
Title of the Research

# A Structure for Exhausts Clean-up and $CO_2$ Utilisation for Reduction of Atmospheric Emissions

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# DECLARATION

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# ABSTRACT

The impacts of atmospheric emissions of greenhouse gases and the need to recover materials and energy from wastes has progressed the subject of carbon capture to continue exploiting new technologies for carbon capture and utilization as best way to curb the effects of atmospheric pollution. This study investigated the photo-dissociation of carbon dioxide into $C + O_2$ in the presence of ultraviolet energy to determine its application for exhausts clean-up and reduction of atmospheric emissions. The experiment was performed by passing carbon dioxide gas (98.9% $CO_2$, Afrox suppliers) through a stainless steel tube (92.5cm x 11cm Packing) containing an ultraviolet bulb (40w, 254 nm, Filters Shop, SA). The experiment was repeated at varying set of reaction conditions such as time, temperature, and pressure. The product gas was collected from the system's outlet and analysed through gas chromatography. The resultant chromatographic peaks were compared to those generated by the standards for carbon monoxide, carbon dioxide, and oxygen gases for qualitative and quantitative analysis. The study also hypothesised that zeolite materials could purify oxygen from ambient air due to their strong nitrogen adsorption capacity that may produce an oxygen-enriched stream. The oxygen-enriched air could then be utilised as feed air for combustion so that the formation of nitrogen oxides by-products avoided, thus lowering the pollution content of an exhaust. The conclusions of the study are such that, the pollution content of exhausts can be lowered through oxy-combustion and breaking carbon dioxide into $C + O_2$ by Ultraviolet energy.

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CEC, capacity of exchange of cations

ESA, Electric Swing Adsorption

EDX, Energy Dispersive X-ray analysis

GC, Gas Chromatography

ICE, Internal Combustion Engine

LSX, Low Silica Zeolite X

MOFs, Metal Organic Frameworks

PSA, Pressure Swing Adsorption

PSI, Polysuccinimide

TSA, Temperature Swing Adsorption

VSA, Vacuum Swing Adsorption

UV, Ultraviolet

XRD, X-ray diffraction Fourier Transform Infra-Red Spectroscopy

# Chapter 1: Background and Motivation

## 1.1 Introduction

The atmospheric emissions of greenhouse gases, chiefly $CO_2$, is one of the most pressing issues and most debated environmental problem today Tan *et al.* (2012). According to the National Oceanic and Atmospheric Administration (NOAA) report, USA, the world has been heating since the 1980s as a consequence of atmospheric emissions due to anthropogenic activities such as the power generation by burning fossils (Tan et al., 2012). According to the World's Environmental Organizations, a critical level of $CO_2$ concentration (400 ppm) was reached by 2013, which was 40% higher than the levels accounted by mid-1800s (Habib et al., 2016, Wang et al, 2017).

Typically, 85% of energy in the world is still sourced from fossils (coal, oil and gas) (Ngoy *et al*, 2014), and predictions are such that, the trend will increase by 2050, since burning fossils is still the most inexpensive way of sourcing energy in large energy-consuming countries (Wang et al, 2017). The impacts of climate change and global warming are heartening the energy transition probably at an expense and pace which cannot be met, that is; in most developing countries, there may be no other alternatives, either to leave people without energy or to implement the cheapest energy sources (fossils). Renewables forms of energy are environmentally cleaner but, they are very capital intensive to start up and not available to all.

When fossils are combusted $CO_2$ is inevitably released as by-products into the atmosphere where it causes chain reactions that influence climate change and global warming (Volkswagen, 2012). Emissions of greenhouse gases have changed the world's climate (Tan et al., 2012, Santos, 2017). According to the "Swiss Sustainable Finance (SSF, 2020)", the global average temperature rise of 2°C is the threshold, but increasing it to 5°C could lead to a loss of US$ 7trillion, whilst an increase up to 6°C could lead to a net loss of the present world's economy value of US$ 13.8 trillion. Thus, the "International Panel on Climate Change (IPCC, 2007)" appeals that the global $CO_2$ emissions must at least be limited to 50% in order to limit the average global temperature to $2^0$C.

Santos (2017) believes that, point-source $CO_2$ capture, also known as $CO_2$ capture from the source of release, is by far the greatest possibility to reduce further release of $CO_2$ into the

atmosphere and it is a selected track towards sustainable application of fossils energy. This statement is well supported by the 8th Trondheim Conference on Carbon Capture, Transport and Storage (CCS) held in Trondheim, Norway in June, 2015 which focused on research and development of CCS technologies (Røkke et al., 2016).

The present technologies for $CO_2$ capture largely focus on power plants; however, a study by Hamed (2015) revealed that, several other sectors like transportation relatively emit large amounts of $CO_2$. The transportation sector emits almost 30% of all annual $CO_2$ emissions (Tan et al., 2012, Santos, 2017). An unexplored gap for carbon capture from movable sources exist (Santos 2017) and this motivates the expansion of existing carbon capture technologies beyond power plants for the overall reduction of carbon emissions whilst opening a window of opportunities for energy and materials recovery from carbon-based wastes like $CO_2$.

The carbon capture technologies at post-combustion stage are highly challenged by operating conditions such as temperature, flow rate, low partial pressure of $CO_2$, and the limiting kinetics of adsorption /absorption materials (Singo et al., 2017). Possibly, the energy penalties of sorbent regeneration have added another challenge that prevented the application of this technology, particularly, on movable sources of emission. Thus, Sullivan and Sivak (2012) believes that, carbon capture technologies expanded to trapping $CO_2$ from delocalized (movable) sources of emission can positively contribute to the relative reduction of annual $CO_2$ emissions targets whilst fostering sustainable application of fossils energy.

## 1.2 Problem statement

According to several literatures, carbon dioxide is the most important greenhouse gas influencing climate change, global warming, and the depletion of ozone layer. This is a survival risk for the humanity. The U.S.A Department of Transportation (2009) discovered that, the amount of carbon emitted by transportation is relatively high, accounting for almost 30% of all annual $CO_2$ emissions. Santos (2017) believes that, carbon capture technologies are still unexplored for delocalized sources of emission like transportation. The emission reduction targets set forth by counties' regulations may not be achieved if carbon capture strategies are directed towards large scale power plants only. Thus, targeting carbon capture to all emission sources (mobile and fixed) could offer a holistic approach towards lowering the levels of atmospheric emissions of greenhouse gases.

Most carbon capture technologies are post-combustion and highly challenged by operating conditions such as temperature, flow rate, low partial pressure of $CO_2$, low kinetics of adsorption /absorption, in addition to energy penalties for regeneration of sorbent materials (Singo et al., 2017). These challenges have possibly limited the application of post-combustion capture technology on movable sources of emission.

In spite of the advent of low-emission alternatives like biofuels, fossils are still the most popular source of transportation energy (Sullivan and Sivak, 2012). Nonetheless, combusting fossils inevitably generate $CO_2$ which has increased the public awareness to the subject of atmospheric emissions. Hence, Andreoli (2017) emphasizes the need to decarbonize the fossils-based energy whilst transitioning to cleaner source of renewable energy. Of course, this may require the development of new carbon capture technologies as means of ensuring cleaner fossils energy for a sustainable energy future. Surely, carbon capture will contribute for mitigation of impacts of atmospheric emissions whilst fostering sustainable application of fossils-based energy (Sullivan and Sivak, 2012). That way, Carbon Capture and Utilization (CCU) could go beyond environmental by unfolding downstream business opportunities that may result in materials and energy recovery from carbon-based wastes like $CO_2$.

## 1.3 Research Aims and Objectives

This study aims to design a structure for reduction of pollution content of exhausts to curb the effects of atmospheric emissions, precisely; the study investigates whether or not the UV-light can break $CO_2$ into $C + O_2$ and what the effects of time, temperature, and pressure are on reaction performance. As well, the study presents the design of an air separator (reactor) for oxygen purification as feed air for combustion (oxy-combustion) as an important component for future applications of the complete design process of the structure.

# Chapter 2: Literature Review

## 2.1 Today's Energy Challenge

Climate change is one of the major challenges the world faces today due to an increased amount of greenhouses being released into the atmosphere, chiefly carbon dioxide ($CO_2$). Amongst humans' activities, the energy consumption accounts for the largest part of greenhouse gases emissions that have reached about 400 ppm by 2014, which is 40% higher than the mid-1800s (Wang *et al*, 2017). Carbon dioxide is inevitably produced as by-product and released into the atmosphere when fossils are combusted to generate energy, and the net effects are the climate change and global warming (Singo et al. 2017). According to Wang *et al* (2017), the burning of fossils is the most inexpensive way of generating energy in large energy-consuming countries. Typically 95% of energy in the world is still sourced from fossils (coal, oil and gas) (Ngoy et al., 2014). Consequently, as fossils continue to be the main source of energy for the world, the use of coal, natural gas, and petroleum will increase.

## 2.2 Sources of Atmospheric Emissions

Transportation alone roughly accounts for 30% of all $CO_2$ emissions in the United States, as illustrated in the figure (2.1) below;

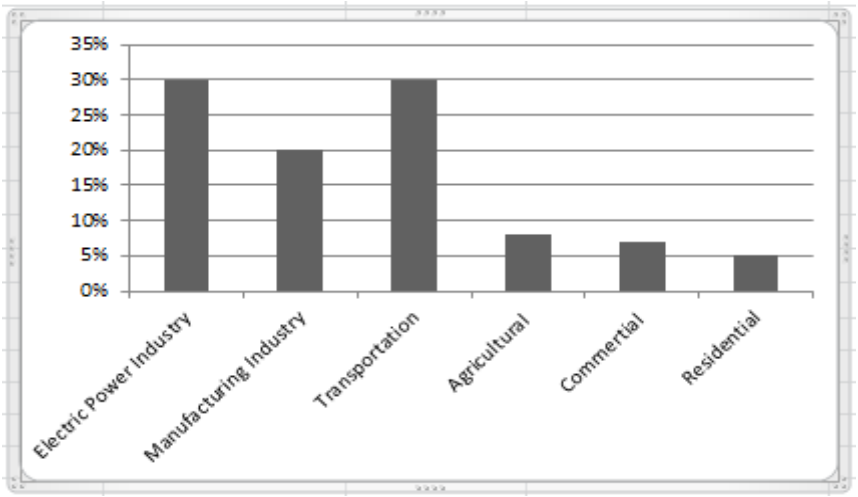


Figure 2.1: Share of Emissions by Sources (Adapted from U.S.A Department of Transportation, 2009)

As depicted in figure (2.1) above, just the road vehicles are responsible for almost 57% all transportation emissions. As vehicles move on roads, an internal combustion takes place inside engines that convert the energy stored in fuels into mechanical energy to rotate the wheels (Ministry of Natural Resources Canada, 2014), $CO_2$ is emitted as a by-product in the process. The Ministry of Resources Canada (2014) estimates that, burning 1 L of gasoline may approximately produce 2.3 kg of $CO_2$ . Hence, an average vehicle of a 60 litters petrol tank would release approximately (2.3 x 60) Kg of $CO_2$ into the atmosphere. The table (2.1) below gives an averaged amount of $CO_2$ emitted by fuel types;

Table 2.1: $CO_2$ Emissions by Fuel Type (Ministry of Natural Resources Canada, 2014).

| Fuel Type | $CO_2$ Exhaust Emissions Kg /L |
|---|---|
| Gasoline | 2,29 |
| E 10 (10% Ethanol + 90% Gasoline) | 2,21 |
| E 10 (85% Ethanol + 15% Gasoline) | 1,61 |
| Diesel | 2,66 |
| B5 (5% biodiesel + 95% Diesel) | 2,65 |
| B5 (20% biodiesel + 80% Diesel) | 2,62 |

The fuel consumption of vehicles is commonly measured in average liters of fuel used per 100 kilometers run (Ve and B2, n.d.). According to the U.S Energy Information Administration "EIA (2011), although the fuel consumption of cars depends strongly on traffic conditions and the driving style, in average a car may consume 5 liters of fuel per 100 km, which implies that, for every 100Km run (5 X 2.3) kg $CO_2$ is released. Thus, a vehicle of 50 litters' tank would emit approximately 115 kg of $CO_2$ in a 1000km run.

