CEDTECH International Journal of Engineering & Applied Science
Volume 3, Number 4, December 2022
http://www.cedtechjournals.org
ISSN: 2756-4533

AN IN-DEPTH STUDY OF CARBON DIOXIDE (CO_2) AND THE MAJOR TECHNIQUES IN THE PRODUCTION, STORAGE AND RE-USE OF CO_2

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ABSTRACT
The focus of this study is to "determine the quantity of CO_2 produced in a local Ethanol plant". However, due to the broad scope of the study, it is presented in part-1 and part-2. Part-1 is presented in this volume and part-2 will be presented in subsequent volumes. The aim of part-1 is to have an in-depth study of CO_2 and the major techniques in the production of CO_2. This part of the study discussed and presented the physical and chemical properties of CO_2. It described the various technologies in the production of CO_2 and showed diverse techniques in removing, storing and re-using the CO_2 produced. This part also gave an insight to the uses of CO_2 in all spheres of life and its harmful effects in the atmosphere and to the human life.

Keywords: *Techniques, Production, Carbon Dioxide, Removal, Storage, Re-used*.

INTRODUCTION
The substance called carbon dioxide (CO_2) is useful if available in desired quantities but very harmful and devastating if available in very large quantities depending on the use and where it is released to. The focus of this study is to "determine the quantity of CO_2 produced in a local ethanol plant". The scope of this study is very broad because of the modeling, simulations and equipment design that will be carried out using Aspen HYSYS software and so the study will be presented in part-1 and part-2. Part-1 is titled "An in-depth study of CO_2 and the major techniques involved in the production of CO_2" while part 2 is titled "The determination of the quantity of CO_2 produced in a local ethanol plant using Aspen HYSYS software". So in this volume, part-1 will be presented and part-2 will be presented in subsequent volumes. The study

is very important to researchers in two ways: firstly, to give a very broad insight to and an in-depth study of CO_2 and secondly to use Aspen HYSYS, CHEMCAD or other similar software to accurately predict the quantity of CO_2 to be produced for various uses.

MATERIALS AND METHODS

Figure 1.0 is a diagrammatic description of CO_2 production in a local ethanol plant using Aspen HYSYS software. In view of the process equipment involved and the nature of the in-depth study on the substance CO_2, the methodology applied in this volume will be descriptive and will be discussed under the following headings: The Historical Perspective of CO_2, What is CO_2, Properties of CO_2, Sources of CO_2, Importance of CO_2, Harmful Nature of CO_2, Capture and Storage of Carbon Dioxide, Biomass Conversion Technology with CO_2 Capture, and Fossil Fuel Conversion Technology with CO_2 Capture.

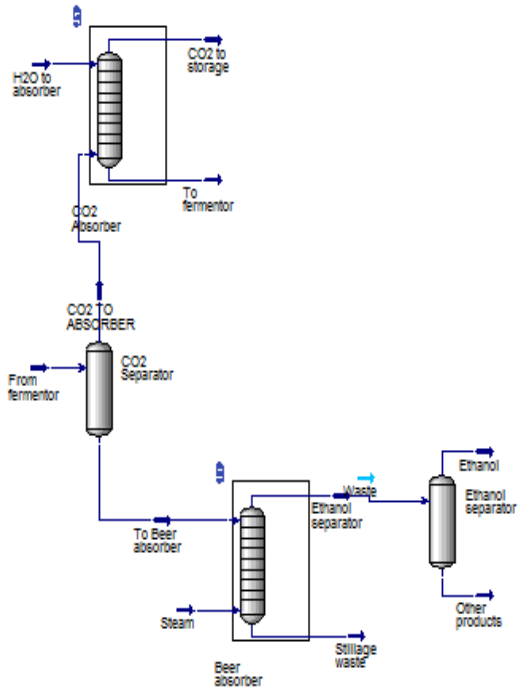

Figure 1.0: CO_2 production in a local ethanol plant using Aspen HYSYS software

The Historical Perspective of CO_2

It was in the 16th century (in the 1750s) CO_2 was identified by a physician called Joseph Black who is a Scottish chemist. Since then the quantity of

CO_2 released into the atmosphere due to human activities has been on the increase the last 150 years (Lenntech, 2009). After the industrial revolution that started in 1850 carbon dioxide in the atmosphere has been on the increase as a result of the activities of human. Many researchers like Jan Baptista van Helmont, Svante Arrhenius, Charles Keeling, etc worked separately on carbon dioxide, burning processes and global warming in the 17 century. (John, 2001; UCAR, 2000; Rebecca and Dlugokencky, 2022)

What is Carbon Dioxide (CO_2)

Carbon dioxide (CO_2) is one of the components of the air and in terms of abundance is far less than nitrogen and oxygen in the atmosphere. Carbon dioxide is a colorless and non-flammable gas at normal temperature and pressure. CO_2 has a faint sharp odor and a sour taste. CO_2 exists as a molecule and a molecule of carbon dioxide is made up of one carbon atom and two oxygen atoms. CO_2 is one of the most important greenhouse gases which bring about global warming. (Lenntech, 2009).

