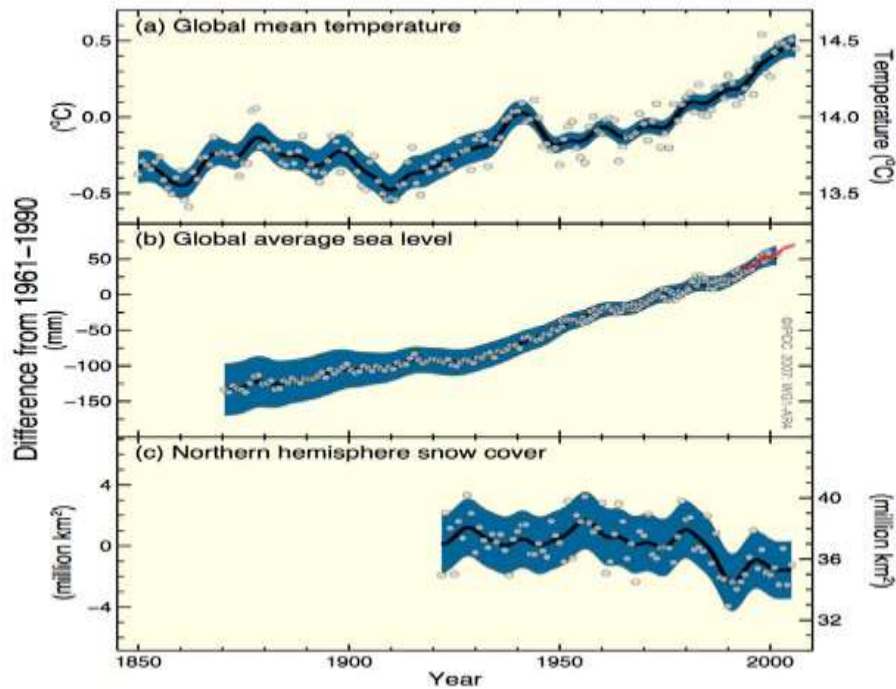


Figure 1.4 Changes in Temperature, Sea Level, and Northern Hemisphere Snow Cover
 Source: IPCC presentation, 2007