## 2.3 The Exhaust's Gas Composition

A typical exhaust gas composition of a petrol engine comprises approximately 4% $CO_2$, 13% Water ($H_2O$), and 71% $N_2$, with only 1-2% other minor constituents such as hydrocarbons (HC), nitrogen oxides (NOx), and carbon monoxide (CO), but a diesel exhaust's gas composition differs slightly comprising 12% $CO_2$, 11% $H_2O$, 10% $O_2$, 67% $N_2$, with only 0.3 % other minor components such as particulate matter (PM), sulphur oxides ($SO_2$), HC, NOx, and CO (Volkswagen, 2012).

The air is a common requirement for combustion of fuels and it is normally composed of 78% $N_2$, 21% $O_2$, with only 1% comprising other gases like Argon (Volkswagen Ag, 2012). Clearly, $N_2$ is by fraction the largest constituent in the ambient air as well as in exhaust's flue gas (see Fig. 2.2), assume W/v% exactly 1g /100cm$^3$. Hence, the $CO_2$ capture (separation) process is mostly between $CO_2$ and $N_2$.

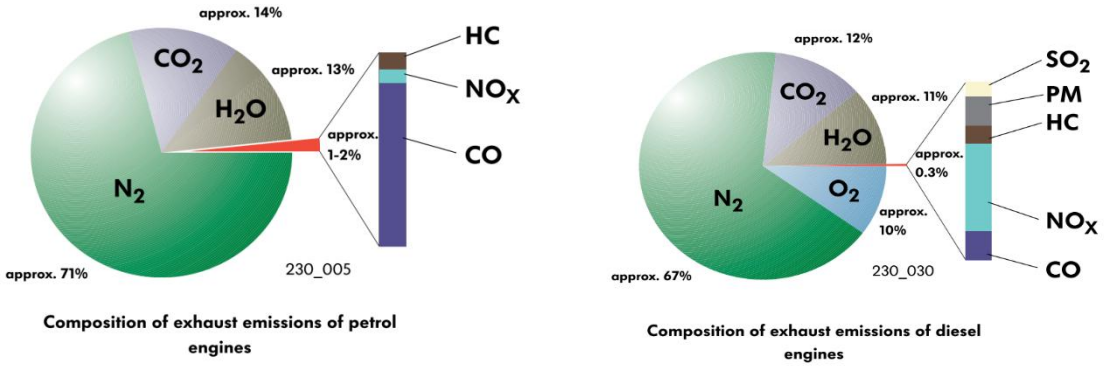


Figure 2.2: Diesel and Petrol Exhaust's Gas Compositions (Volkswagen Ag, 2012).

## 2.4 Emissions Reduction Schemes for Road Transportation

According to Volkswagen (2012), there have been a few resolutions aimed to curb gases emissions by road traffic; however, the number of private and freight car owners increasing every year, as well as the size upgrades and automation of modern vehicles have cancelled out any positive benefits for emissions reduction (Volkswagen, 2012). Evidently, an effective reduction of gases emissions may require the development of exhaust treatment technologies in addition to improved designs of more fuel-efficient engines.

The use of less-emissive alternative fuels such as ethanol, hydrogen, and natural gas as well as the switching of public attitudes and behaviors must all become part of emissions-reduction strategy in addition to exhausts treatment technologies (Hodges, 2009b, Sullivan and Sivak, 2012). Hodges (2009b) affirms that, the public transportation emits less greenhouse gases per passenger than single-occupancy (private) vehicles. For example, the rail transportation emits 60 to 70% less greenhouse gases, and the buses emit 33% less (Hodges, 2009b). These benefits are understood based on a larger number of passengers in trains and buses sharing the same unit rather than a fewer number of occupants in private vehicles. Thus, the switching of public attitudes and behaviors from private to more public

transport use could become one of the greatest approaches for an individual reduction of carbon footprint. According to Sullivan and Sivak (2012), reducing the pollution content of exhausts is a practical emissions-reduction strategy given that, fossil are still the most inexpensive form of energy in the foreseeable automotive future.

## 2.5 Carbon Capture and Storage Projects

There are at least three basic steps in Carbon Capture and Storage (CCS) process, namely; the $CO_2$ separation from other gas constituents, transportation, and storage in a manner that must prevent $CO_2$ from back release into the atmosphere (Fig.2.3).

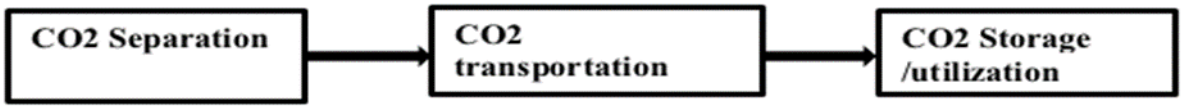


Fig. 2.3: CCS Process (Adapted from Ronca, 2019)

Carbon capture is gradually gaining an acceptable entry as technology option to reduce greenhouse gas emissions along with other strategies such as the use of energy alternatives, and the energy efficiency schemes that emit less or permit consumption of less amount of energy (Feron and Hendriks, 2005). Feron and Hendriks (2005) believe that, carbon capture technologies will make it possible to sustain the use of fossils, while drastically reducing carbon emissions.

Ronca (2019) declared that, carbon capture existed since a few decades ago for gas and oil enhanced recovery rather than for environmental protection. Therefore, the idea of carbon capture for environmental reasons is still novel. Figure (2.4) blow depicts a few carbon capture and storage projects across the globe.


Fig 2.4: CCS Projects across the Globe (MapLink Tale Atlas, 2012)

## 2.6 Carbon Capture Routes

There are at least three common technological routes for carbon capture, namely; the post-combustion, pre-combustion, and the oxy-fuel combustion as discussed below;

### 2.6.1 Post-Combustion

In post-combustion $CO_2$ is sequestrated from the exhausts' flue gas after combustion (Ronca, 2019). Here, $CO_2$ is separated under low pressure and low concentrations, typically 1bar and 3-20% content, from a mixture of other impurities such as Nitrogen oxides (NOx) and Sulphur oxides (SOx) (Feron and Hendriks, 2005). Wang *et al.* (2016) thinks that, post-combustion is one of the most practical carbon capture techniques because it is an "end-of-pipe" and last stage combustion process. Advantages of this process includes the possibility of retrofitting old systems by simply adding a "filter" that can trap desired constituents of exhausts flue a gas like $CO_2$ as it travels up a chimney or smokestack (Ronca, 2019). Ronca (2019) explained that, the filter is actually an absorbent or solvent for $CO_2$ which must later

be heated to release water vapor and a concentrated stream of $CO_2$. This technology can prevent 80 to 90% of a power plant's carbon emissions from entering the atmosphere (Ronca, 2019). Adsorption, usually called "scrubbing process", is currently the most promising technology for $CO_2$ capture but energy-intensive, and various optimization methods have not changed the fact that this technology may lay more burdens on power (Wang *et al* 2017). This recalls the need for further investigations.

### 2.6.2 Pre-combustion

In pre-combustion, $CO_2$ is trapped before combustion (Ronca, 2019). According to the U.S Department of Energy (n.d.), this technology is mostly used for gasification including the "integrated gasification combined cycle power plants (IGCC)" where solid coal is heated under pressure in pure oxygen which results in "Syngas" (hydrogen and carbon monoxide). Consequently, $CO_2$ is captured from a gas mixture with predominantly $H_2$ gas at high pressure (15-40 bar) and $CO_2$-content of 15-40% (Feron and Hendriks, 2005). This Syngas is treated with steam which produces more hydrogen along with $CO_2$, then; separation takes place using an adsorbent, usually amines (Ronca, 2019). Ronca (2019) affirms that, the pre-combustion technology is already in use for natural gas power plants and points out a few advantages over post-combustion $CO_2$ capture, precisely; pre-combustion is lower in cost and provides much higher concentration of $CO_2$ than post-combustion, 15-40% of content, comparably to 3-20% in post-combustion. However, several authors believe that, this technology cannot be used to retrofit old power plants, and it has mostly been applied to coal and natural gas power plants (Jansen *et al*, 2015). Further, Ronca (2019) argues that, the pre-combustion $CO_2$ capture does not guarantee prevention of a power plant's emissions of $CO_2$ into the atmosphere, because it not designed purely for environmental reasons.

### 2.6.3 Oxy-combustion

In this technology, the burning a fossil takes place in nearly pure oxygen which produces flue gas with high $CO_2$ concentration that is almost ready for transport and storage (Wang *et al.* 2017). Ronca (2019) thinks that, since firing a fuel in pure oxygen (oxy-combustion) results in a gas mixture comprising mostly steam and $CO_2$, this technology offers a cost benefit over post-combustion separation as the steam and $CO_2$ can simply be separated by cooling. However, Ronca (2019) acknowledged that, the oxygen required for this technique may

increase costs. This calls for further developments and new approaches in hopes of bringing this cost down. Wang *et al.* (2017) believe that, oxy-combustion can eliminate 90% of a system's emissions into the atmosphere. Considering the ongoing country's stringent regulations and specifications limiting nitrogen and sulphur content to 10ppm in fuels, the air might remain the most important source of nitrogen contaminants in combustion process. This motivates the reason why combusting a fuel in pure oxygen would effectively reduce the pollution content of exhausts in addition to making the $CO_2$ capture process much easier.

## 2.7 Methods and Materials for Carbon Capture

The development of materials and technologies for $CO_2$ capture has been increasing in the past decade (Habib et al., 2016). Habib et al. (2016) points out the size exclusion and the electrostatic interactions properties of sorbent materials as the most important chemical and physical properties defining the selectivity and specificity of adsorption. However, certain molecules do not differ much in terms of size; For example, the diameter of $CO_2$ is 3.30 Å, whereas $N_2$ is 3.64 Å making only less than 0.4 Å size difference (Habib et al., 2016). Perhaps the electronic interactions, rather than size exclusion, remain the most important base for separation of molecules. A few technologies and bases under which molecules can be separated are discussed in detail in the next sections below.

### 2.7.1 Adsorption versus Absorption

Both adsorption and absorption are used for separation of molecules and elements in a mixture (Breeuwsma and Lyklema, 1973, Chitsiga *et al.*, 2016). Two types of adsorption can be identified; the physical adsorption, uses intermolecular forces of interaction, often termed van der Waals adsorption, whereas, chemisorption or chemical adsorption involves rearrangement of electrons between the interacting gas and the sorbent with a consequent formation and rupture of chemical bonds (Breeuwsma and Lyklema, 1973). According to Chitsiga *et al* (2016), the isotherms and the equilibrium of adsorption are usually influenced by the adsorbent's properties such as the surface area, pore size, pore volume, and the functional groups. Most adsorption technologies present the adsorbent either as membranes like polymeric membranes, $O_2$-conducting membrane, facilitated transport membrane or in a crystalline form (beads, pallets, or powder**)** (Wang *et al* 2017)**.**

### 2.7.2 Sorbent Materials for $CO_2$ Capture

Several adsorbents such as amines grafted polysuccinimide (PSI), zeolites, amine-rich nanosilicates, carbon-based adsorbents, metal organic frameworks (MOFs), and alkali-metal-based materials are in use for $CO_2$ adsorption and widely reported in the literature (Chitsiga *et al* 2016). Chitsiga et al. (2016) state that, zeolites have a high capacity for $CO_2$ adsorption of 98g $CO_2$/ kg adsorbent, although carbon-based adsorbents perform slightly better than zeolites with an adsorption capacity of 374g $CO_2$/kg adsorbent. Nevertheless, zeolites and carbon-based adsorbents may demand high-pressure conditions, up to 10 bar, to obtain these capacities (Chitsiga et al., 2016). Chitsiga et al. (2016) think that, amines-grafted PSI is an attractive option for $CO_2$ capture due to its ability to work approximately at atmospheric conditions. However, Wang *et al* (2017) claim that, the energy costs associated with amines regeneration are quite high, this fact is motivating scientists to find alternatives.