The Properties of CO_2

There are several physical and chemical properties of CO_2. It is most often exists as gas. It is liquid when CO_2 is dissolved in water with a pressure higher than normal. It can be solid when the temperature is below -78 °C. Table 1.0 is a summary of the properties of CO_2. See detailed description of the properties of CO_2 elsewhere (Lenntech, 2009; John, 2001).

Table 1.0: Summary of the Properties of CO_2

Property	Value
Mw	44.01
Sg (at 21°C)	1.53
Cd (in kg/m^3)	468
Ca in air (in ppm)	370,3 * 10^7
St	High
Lq (in kPa)	< 415.8
Sd Solid (in °C)	-78
HCS (in mol/ kg * bar)	298.15
Ws (vol/vol at 20 °C)	0.9

Mw =Molecular weight; Sg =Specific gravity; Cd = Critical density; Ca = Concentration; St = Stability; Lq =Liquid; Sd= Solid; HCS = Henry constant for solubility; WS = Water solubility

The Sources of CO_2

Natural sources

There are two main sources of CO_2 in the atmosphere: Gasses from volcanic rocks and wild-fires. Respiration is another natural source. Respiration is a process whereby plants and animals take in oxygen for the oxidation of food to obtain energy and liberates CO_2. The respiration reaction is given in equation (1). The opposite of respiration is photosynthesis and the reaction is in equation (2).

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O \quad (1)$$

$$6CO_2 + 6H_2O + Sunlight \rightarrow C_6H_{12}O_6 + 6O_2 \quad (2)$$

Synthetic Sources of CO_2

Combustion Process

CO_2 is formed from combustion of materials or burning of substances. Combustion may be as a result of burning of substances (e.g. fossil fuels, wastes, land, forest, bush, agricultural products, in internal combustion engines, etc). When the supply of oxygen is insufficient or there is excess carbon, the result is incomplete combustion that produces carbon monoxide (CO). Carbon monoxide is hazardous to the human life which reacts with oxygen (or oxidizes) to form carbon dioxide. Humans also produce carbon dioxide from cement production activities.

Fermentation Process

Figure 2.0 shows how CO_2 is produced from fermentation in an ethanol plant. The primary objectives of this set-up is to identify the process equipment that would be needed to capture CO_2 from ethanol plants, to measure the quantity of CO_2 that will be produced and to estimate the total costs associated with the process. The reason for the setup was to produce CO_2 to be sold to industrial consumers or transported for EOR operations. (Ray et al., 2018 and Bamikole et al., 2012).