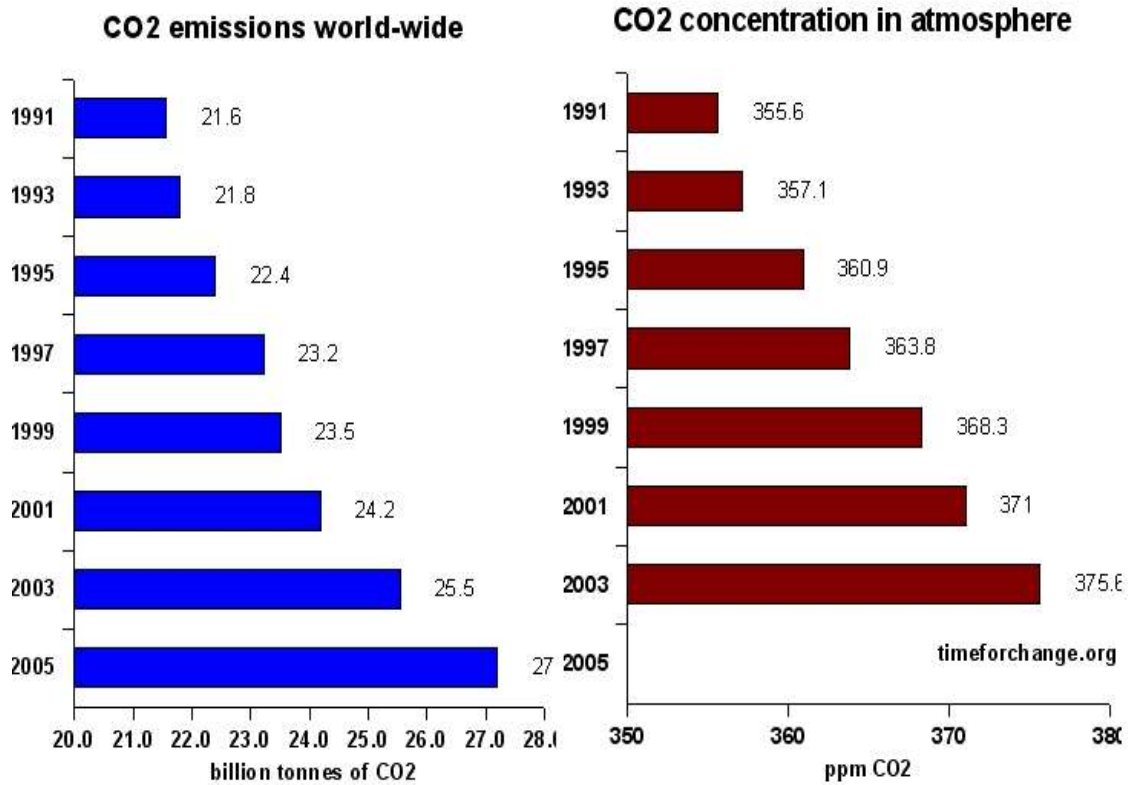


Figure 2.1 Global CO₂ Emissions and Concentrations
 Source: timeforchange .org

World temperature increase in °C

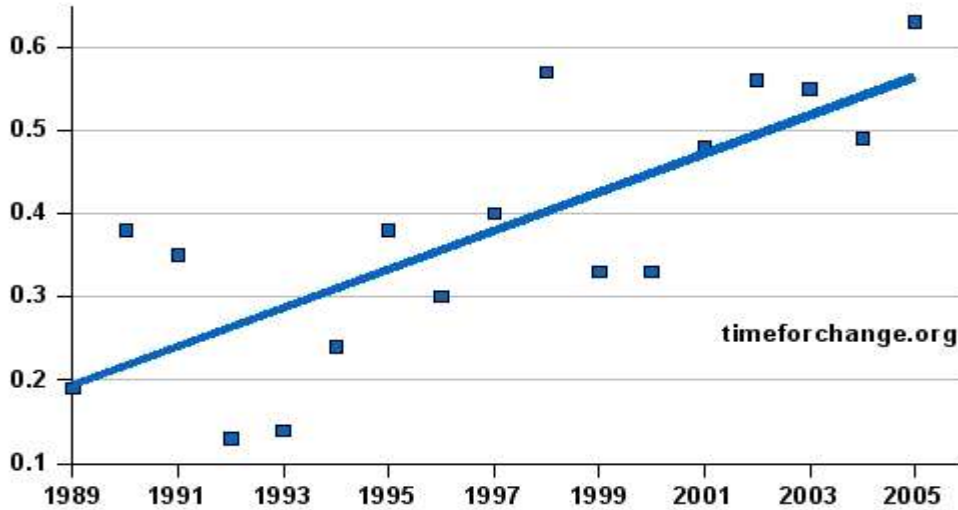


Figure 2.2 increase in world temperature

Source: timeforchange.org