Membrane-based physical adsorption are an emerging and very promising technology, unlike chemical adsorption, in most cases, here no chemical reaction takes place in a membrane or column-based separation, and no energy consumption is expected, rather, molecules are separated on basis of sieving (Wang et al., 2017). Adsorption processes are usually reversible, that is; the adsorbent can be recuperated by desorption using Temperature Swing Adsorption (TSA), Pressure Swing Adsorption (PSA), Electric Swing Adsorption (ESA) or Vacuum Swing Adsorption (VSA) (Chitsiga et al., 2016).

In addition to adsorption, Wang *et al* (2017) mentions a few other separation methods including absorption of liquid or gases, cryogenic liquefaction, distillation, direct decarbonisation and biotechnology (e.g. algae production), as summarised in figure (2.5) below.

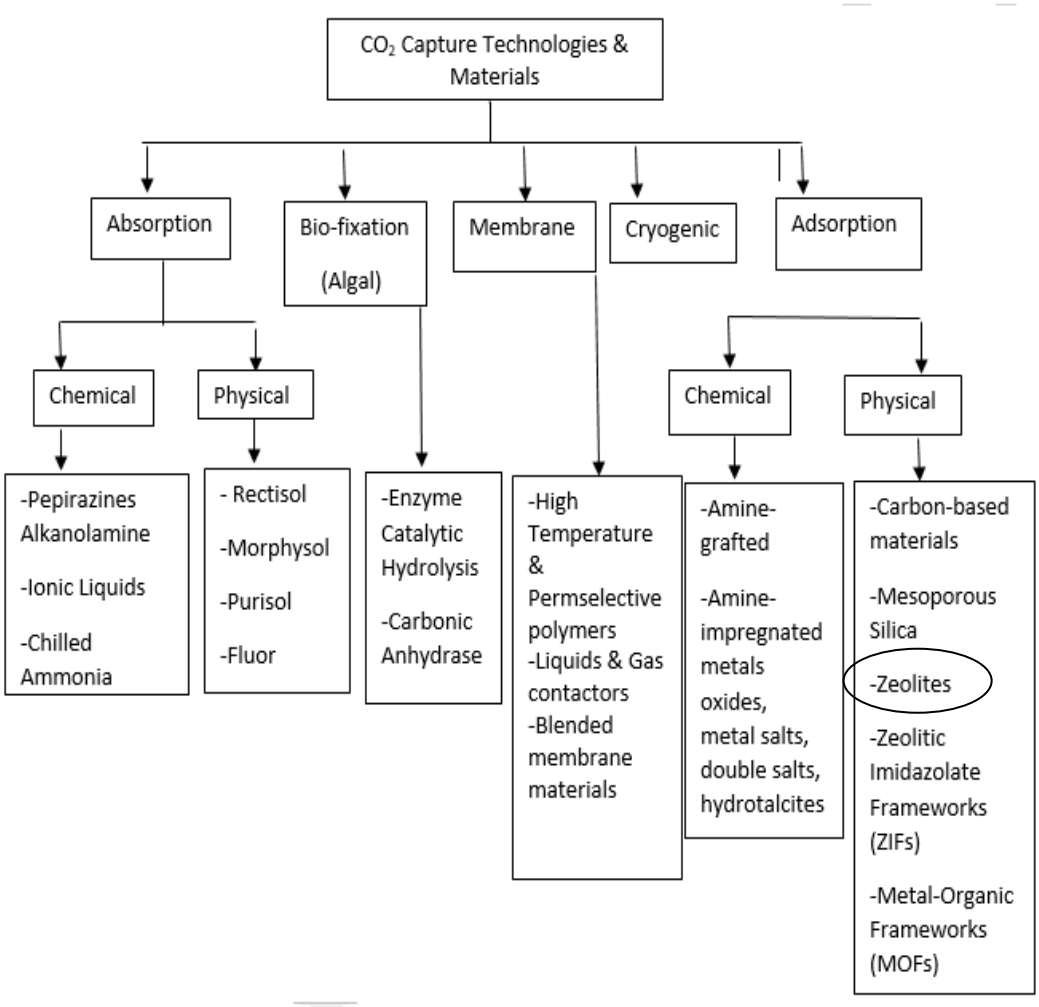


Figure 2.5: Technologies and Materials for $CO_2$ Capture (Adapted from Habib et al., 2016)

Physical sorbents selectively separate chemical species like gases passing through an adsorption bed faster than the other, and this exclusion phenomena gives clear advantages compared to chemical adsorption processes because no energy is required for regeneration (Yoro and Daramola, 2017). Yoro and Daramola (2017) stated that, although physical adsorption is relatively a new technology, its selectivity, flexibility, and low cost makes it widely known compared to conventional separation methods.

Figure (2.6) below depicts a process of separation by physical adsorption in a cylindrical bed.

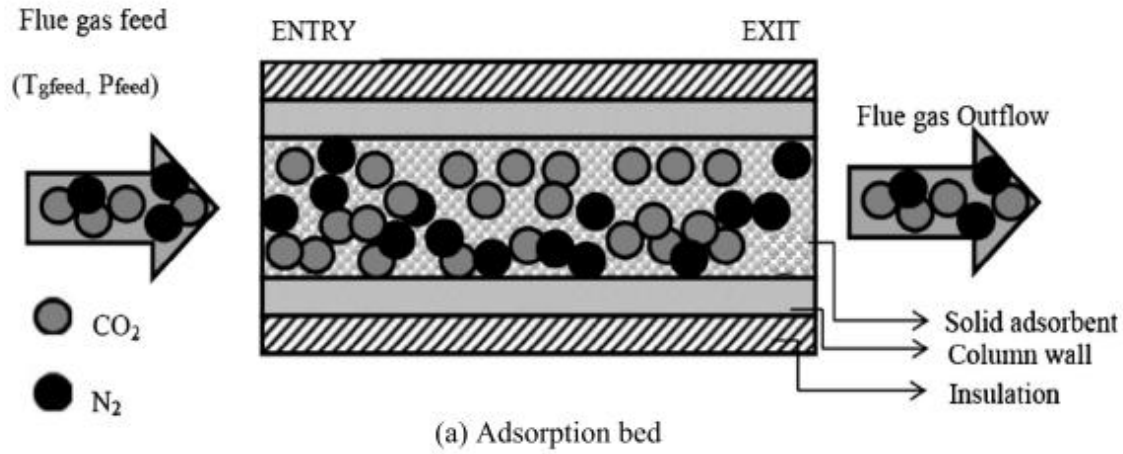


Fig. 2.6: Separation of $CO_2$and $N_2$ Gases in a Cylindrical bed (Habib et al., 2016)

## 2.8 Zeolites

Zeolites are a "group naturally occurring crystalline and microporous (0.1 -1 nm) of hydrated aluminosilicate materials composed of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedral", having a chemical formula of Ma/*n*[(AlO2)a (SiO2)b] *w*$H_2O$ (Petrov & Michalev, 2012, Von-kiti, 2016), where M the is exchangeable metal cation of valence *n, w* is the number of water molecules present in the unit cell, and *a/b* are the variable number of aluminate or silicate which gives the total number of tetrahedral in a unit cell (Von-kiti, 2016). Since their introduction around the 1950s, zeolites have found a wide industrial application as catalysts, ion exchange, sorbents, drying and separation, and water purification (Hutson et al., 2000).

Each zeolite structure is unique but they all possess void spaces that create an environment for ion exchange and adsorption purposes (Von-kiti, 2016). Santos, Cruz, Regala, Magalhães, and Mendes (2007) discovered that, synthetic zeolites type A (5A) and X (13X, NaX, LiX, and LiLSX) can be used for oxygen production from air, because nitrogen is strongly adsorbed by zeolites due to its quadrupole moment being roughly 4 times greater than that of oxygen.

Zeolite frameworks are basically made of silicon and aluminium atoms, so-called T-atoms (T=Si or Al), surrounded by four oxygen atoms which forms a tetrahedral in a crystal lattice with a net negative charge on the structure giving zeolites a tendency of large cation

exchange capabilities (Von-kiti, 2016). According to Von-kiti (2016), the negative charge on zeolite structure is mostly due to the presence of aluminium ion in the framework which can be compensated by adding more cations such as $Na^+$, $Li^+$, and $K^+$ to the framework. Figure (2.7) below illustrates zeolites building units.

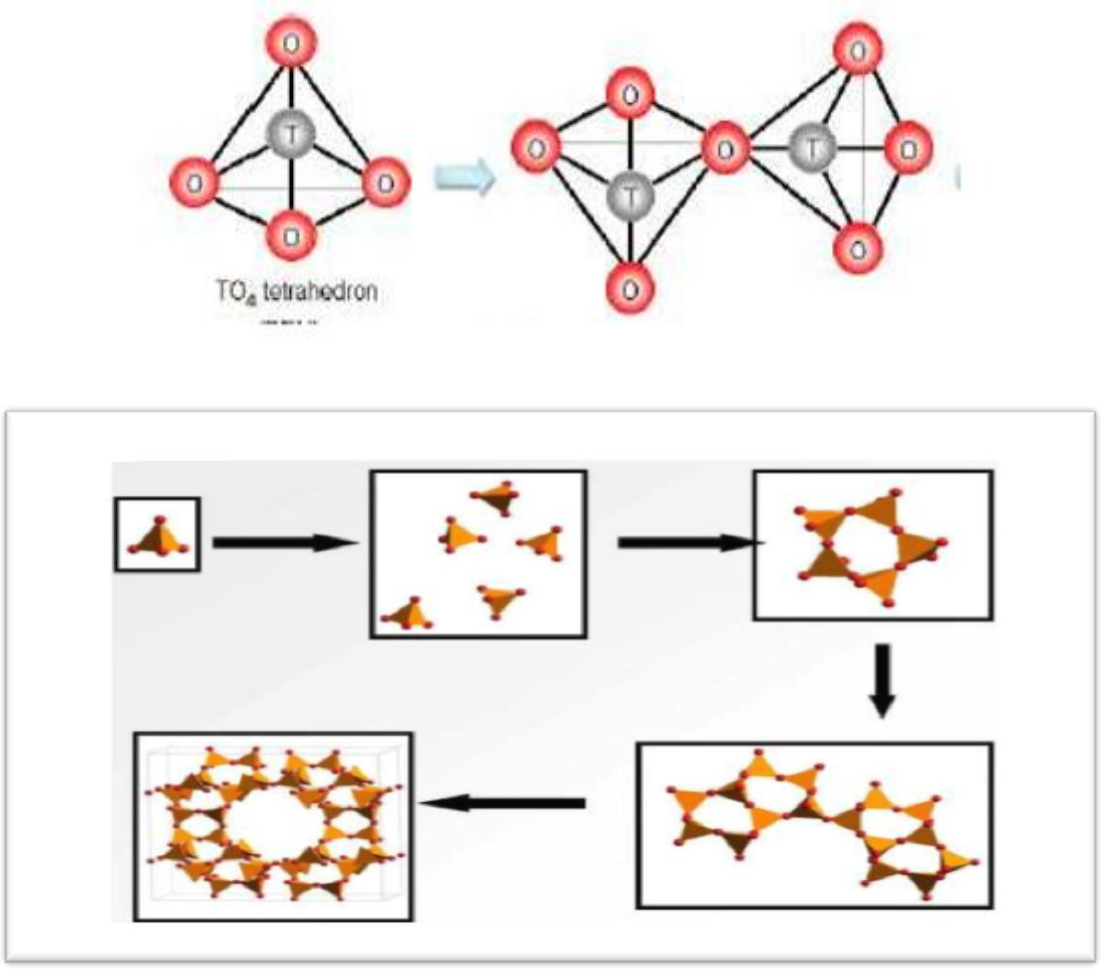


Figure 2.7 Zeolites' Building Blocks (Von-kiti, 2016)

The interconnections of zeolites, by shared oxygen atoms, generates channels of diameter between 3 to 10 Å which confers zeolites different classifications as Sodalite and Gsmodine (small pore size up to 4Å), MFI (medium size up to 5.5 Å), Mordenite and Faujasite (large pore size up to 7.5Å), and, most recently, Clevorite (up to 9Å) (Von-kiti, 2016). Further work by Hutson et al. (1999), demonstrated synthesis of two zeolites differing only in Si /Al ratio. These were Praxiar, SI/Al ratio of 1.0, sometimes referred to as LSX (low Silica X zeolite or simply Li-X zeolite) and Linde, Si /Al ratio of 1.25.