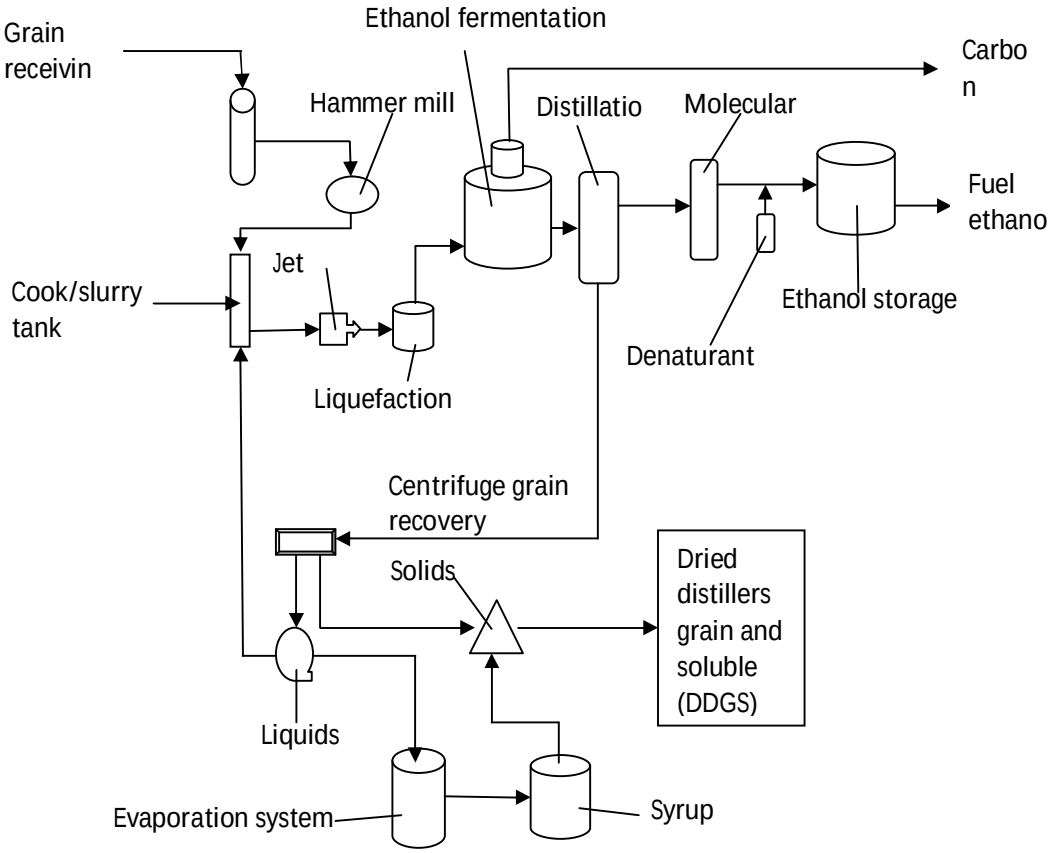

Figure 2.0: An Ethanol Plant

The Importance of CO_2

Humans use CO_2 in diverse ways. The following are some of these uses:

i. In beer and soft drinks, causing 'fizzy' in them.
ii. In yeast and baking powder, making cake to rise.
iii. In some fire extinguishers.
iv. It stops oxygen from burning materials and so has the capacity to stop substances to continue burning.
v. It is used to decaffeinate coffee.
vi. Dry Ice is the solid form of CO_2 which is used in theatres to build stage fogs.
vii. As greenhouse gasses for greenhouse.
viii. It reacts with the water in the ocean, producing carbonic acid that lowers the ocean's pH.
ix. As a refrigerant.
x. For inflating life jackets, bicycle tires and rafts.

xi. For coal blasting.
xii. For plastics and foaming rubber.
xiii. In the growth of plants in greenhouses.
xiv. In immobilizing animals before slaughter.
xv. In carbonated beverages.
xvi. In reservoirs. (UCAR, 2000).

The harmful nature of CO_2Human processes emissions since the industrial revolution in 1850 have caused greenhouse gasses (chlorofluorocarbon's and carbon dioxide) which are harmful to the environment. The increase of these gases has led to rise in temperatures and a greenhouse effect referred to as global warming and global warming have been suspected to cause increases in melting of ice caps and in storms. These melting of ice caps and storms will in turn cause flooding and other problems.

Carbon dioxide also poses some health dangers. Three (3) are discussed here: (1) Asphyxiation. -This is handling carbon dioxide in a confined or unventilated area. This reduces the oxygen available for human health and it is dangerous. (2) Frostbite. - This is caused by handling Solid carbon dioxide for few seconds without appropriate protection which may cause serious harmful effects. CO_2 from fire extinguisher can cause related effects. (3) Kidney malfunctioning or coma. - This is as a result of increase in carbon dioxide concentrations in the human system. Whenever the equilibrium is disturbed, life threatening situations of all kinds may occur.

Capture and Storage of Carbon Dioxide

This is also called Carbon dioxide Capture and Storage (CCS) is a term used for varieties of technologies for reducing CO_2 emissions to the atmosphere. It consists of three distinct stages: CO_2 capture, transport and storage.

There are four CO_2 capturing categories, IEAGHG, 2011. They are as follows:

i. Post-combustion capture;
ii. Pre-combustion capture;
iii. Oxyfuel combustion capture;
iv. Capture from industrial processes

We describe these technologies briefly below and the separation techniques are also briefly tabulated in Table 2.0.

Post-combustion Capture

This technique is used to capture CO_2 from the flue gas of a combustion process such as combustion in a boiler, gas turbine or industrial process yielding CO_2. Capture techniques and mechanisms used are shown in Table 2.0.

Pre-combustion Capture

These are technologies that capture CO_2 before the combustion of the fuel. In these techniques, sometime a syngas (hydrogen and carbon monoxide) is formed from a carbonaceous fuel. It is called reforming or partial oxidation for gaseous fuels and gasification for solid fuels. CO_2 is later recovered from the carbon monoxide (CO) through a water gas shift reaction as shown in Table 2.0.