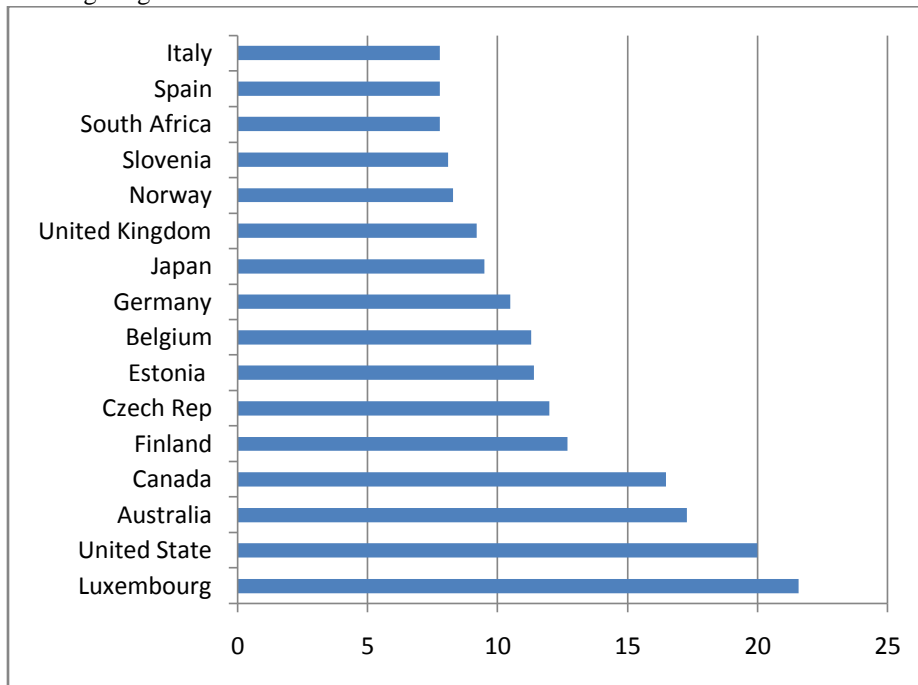


Figure 2.3 CO₂emission per capita 2002

Source: Statista.com/statistics

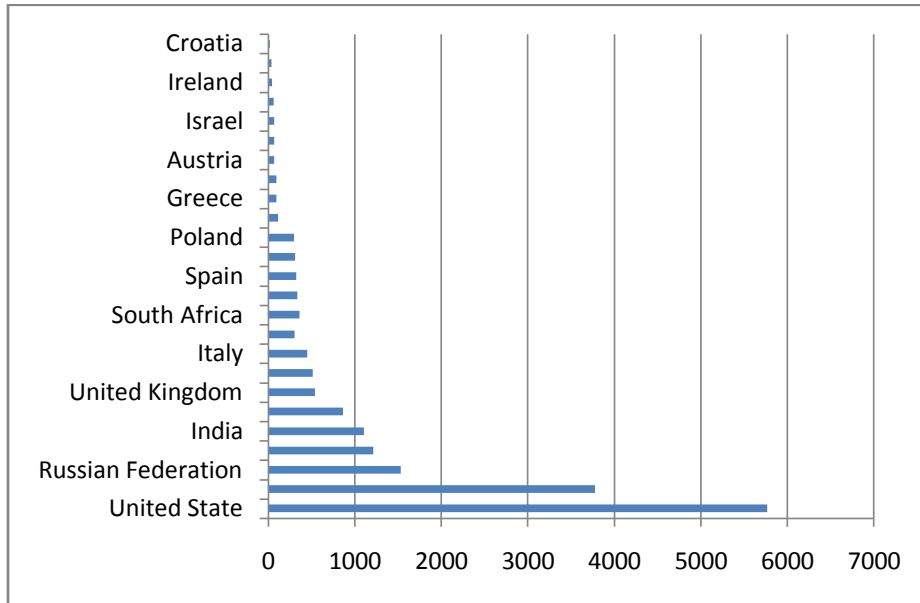


Figure 2.4 Total CO₂ Emissions 2002

Source: Statista.com/statistics

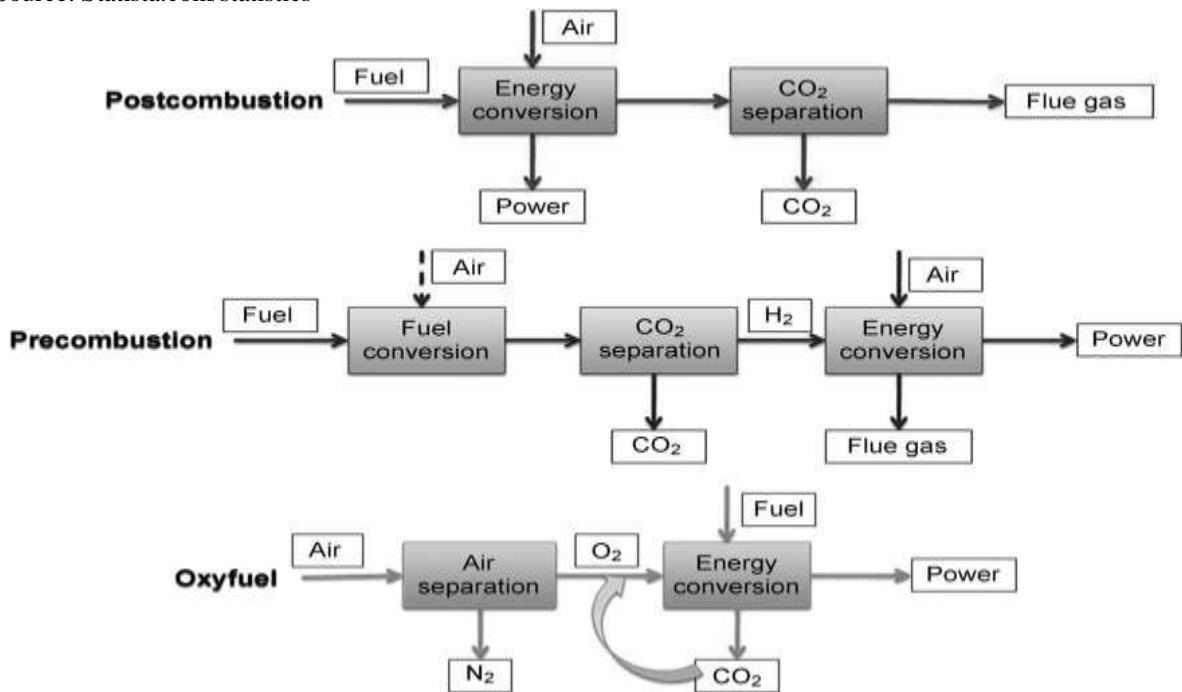