## 2.9 Gases Adsorption with Zeolite Sorbents

Zeolites have a number of applications as catalysts (e.g. petrochemical industry), sorbents (gas separation), and ion exchange (water purification and environmental decontamination of heavy and radioactive metals e.g. mining) (Von-kiti, 2016). According to Santos *et al.* (2007), zeolites are very effective in gases separation, for example, zeolites can produce up to 99.5% oxygen purity recovering about 62% oxygen from air. This property represents an attractive possibility for enhanced combustion with inherent benefits of firing a fuel in pure oxygen. As demonstrated by Hamed (2015), "Pressure Swing Adsorption (PSA)" can be applied for gases separation through small beds and the technique can be adapted to small scale applications with minimal amount of sorbents. Zeolites are fit candidates for PSA technology, because of their favourable results in gas separations, and low cost (Siriwardane et al., 2003). Amongst a few advantages of zeolites are the easy of modification to fit specific needs for applications, and a high chemical and thermal stability (Von-kiti, 2016). Besides, Von-kiti (2016) discovered that, zeolites are also effective materials for separation of $CO_2$, water, and sulphur compounds from natural gas streams.

Siriwardane *et al* (2003) pointed out that, the energy costs and lack of technical feasibility on existing $CO_2$ capture technologies have led the need for the development of improved $CO_2$ capture technologies that can make the $CO_2$ capture process more viable. The outstanding ability of zeolites to adsorb nitrogen over oxygen, as proven by Hamed (2015), could be used to produce an oxygen enriched stream from air to enhance combustion. For instance, studies by Rege and Yang (1997) revealed that, LiX zeolites have an exceptional efficiency to separate nitrogen and oxygen gases even at pressures lower than 2 bars. Actually it has long been known that $Li^+$ is amongst cations that have the highest affinity for nitrogen. Hutson *et al.* (2000) also found that, nitrogen adsorption capacity was higher in low-silica X-type zeolite (an alumina saturated-type zeolite with low Si/Al ratio over that of typical commercial zeolite type A. However, it must be noted that, adsorption of gases by zeolites is strongly affected by the presence of water, which explains the reason why zeolites have been employed as drying agents. Because of this, any water present in the gas mixture, or in the zeolite itself prior to adsorption, may result in decline in the adsorption capacity (Hutson et al., 2000).

Combusting fuels in pure oxygen will eventually produce a concentrated stream of $CO_2$, whilst the NOx impurities are avoided, this will consequently make the $CO_2$ capture process

much easier. However, this is only a step towards a successful $CO_2$ capture. $CO_2$ must be collected or utilised to prevent atmospheric emissions. According to Ojuva (2015), future challenges for $CO_2$ capture will indeed lie on developing inexpensive technologies that use low-cost materials, with less or no maintenance costs. Figure (2.8) below shows a bed packed with zeolites granules which can be used for adsorption in gases separations.

Figure 2.8: Packed bed of Zeolite Granules (Adapted from Rege and Yang, 1997)

A comparison study by Rege and Yang (1997) revealed that, oxygen recovery and purity by LiX zeolites is higher than Zeolite Nax (13X), although the temperature in Lix was four times higher than that of Nax. The oxygen product at various pressure rations (isotherms) was an important parameter on which performance of different zeolites could be compared on the PSA unit. The oxygen recovery by LiX was satisfactory even at adsorption/purge pressure ratio as low as 2, whereas for Nax a pressure drop below 4 was almost impossible to maintain a product purity above 95% (Rege and Yang, 1997).

### 2.9.1 Ion Exchanged Zeolites

Through an ion exchange process, ions on zeolite can be replaced by nearly similar charged ions without permanently changing the structure of the solid (See Fig. 2.9) below.

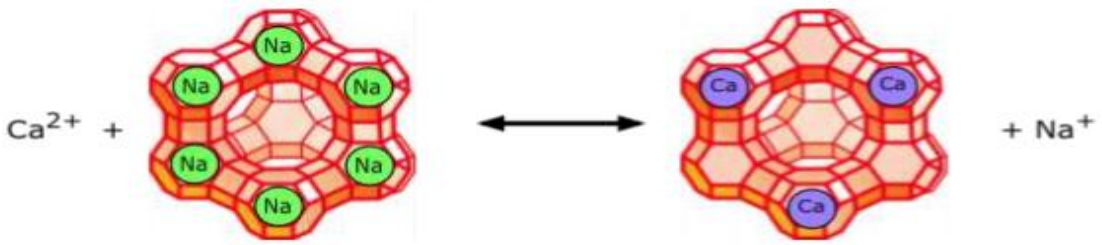


Figure 2.9: Zeolites Ion-exchange Reaction (Von-kiti, 2016).

No net change takes place in the structure, but replacement of the adsorbed ions on zeolite by others. Hutson *et al*. (1999) discovered that, the sodium-form of zeolite exchanges more readily with most cations, hence, all zeolites were first converted to $Na^+$ form with sodium chloride solution as source of $Na^+$ ions and the resultant Na+ zeolite was then used as starting material for all other synthesis (ionic exchanged with other cations). Lithium-x (Li-X) zeolite is an example of exchanged zeolite that offers the best performance on $N_2$ adsorption for air separation (Hutson *et al*., 1999).

Since the silicate group on zeolite is electroneutral, possibly, it is the aluminate group with its net negative charge that introduces non-framework cations such as $Na^+$, $Ca^+$, $Li^+$, and others. This way, from any starting zeolite material, zeolites can ionic-exchange to various other zeolites forms. This makes it obvious that, high alumina content zeolites may have greater capacity of exchange of cations. Hutson *et al*. (1999) thinks that, a low Si/Al zeolite (or simply high alumina zeolite) should contain at least 96 aluminium atoms per zeolite unit cell, whereas, having only 86 aluminium atoms per unit cell is not aluminium saturated. Thus, by adjusting the Si/Al ratio and subjecting the zeolite to an appropriate cation exchange may yield a significant increase in adsorption capacity of zeolites in addition.

## 2.10 Does UV- light break $CO_2$ into C + $O_2$?

One of the best ways to curb the effects of $CO_2$ is to utilize it, thus, Dubey (2016) introduced a basic principle to break $CO_2$ using Ultraviolet (UV) light. Dubey (2016) is convinced that, this technique can convert the hazardous air pollutant ($CO_2$) into eco-friendlier elements (C + $O_2$) with commercial benefits. According to Dubey (2016), the ionisation of carbon produces carbon allotropes and $O_2$ from $CO_2$ with at least 11.3 eV provided by UV-visible light. A similar study, conducted by Jackson *et al.* (2014), roughly used the same thermochemical threshold (about 11.44 eV) of energy to reach the formation of C + $O_2$. Till recently, Jackson *et al.* (2014) thought that, the photodissociassion of $CO_2$ could only yielded CO + ½$O_2$. But, it is now evident that, there is an exit mechanism to produce C + $O_2$. Figure (2.5) below illustrates the photo-fragment excitation spectra with UV-rays over a range of energy (6.03 eV to 11.44 eV).

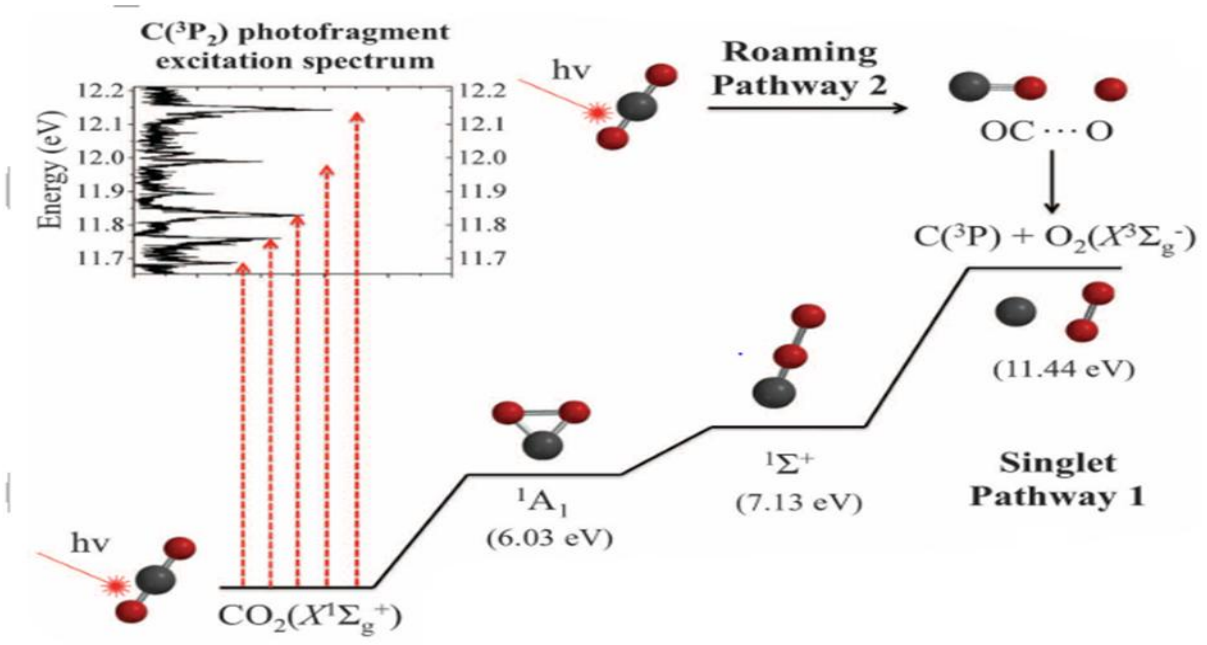


Fig. 2.10: $CO_2$ Photodissociation Pathways (Jackson et al, 2014).

# Chapter 3: Research Methodology

The diagram below (figure 3.1) introduces a detailed description of the methodology design (Air purification, oxy-combustion, $CO_2$ utilization).