Oxyfuel Combustion Capture

This technique removes nitrogen from the combustion medium and allows combustion to take place with oxygen and the final result is a flue gas containing CO_2 and H_2O (Table 2.0).

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Capture from Industrial Processes

Examples of industrial processes where CO_2 is captured include the following: Production of cement, iron and steel, ethelene (oxide), ammonia, hydrogen, natural gas sweetening processes and refinery processes.

Table 2.0: CO_2 Separation Techniques

Separation techniques	Post-combustion	Oxyfuel-combustion	Pre-combustion
Chemical and physical absorption	Chemical solvents		Physical solvents Chemical Solvents
Membranes	Polymer, Ceramic Hybrid, Carbon	Polymer	
Adsorption	Zeolites Active carbons Sorbent types: "molecular basket"	Zeolites Active carbons Adsorbent for separation of O_2/N_2	Zeolites Active carbons Aluminum and silica gel
Cryogenic		Distillation	

Biomass Conversion Technologies with CO_2 capture

The use of biomass for the production of energy and biofuels (e.g. ethanol) produce CO_2 emissions. Biomass processes include the following: pulp and paper production, production of biofuels from starch (corn), Sugar (sugarcane) and boil crops (palm and rapeseed oil). Four examples of biomass conversion technologies with CO_2 capture is mentioned below and are also shown in figure 3.0 (IEAGHG, 2011).

i. Biological processing (e.g. fermentation) for fuel production and CO_2 capture
ii. Biomass gasification with shift and pre-combustion CO_2 separation to produce hydrogen and rich syngas, which can be used for the production of chemicals, fuels and power
iii. Production of power and heat by combustion combined with post combustion capture
iv. Production of power and heat based on oxyfuel combustion.

v.