Figure 2.5 Post-, pre- and oxyfuel combustion processes.

Source: Alessandra D.M. et al, 2006

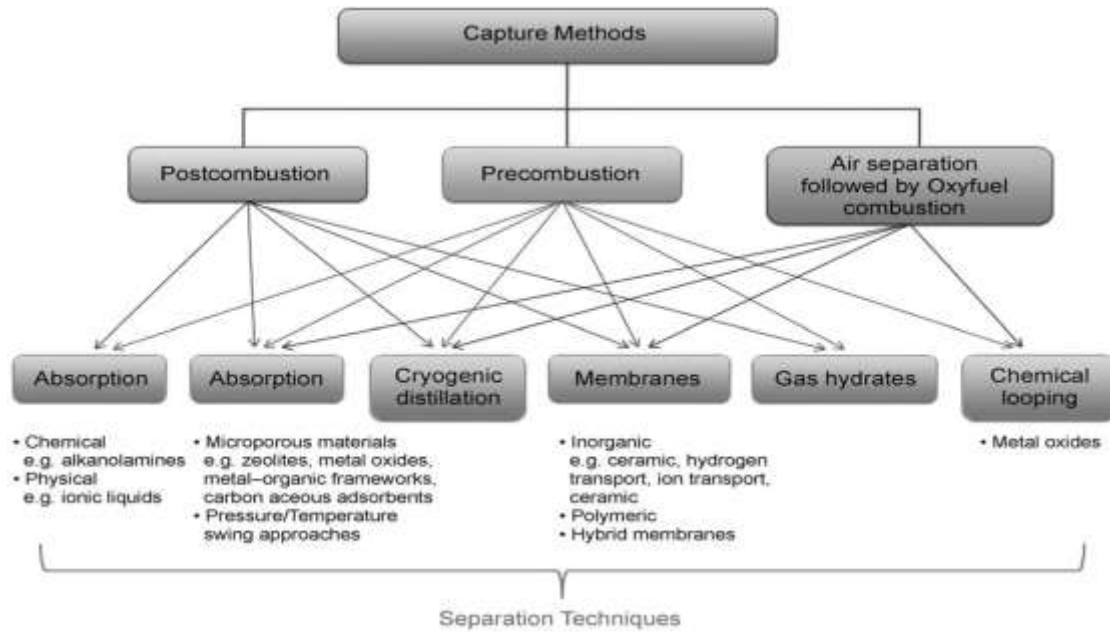


Figure 2.2 Materials for CO₂ capture in the context of postcombustion, precombustion, and oxyfuel processes. Source: Alessandra D.M. et al, 2006