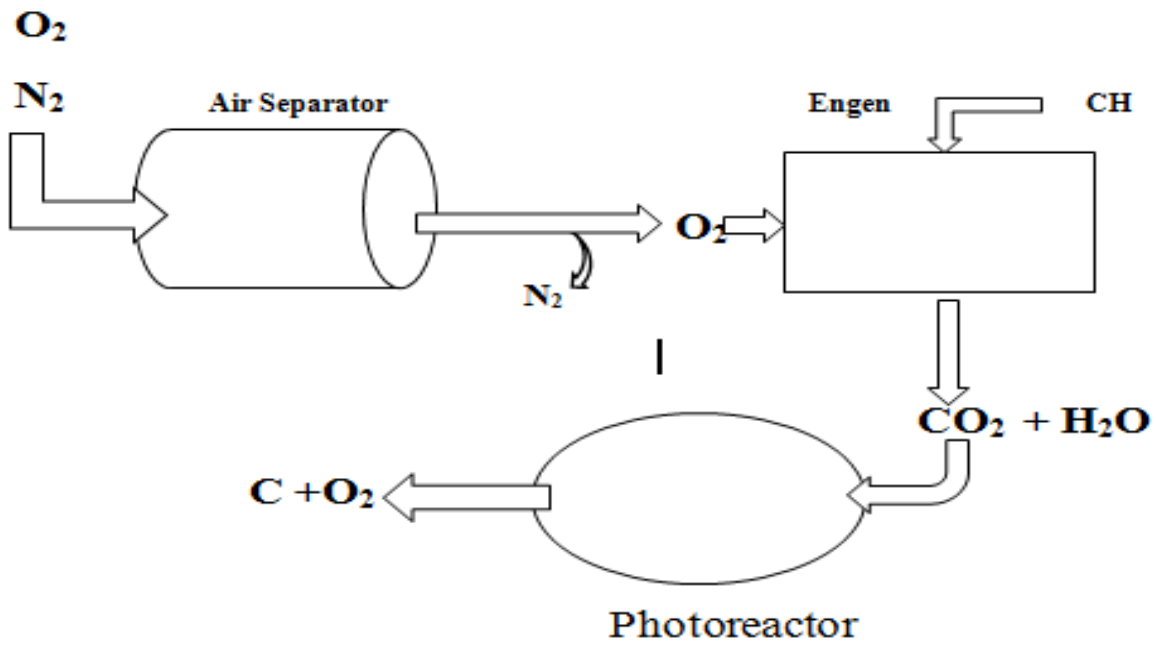


Fig 3.1: Methodology Design Flow Diagram

## 3.1 Hypothesis

This study hypothesizes that burning fuels in pure $O_2$, also known as oxy-combustion, may reduce the pollution content of exhausts, because excluding nitrogen from feed air stops it from entering the combustion chamber and, consequently, nitrogen oxides such as NO and $NO_2$, commonly known as NOx are avoided, and $CO_2$ is concentrated in the exhaust stream. It is further hypothesized that, this technology may significantly reduce the costs associated with tail pipes post-combustion $CO_2$ separations methods, because concentrated $CO_2$ and steam ($H_2O$) can simply be separated by cooling and collected.

## 3.2 Method

### 3.2.1 $CO_2$ Breaking in UV-light

The splitting of $CO_2$ into C + $O_2$ under the effect of UV-light was investigated by passing $CO_2$ gas (98.9 %, Afrox supplier) through a stainless steel tube (92.5cm x 11cm Packing) containing a UV-bulb (40w, 254nm). The reaction was subject to a set of varying conditions such as temperature (25-50°C, manual thermometer), time (0-30mins, Stop Watch), and pressure (0-2 bars, pressure regulators on the gas cylinder) and the product gas was collected for analysis. The analysis of gas was performed by chromatography (GC, Bruker 430-GC, TCD, $N_2$ mobile phase) and the resultant chromatography peaks were compared with those generated by the standards ($CO_2$, CO, and $O_2$) previously run under same experimental conditions. The experiment provided sufficient qualitative data, even though with good quantitative insights inferred from peak areas displayed by chromatograms.

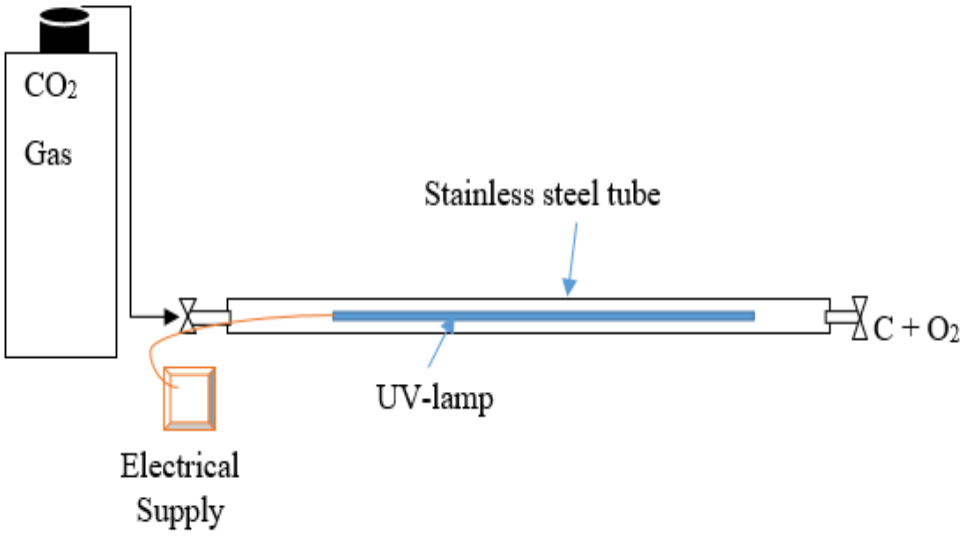


Figure 3.3: UV Reactor System

The mechanism below (figure 3.4) depicts the light-induced $CO_2$ breaking mechanism.

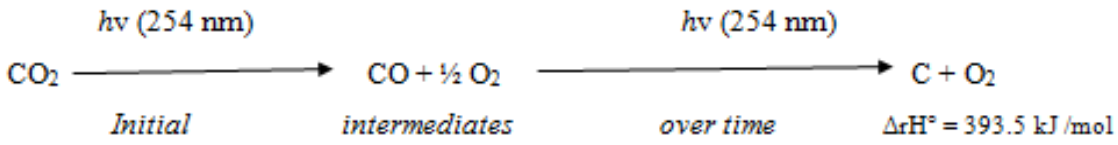


Figure 3.4: UV light-induced $CO_2$ Breaking Mechanism

## 3.2.1 Construction of an Air Separator Unit

An air separator unit (small scale reactor) was constructed of two columns packed with zeolites sorbents (3A, Sigma-Aldrich) to purify oxygen from air (See Fig. 3.5 below and the Appendix (p49).

Table 3.2: Air Separator Unit Specifications and Operating Conditions

| Unit Specifications | | Assessories | | Operating Conditions | |
|---|---|---|---|---|---|
| Column height /cm | 14 | Manual valves | 2 | Temperature /°C | 25 |
| Column radius /cm | 3 | Pressure gauges | 2 | Saturation time /Secs | 5 |
| Column thickness /cm | 0.002 | Air flow meter | 1 | Purge time /Secs | 5 |
| Catalyst amount /g /column | 478 | Drying unit | 1 | Maximum Pressure Variation /bar | 6 |
| Total Catalyst amount /g | 956 | | | | |
| Total Catalyst Volume /cm3 | 395.6 | | | | |
| Total Catalyst Surface Area | 320.3 | | | | |