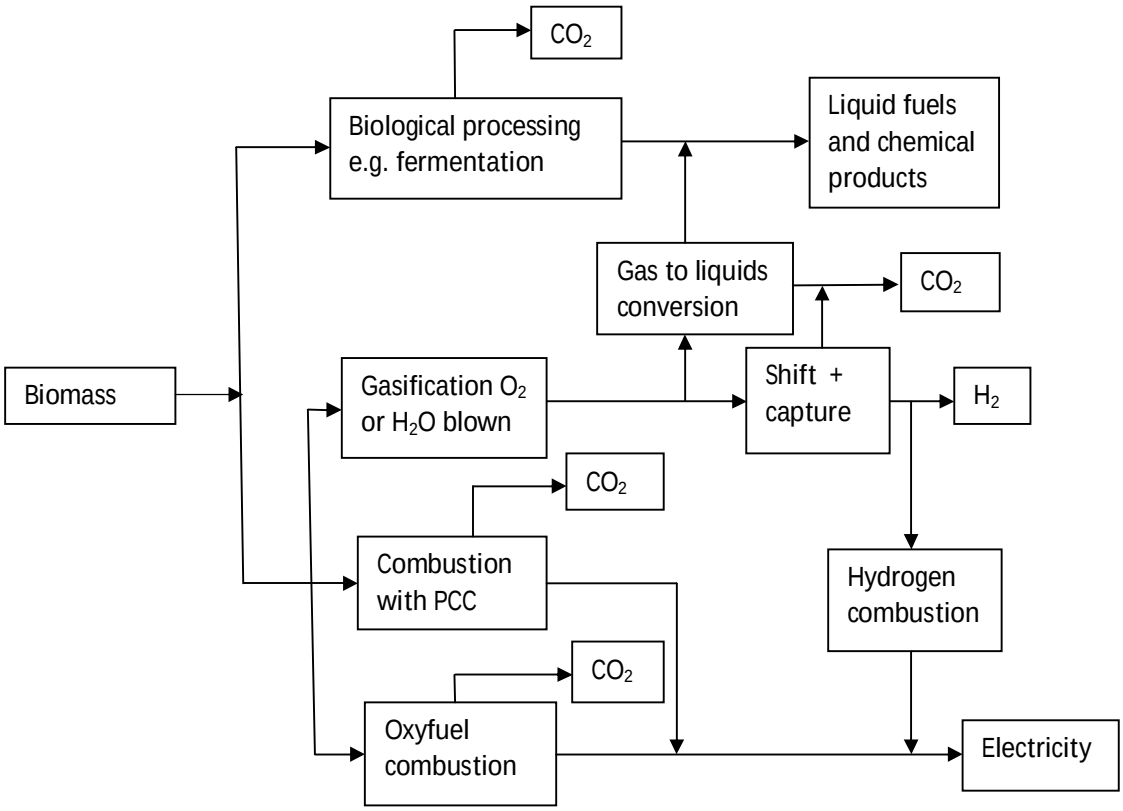

Figure 3: Biomass Conversion Technologies

Eero and Tero, 2020 stated that Even though fossil emission could be decreased or even eliminated, there is a need to start removing CO_2 from the atmosphere. The removed CO_2 could be either stored permanently to a reservoir (Carbon Capture and Storage) or utilized as a raw material in a long-lasting product (Carbon Capture and Utilization). The capture of CO_2 could be done by direct air capture, or capturing CO_2 from biogenic sources. A similar reactor setup used by Eero and Tero, 2020 is shown in figure 4.0. The gas inlet is at the bottom of the reactor, and the liquid inlet is at the top. Part of CO_2 from the inlet gas is absorbed into water.

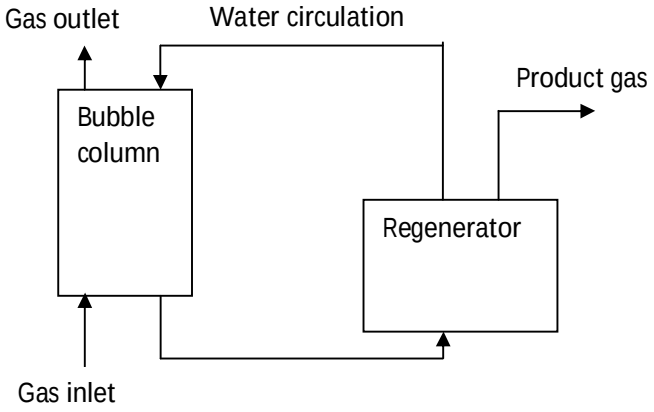

Figure 4.0: CO_2 Absorption Column using Water

Raschig USA (2022) stated that ethanol (CH_3CH_2OH) is widely produced as a fuel additive in the USA. Fermentation is the basic process that makes ethanol and in fermenters microorganisms consume the feed stock (be it corn, sweet sorghum, sugarcane or others) and produce gases and ethanol as a byproduct. Ethanol is a relatively volatile liquid at normal temperature and pressure. The primary constituent of the off gas is CO_2. Acetaldehyde and other volatiles are also present in the fermenter off gas. In an ethanol plant a packed bed wet scrubber is always used to clean the off gas from the fermenter.

Fossil Fuel Conversion Technologies with CO_2 Capture

A fossil fuel is formed in the earth's crust from the remains of dead plants and animals that is taken and burned as a fuel. The three major fossil fuels are coal, crude oil and natural gas. The three main uses of fossil fuels are to be burned to give heat (e.g. for cooking or heating), to power engines, or to produce electricity. The burning of fossil fuels also generate carbon dioxide (CO_2) which is captured for future use. (Wikipedia, 2022).

RESULTS AND DISCUSSION

As stated in the introduction, the study is enormous and it is to be presented in parts. In view of this and to stay within the limits of this part, the discussion will be on the tables and the figures presented in the methodology.

Table 1.0 shows the summary of the properties of CO_2. This table shows that CO_2 is a gas and its solubility in water can only be made possible with a high pressure. The reason water is mentioned here is because we will use water to absorb CO_2 produced in bubble columns, flash columns and distillation columns and later capture the CO_2 in separation columns using their boiling temperatures differences and at lower pressures. Table 2.0 shows some of the known separation techniques to capture the produced CO_2. In part-2 of this study, we will use the physical absorption technique to capture CO_2 produced in an ethanol plant.

Figure 1.0 shows a diagrammatic description of CO_2 production in a local ethanol plant using Aspen HYSYS software. In this local ethanol plant, CO_2 released from the fermentation process was sent to the CO_2 separator where CO_2 and other gasses were separated from other fermented products (beer and others) and were sent to the CO_2 absorber where water was used to absorb the CO_2 and was sent for measurement, storage and use. Figure 2.0 shows an ethanol plant where CO_2 is released. In figure 3.0, Biomass conversion techniques were shown where there are many routes to the production of CO_2. The fermentation technique will be considered in part-2 of this study. Figure 4.0 shows CO_2 absorption column using water. In part-2 of this study, we will show how the quantity of CO_2 in this absorption column produced in a local ethanol plant is determined using Aspen HYSYS software.

With the above, one can conclude that an In-depth study on CO_2 is very important. This is because of the following reasons. The study

1. Gave understanding of the physical and chemical properties of CO_2.
2. Described the various technologies used in CO_2 production.
3. Gave insight to the uses of CO_2 in all spheres of life and its harmful effects in the atmosphere and to the human life.
4. Showed various techniques CO_2 so produced can be removed, stored and re-used.

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