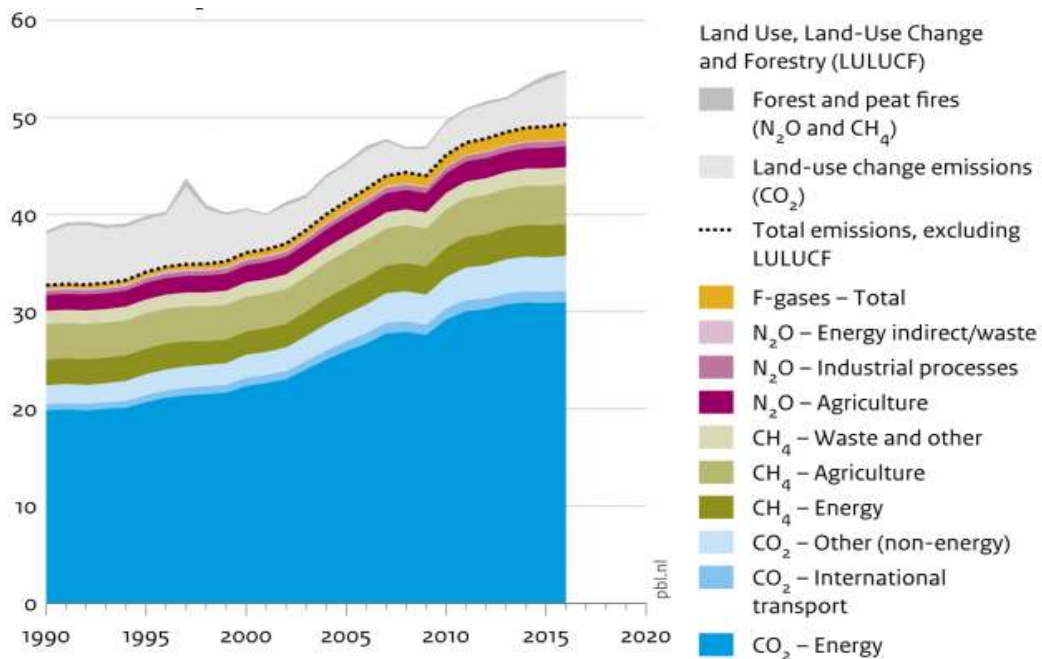


Figure 2.6 Global Greenhouse Gas Emissions, per type of gas and source, including LULUCF Gigatonnes

Source: EDGAR v4.3.2 (- JRC/PBL 2017), Houghton and Nassikas (2017)

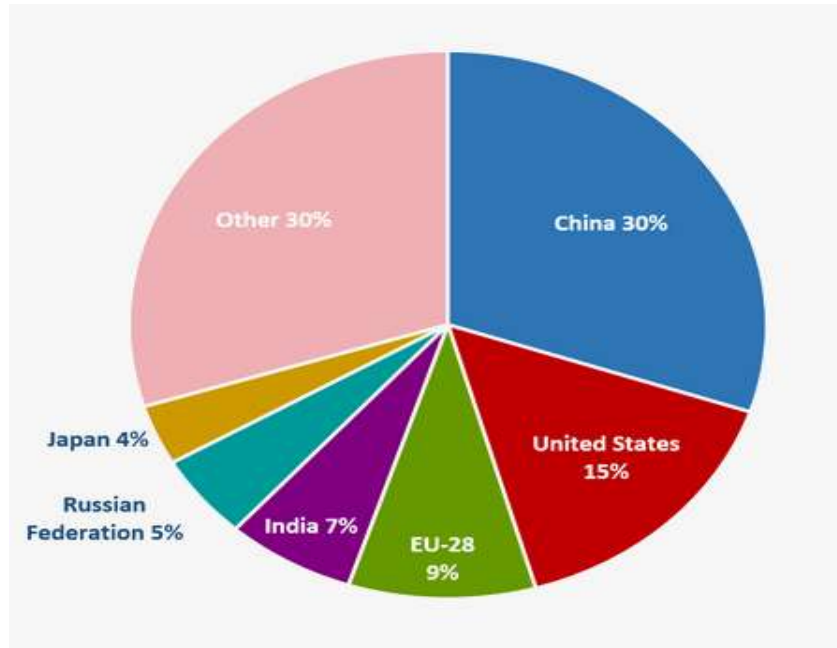


Figure 2.7 2014 Global CO2 Emissions from Fossil fuel Combustion and Some Industrial Processes
 Source: Boden, T.A., Marland, G. and Andres R.J. (2017)