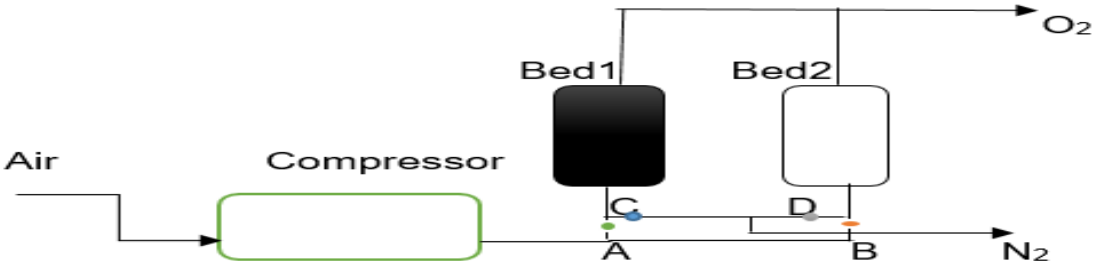


Figure 3.5: Air Separator Unit flow Diagram

# Chapter 4: Results and Discussion

## 4.1 Chromatographic Peaks of Standards

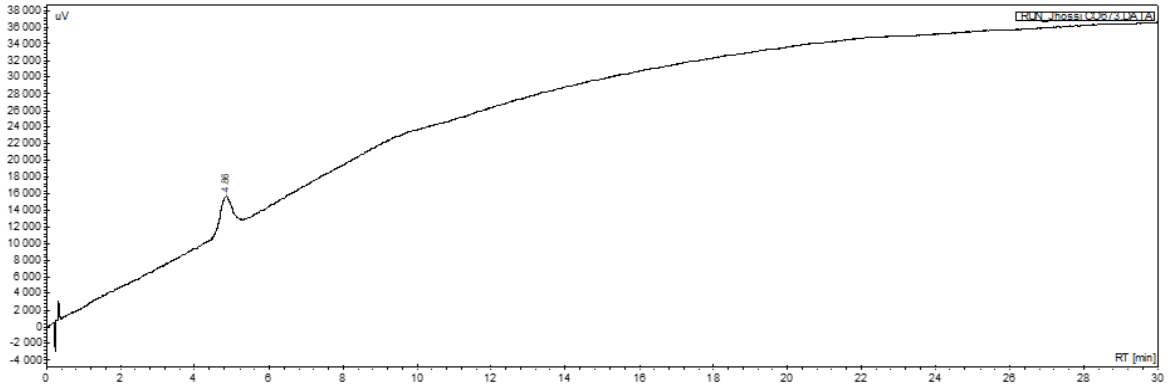


Fig. 4.1: Peak of CO

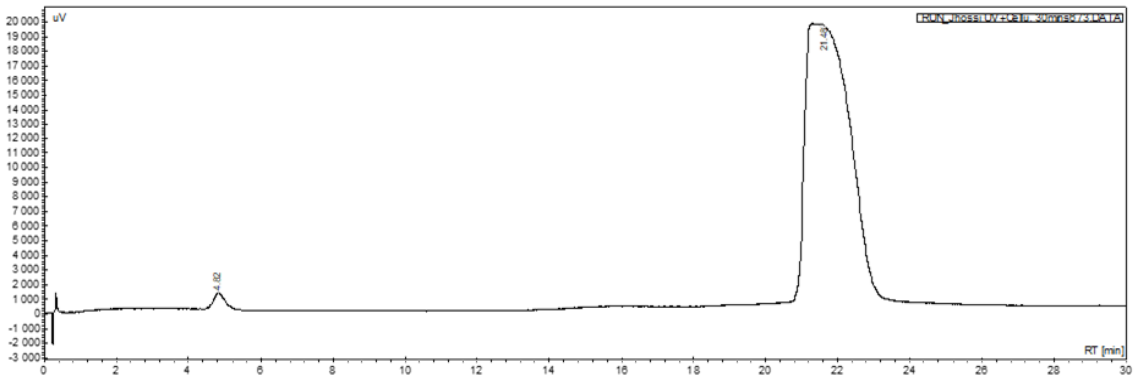


Fig. 4.1: Peak of $CO_2$

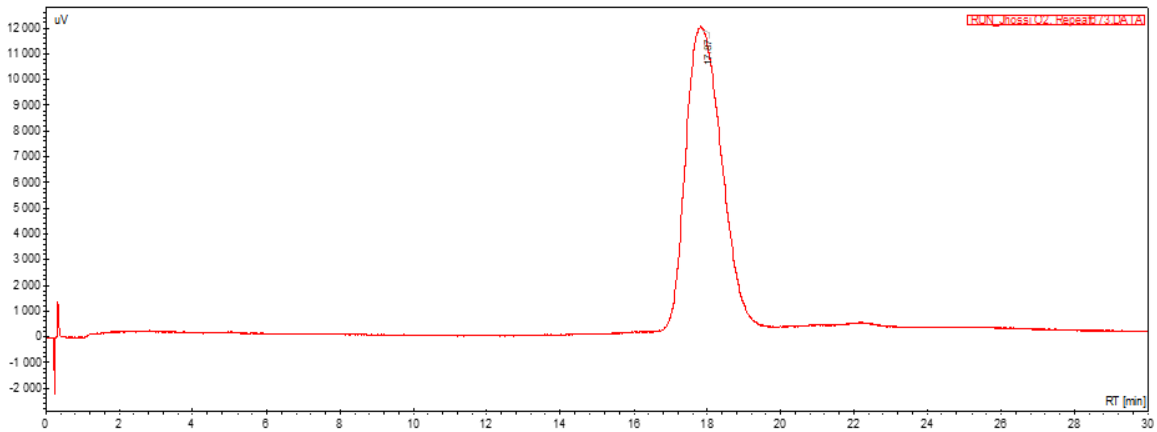


Fig. 4.3: Peak of $O_2$

Table 4.1: Retention Times and Areas (Peaks) of Standards

| Gas Standard | TR (min) | Area (%) |
|---|---|---|
| $CO_2$ | 4.82 | 66.5 |
| CO | 22.07 | 6.6 |
| $O_2$ | 18.01 | 26.6 |

Whilst the peak retention times TRs of standards are compared against those of the analytes for qualitative analysis (identification), the actual areas of peaks could be correlated to the composition of gas constituents as the equation (4.1) below shows;

$A_A/T_A = \%\ A$ Eq. 4.1

$A_A$ is the area of the analyte, $T_A$ is the total number of areas in a chromatogram, and %A is the analyte percentage. Assume exactly 1g /100 $cm^3$.

## 4.2 Chromatographic Characterization of Product Gas

### 4.2.1 Effects of Varying Time on Reaction Performance, Stopped Flow, 25 °C

#### 4.2.1a Qualitative Analysis

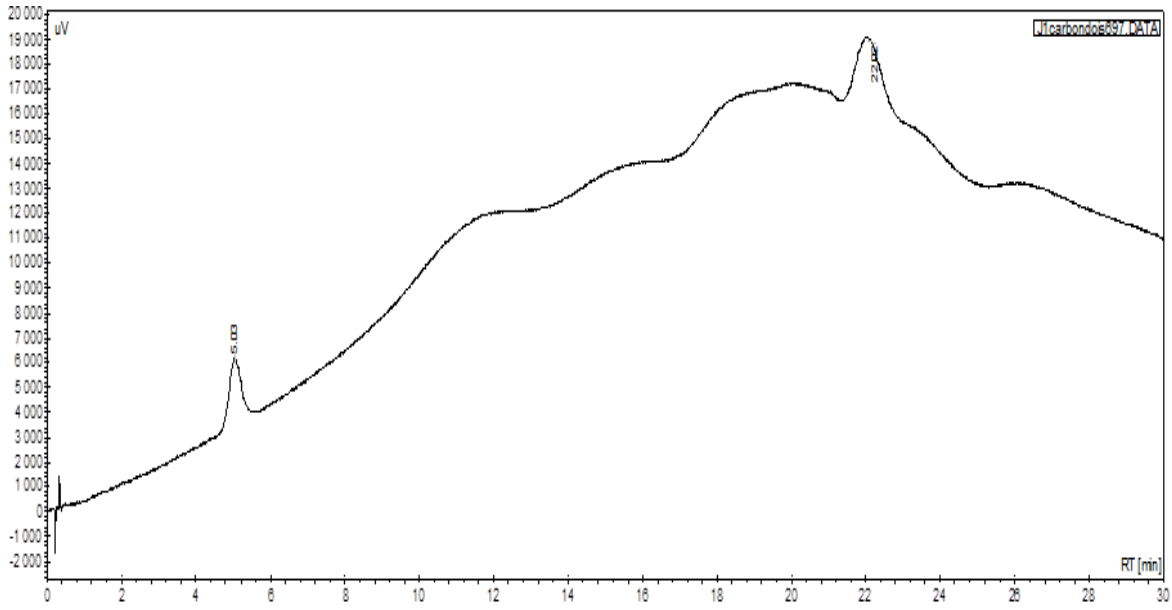


Fig. 4.4: Reaction at 0 min

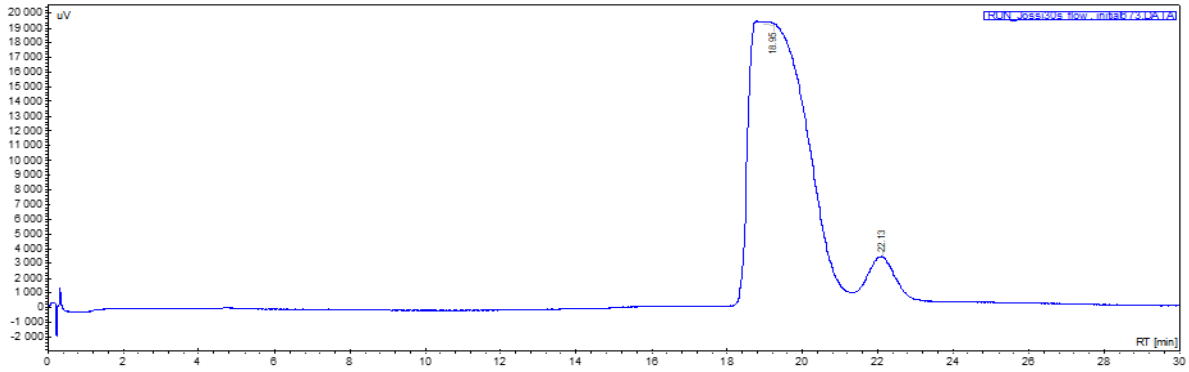


Fig. 4.5: Reaction after 5 min

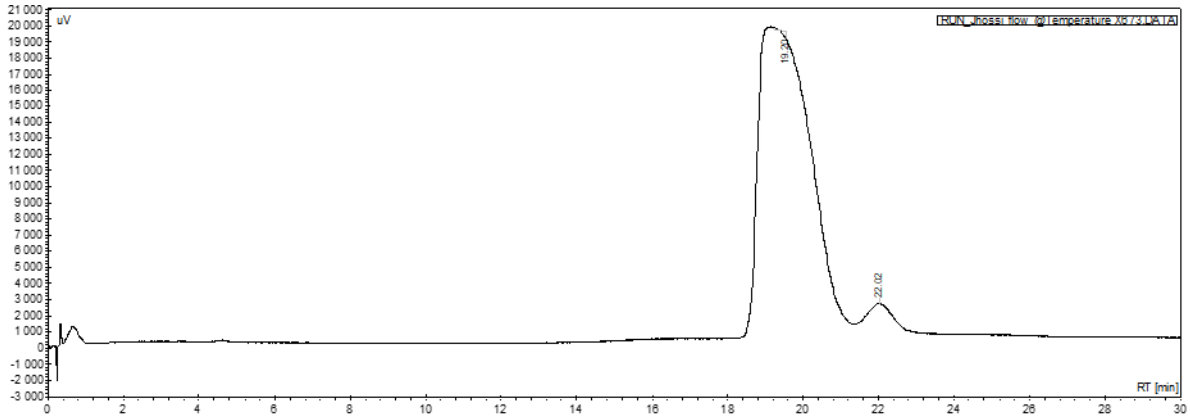


Fig. 4.6: Reaction after 10 min

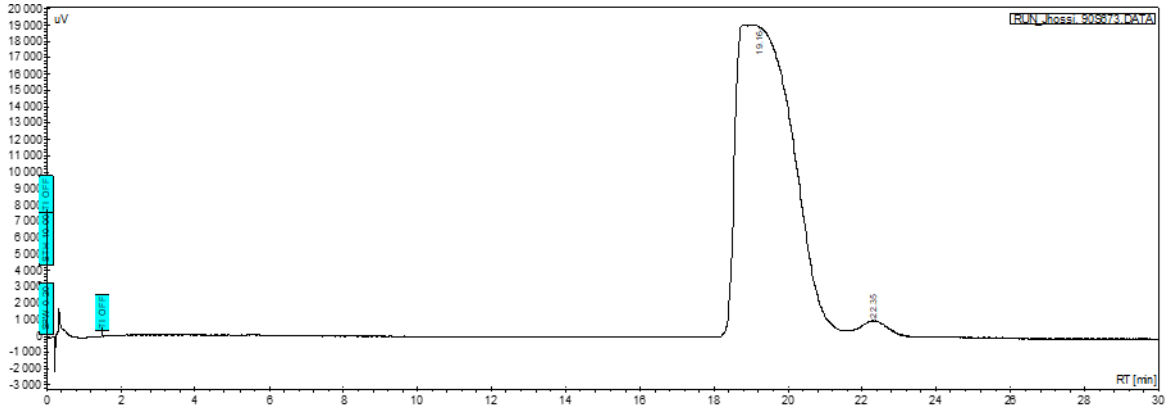


Fig. 4.7: Rection After 15 min

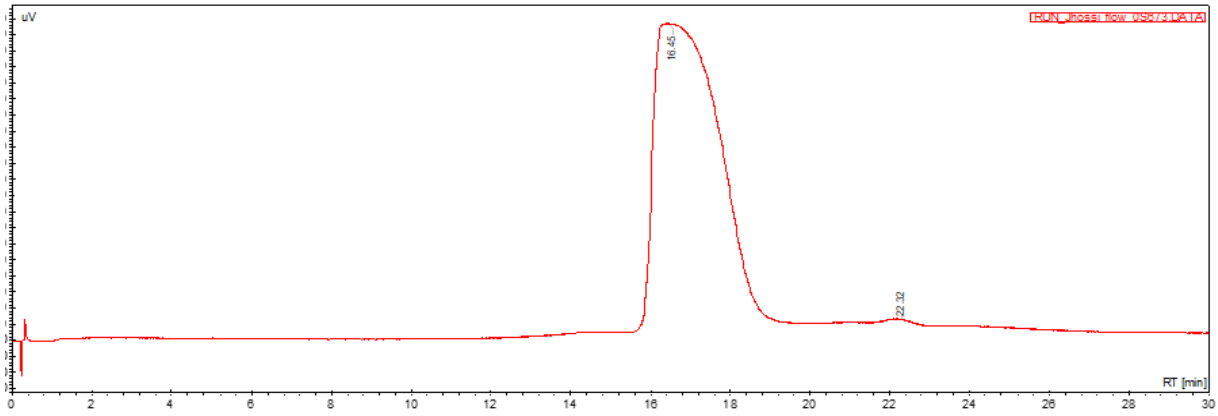


Fig. 4.8: Reaction After Time 20 min

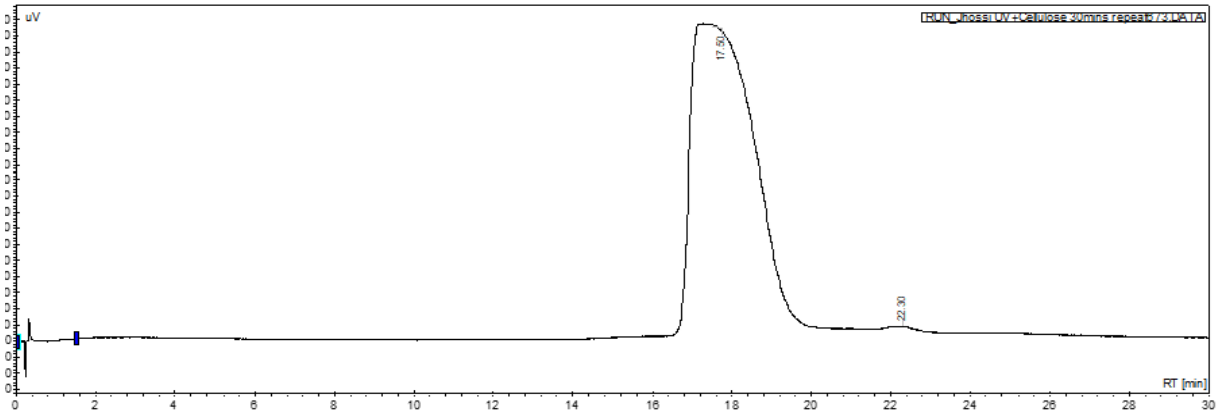


Fig. 4.9: Reaction After 25 min

Table 4.2: Retention Times Values (Fig. 4.4-4.9)

| | TRs (min) | | |
|---|---|---|---|
| Time interval (min) | $CO_2$ | CO | $O_2$ |
| 0 | 22.02 | 5.03 | 0 |
| 5 | 22.05 | 0 | 18.83 |
| 10 | 22.35 | 0 | 18.9 |
| 15 | 22.24 | 0 | 18.54 |
| 20 | 22.24 | 0 | 18.96 |
| 25 | 22.24 | 0 | 18.04 |

4.2.1b Quantitative Analysis

Table 4.3: Peak Areas Correlation to Composition at Varying Reaction Time (Eq. 4.1)

| Component | Area % | Mole % (W/v) |
|---|---|---|
| | At 0 min | |
| $CO_2$ | 62.06 | 66.96 |
| CO | 30.62 | 33.04 |
| $O_2$ | 0 | 0 |
| Total | 92.68 | 100.00 |
| | At 5 min | |
| $CO_2$ | 5.15 | 5.16 |
| CO | 0 | 0.00 |
| $O_2$ | 94.68 | 94.84 |
| Total | 99.83 | 100.00 |
| | At 10 min | |
| $CO_2$ | 19.72 | 32.88 |
| CO | 0 | 0 |
| $O_2$ | 40.26 | 67.12 |
| Total | 59.98 | 100.00 |
| | At 15 min | |
| $CO_2$ | 0.01 | 0.01 |
| CO | 0 | 0 |
| $O_2$ | 99.79 | 99.990 |
| Total | 99.8 | 100.00 |
| | At 20 min | |
| $CO_2$ | 0.004 | 0.004 |
| CO | 0 | 0 |
| $O_2$ | 99.79 | 99.996 |
| Total | 99.794 | 100.00 |
| | At 25 min | |
| $CO_2$ | 0.004 | 0.004 |
| CO | 0 | 0 |
| $O_2$ | 99.97 | 99.996 |
| Total | 99.974 | 100.000 |

Table 4.4: Summary of Product Gas Composition at Varying Time of Reaction

| | Mole % (W/v) | | |
|---|---|---|---|
| **Time (min)** | **[$CO_2$]** | **[CO]** | **[$O_2$]** |
| 0 | 66.96 | 33.04 | 0 |
| 5 | 5.16 | 0 | 94.840 |
| 15 | 0.01 | 0 | 99.990 |
| 20 | 0.004 | 0 | 99.996 |
| 25 | 0.004 | 0 | 100 |

4.2.1c Discussion (Fig. 4.4-4.9)

A qualitative analysis based on peaks (Fig. 4.4-4.9) above reveals the effects of UV-light on $CO_2$. As observed (in Fig. 4.4), at the start of reaction (zero minute), no oxygen is produced but CO and $CO_2$ (See RTs values 5.03 and 22.02 characteristic of CO and $CO_2$ respectively). This is evidenced in the reaction mechanism (Fig. 3.4) whereby $CO_2$ breaking produces CO + ½ $O_2$ intermediates at the very beginning of the reaction.

After 5 minutes, two peaks consistently appear in the chromatograms (Fig. 4.5-4.9), one around TR zone (18 min) characteristic of $O_2$, and the other around TR zone (22 min) characteristic of $CO_2$. As the reaction proceeds over time, $CO_2$ peak area becomes smaller whereas the oxygen peak maintains a large area. This in fact confirms $CO_2$ being consumed as $O_2$ is produced.

The area correlations displayed in table (4.2) above reveals oxygen as the most predominant component in the product gas (94%). $CO_2$ declined dismally from 69.25 % (reaction at 0 min) to less than 1 % after 10 mins. This could be an indication of a no instantaneous kinetic reaction as the concertation of the products increases with time. More insights will be drawn from the coming sections for better understanding of this phenomenon with varying the temperature and pressure of reaction.

## 4.2.2 Effects of Varying Temperature on Reaction Performance

### 4.2.2a Qualitative Analysis

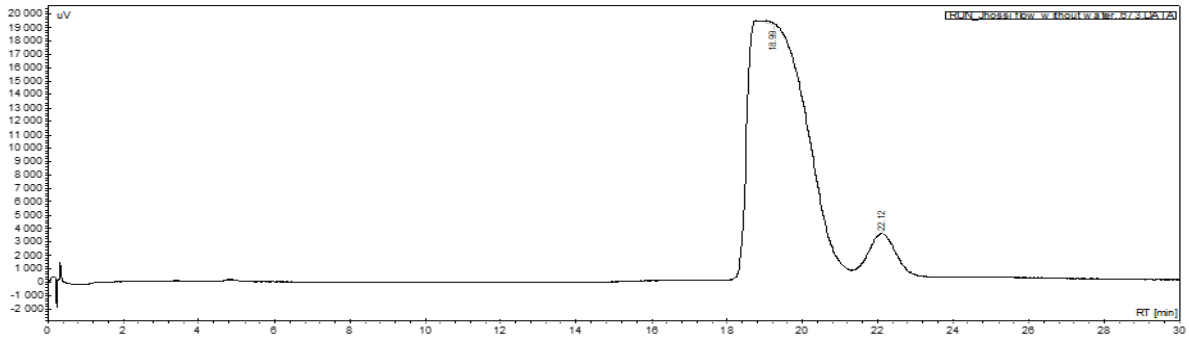


Figure 4.10: Reaction at 25°C

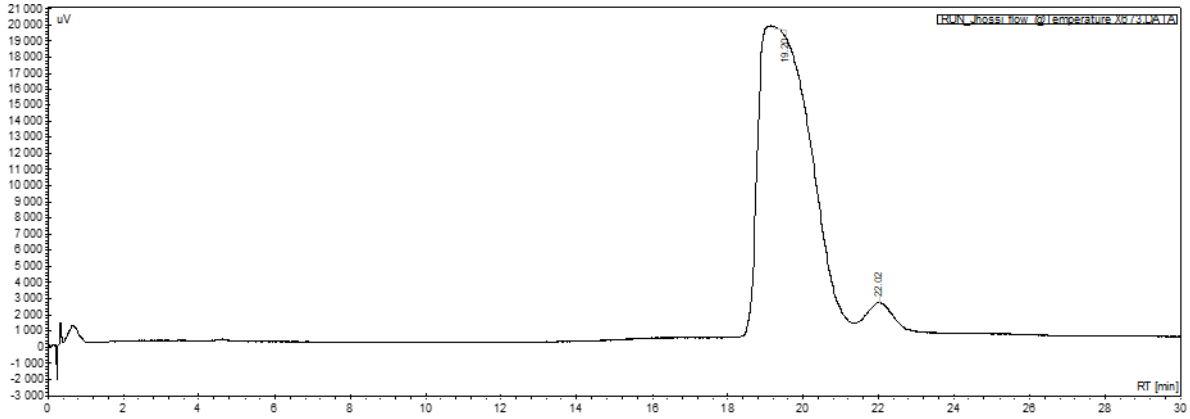


Figure 4.11: Reaction at 30°C

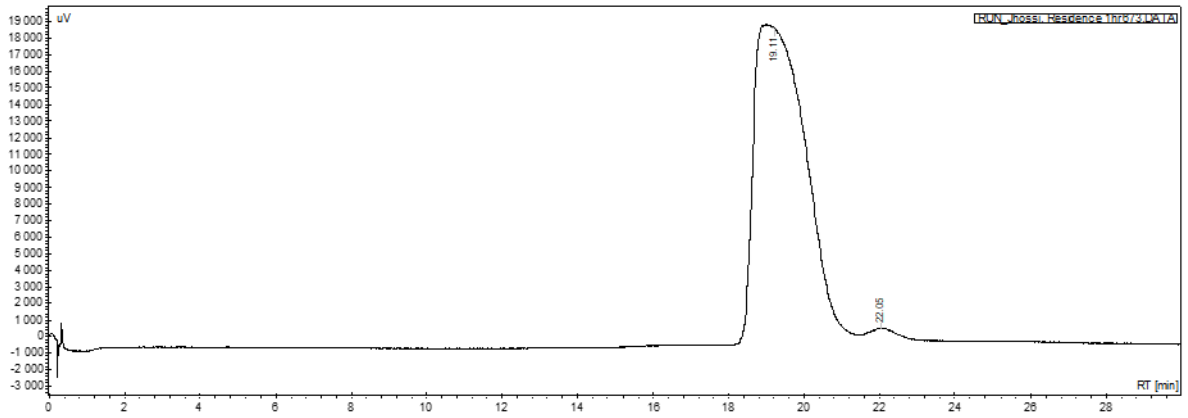


Figure 4.12: Reaction at 35°C

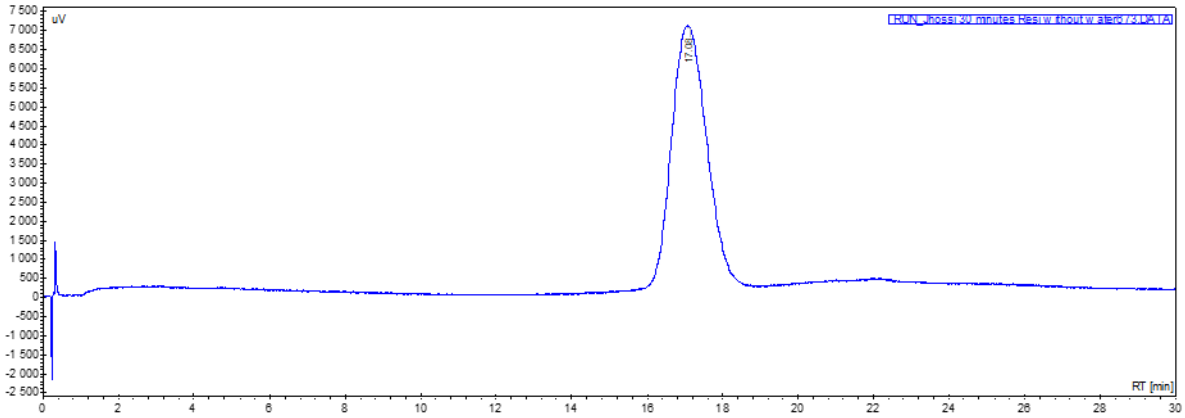


Figure 4.13: Reaction at 50°C

Table 4.5: Retention Times Values (Fig. 4.10-4.13)

| | TRs (min) | | |
|---|---|---|---|
| T /°C | $CO_2$ | CO | $O_2$ |
| 25 | 22.1 | NO | 18.1 |
| 30 | 22 | NO | 18.9 |
| 35 | 22 | NO | 17.9 |
| 50 | NO | NO | 18.7 |