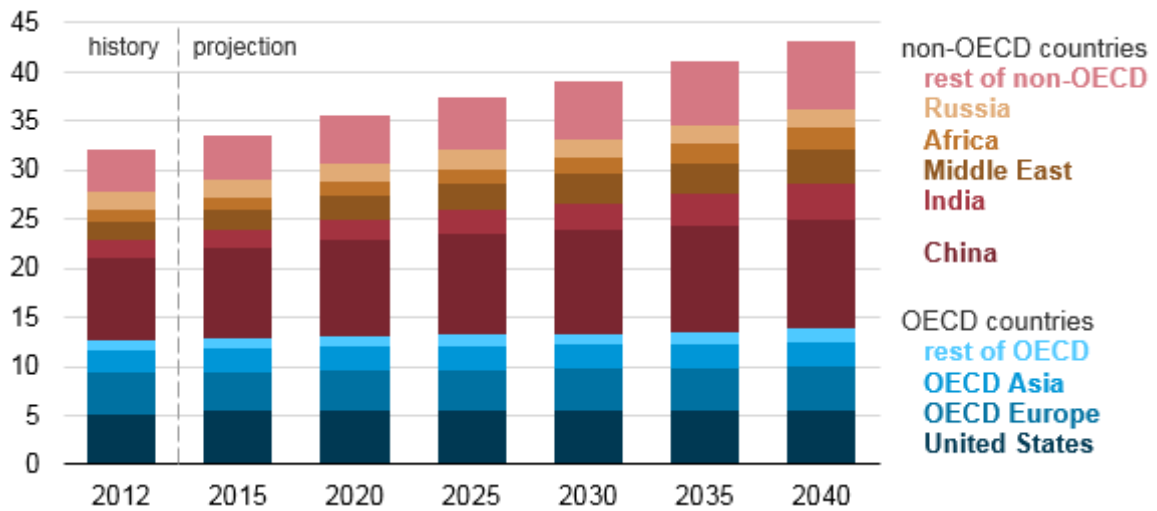


Figure 2.8 Energy Related CO2 Emissions by country or regions 2012- 2040 in Billion metric tons
 Source: US Energy information Administration, International Energy Outlook, 2016.

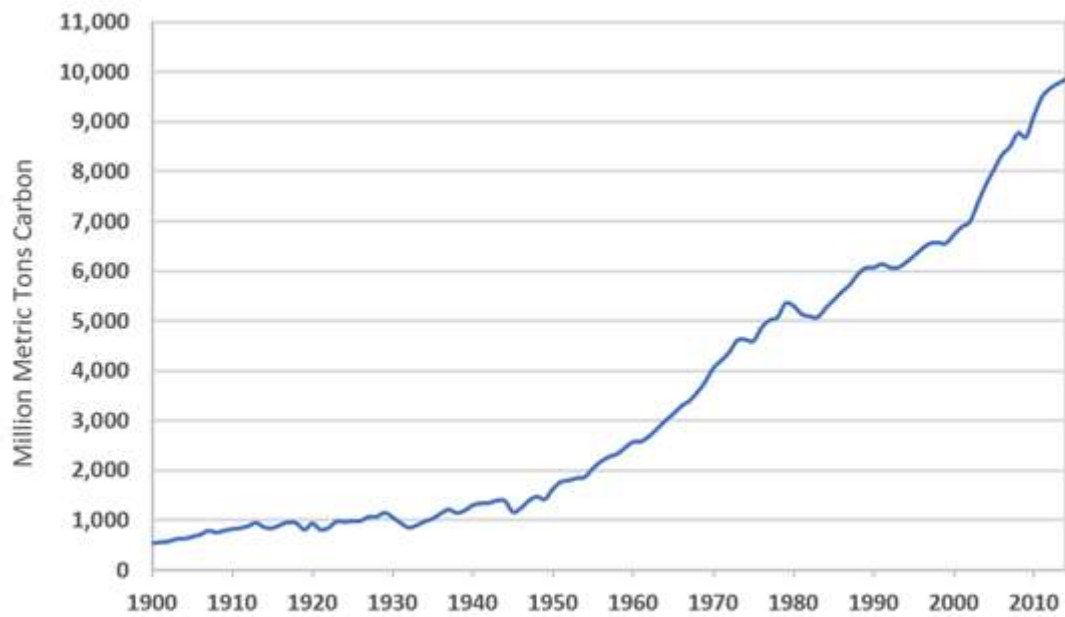


Figure 2.9 Global Carbon Emissions from Fossil Fuels, 1900- 2014

Source: Boden, T.A., Marland, G. and Andres R.J. (2017)



Figure 3.1 Jenkins CO₂ Capture and Sequestration Unit



Figure 3.2 The Reactor



Figure 4.1 Precipitates of CaCO_3