4.2.2b Quantitative Analysis

Table 4.6: Peak Areas Correlations to Gas Composition at Varying Temperatures

| Component | Area % | Mole % (W/v) |
|---|---|---|
| | At 25 °C | |
| $CO_2$ | 4.78 | 4.85 |
| CO | 0.00 | 0.00 |
| $O_2$ | 93.68 | 95.15 |
| Total | 98.46 | 100.00 |
| | At 30 °C | |
| $CO_2$ | 19.72 | 17.93 |
| CO | 0.00 | 0.00 |
| $O_2$ | 90.26 | 82.07 |
| Total | 109.98 | 100.00 |
| | At 35 °C | |
| $CO_2$ | 0.004 | 0.004 |
| CO | 0.000 | 0.000 |
| $O_2$ | 99.790 | 99.996 |
| Total | 99.794 | 100.000 |
| | At 50 °C | |
| $CO_2$ | 0 | 0.00 |
| CO | 0 | 0 |
| $O_2$ | 99.97 | 100.00 |
| Total | 99.97 | 100.00 |

Table 4.7: Summary of Gas Composition at Varying Temperatures

| | Mole % (W/v) | | |
|---|---|---|---|
| T (°C) | $[CO_2]$ | [CO] | $[O_2]$ |
| 25 | 4.850 | 0.000 | 95.145 |
| 30 | 17.930 | 0.000 | 82.070 |
| 35 | 0.004 | 0.000 | 99.960 |
| 50 | 0.000 | 0.000 | 99.970 |

### 4.3.1c Discussion (Fig. 4.10-4.13)

The temperature at 50°C noticeably displays the most arguable peak (Fig. 4.13); here, $CO_2$ goes completely out of picture with only one peak left (obviously $O_2$). Because it takes roughly 10 to 15 minutes for the temperature of the system to rise above 30°C, it is possible that the net effects are brought by the reaction being driven to completion over time rather than by the rise of temperature inside the system. Further, the rise of temperature could be caused by incident UV-rays inside a sealed tube rather than the reaction itself which is believed to be endothermic.

Based on the data in table (4.5) above, it is tempting to state any temperature dependence on reaction performance because, the reaction occurs perfectly at 25°C and 30°C completely drives $CO_2$ to less than 1% composition with $O_2$ reaching above 99% in composition. Since the reaction was performed under stopped flow, obviously longer residence allowed more reactants to be converted into products. The results in the coming sections assesses the the effects of pressure variation and may offer more insights on the UV $CO_2$ breaking phenomena.

## 4.2.3 Effects of Varying Pressure on Reaction Performance

### 4.2.3a Qualitative Analysis

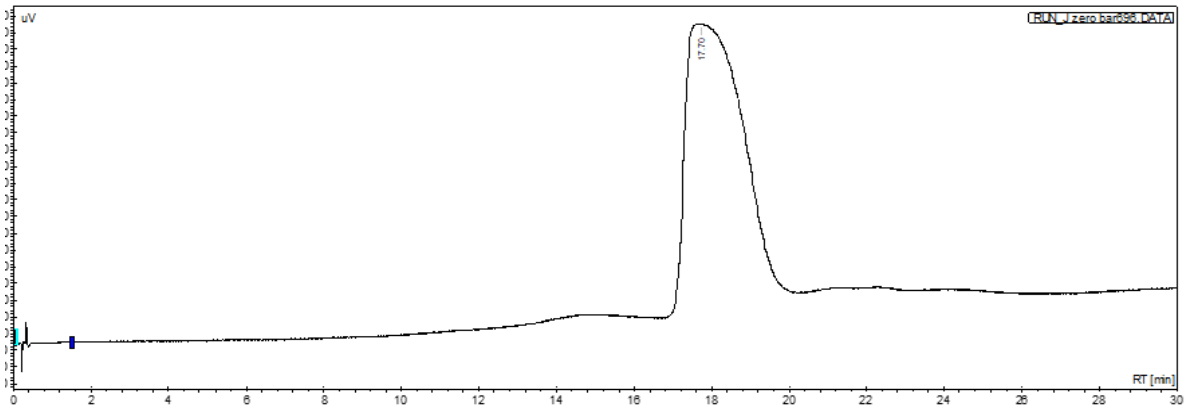


Figure 4.14: Reaction at 0 bar, 50°C

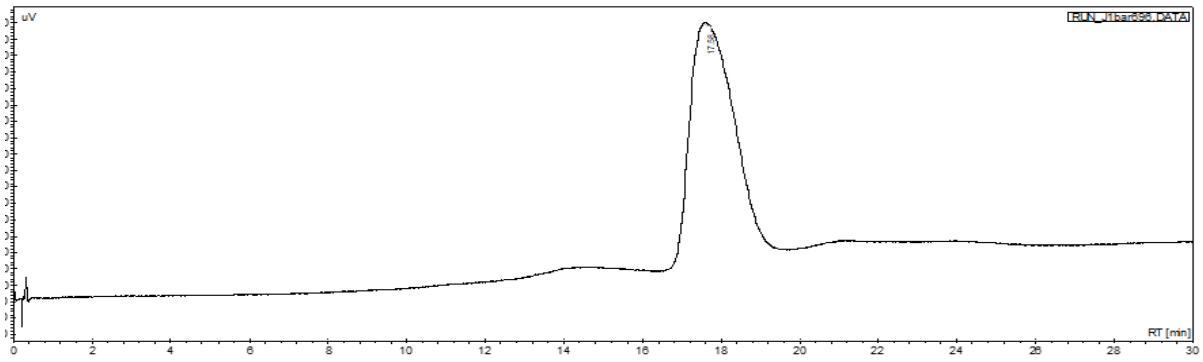


Figure 4.15: Reaction at 1 bar, 50°C

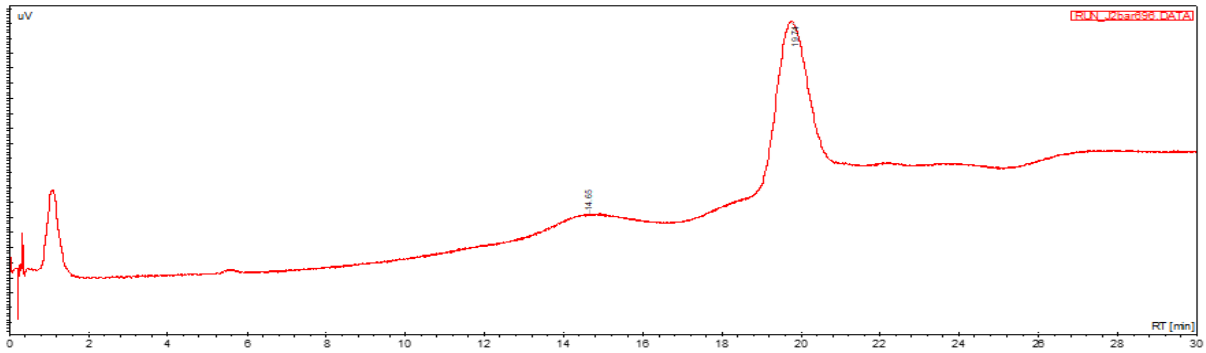


Figure 4.16: Reaction at 1.5 bars, 50°C

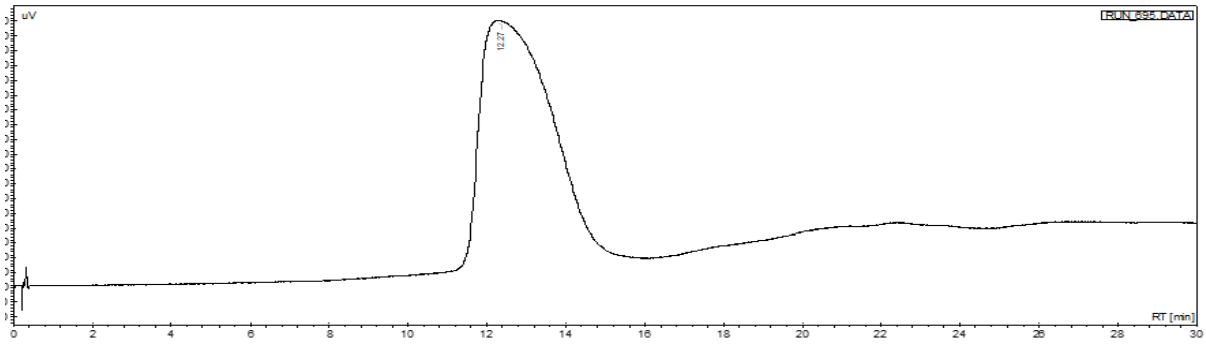


Figure 4.17: Reaction at 2 bars, 50°C

Table 4.8: Retention Times Values (Fig. 4.14-4.17)

| | TRs (min) | | |
|---|---|---|---|
| P (bars) | $CO_2$ | CO | $O_2$ |
| 0 | NO | NO | 17.7 |
| 1 | NO | NO | 17.58 |
| 1.5 | NO | NO | 18.74 |
| 2 | NO | NO | NO |

4.2.3b Quantitative Analysis

Table 4.6: Peak Areas Correlations to Gas Composition Varying Pressures

| Component | Area % | Mole % (W/v) |
|---|---|---|
| | 0 bar | |
| $CO_2$ | 0,00 | 0,00 |
| CO | 0,00 | 0,00 |
| $O_2$ | 100,00 | 100,00 |
| Total | 100,00 | 100,00 |
| | 1 bar | |
| $CO_2$ | 0,00 | 0,00 |
| CO | 0,00 | 0,00 |
| $O_2$ | 100,00 | 100,00 |
| Total | 100,00 | 100,00 |
| | 1.5 bars | |
| $CO_2$ | 0,000 | 0,000 |
| CO | 0,000 | 0,000 |
| $O_2$ | 86,990 | 100,000 |
| Total | 86,990 | 100,000 |
| | 2 bars | |
| $CO_2$ | 0,00 | 0,00 |
| CO | 0,00 | 0,00 |
| $O_2$ | N/A | 0,00 |
| Total | | 0,00 |

Table 4.7: Summary of Gas Composition at Varying Pressures

| | Mole % (W/v) | | |
|---|---|---|---|
| **P (bars)** | **[$CO_2$]** | **[CO]** | **[$O_2$]** |
| 0 | 0.000 | 0.000 | 100.00 |
| 1 | 0.000 | 0.000 | 100.00 |
| 1.5 | 0.000 | 0.000 | 100.00 |
| 2 | 0.000 | 0.000 | NO |

### 4.2.3c Discussion (Fig. 4.14-4.17)

The peaks displayed above (Fig. 4.14-4.16) and the data in tables (4.6, 4.7) shows a remarkable departure from normality of peaks characteristic of $O_2$, CO, and $CO_2$ at pressures above 1 bar. An unidentified peak appears at pressures of 2 bars (Fig 4.17). This could be an indication of $O_2$ production not occurring at conditions of pressures above 1 bar with UV-light as catalyst. It should be noted that, at these same conditions the peaks characteristic of CO and $CO_2$ disappear completely from the gas composition or they are not observable (NO). Therefore, this does not give enough conclusive evidence as to whether or not the reaction does not occur at said conditions. Whilst it is possible that raising the pressure above 1 bar could be suboptimal for $CO_2$ breaking under the effect of UV-rays, more data is necessary with variation in analytical method to arrive to more convincing conclusions.

# Chapter 5: Gap Analysis, Conclusions and Recommendations

## 5.1 Gap Analysis

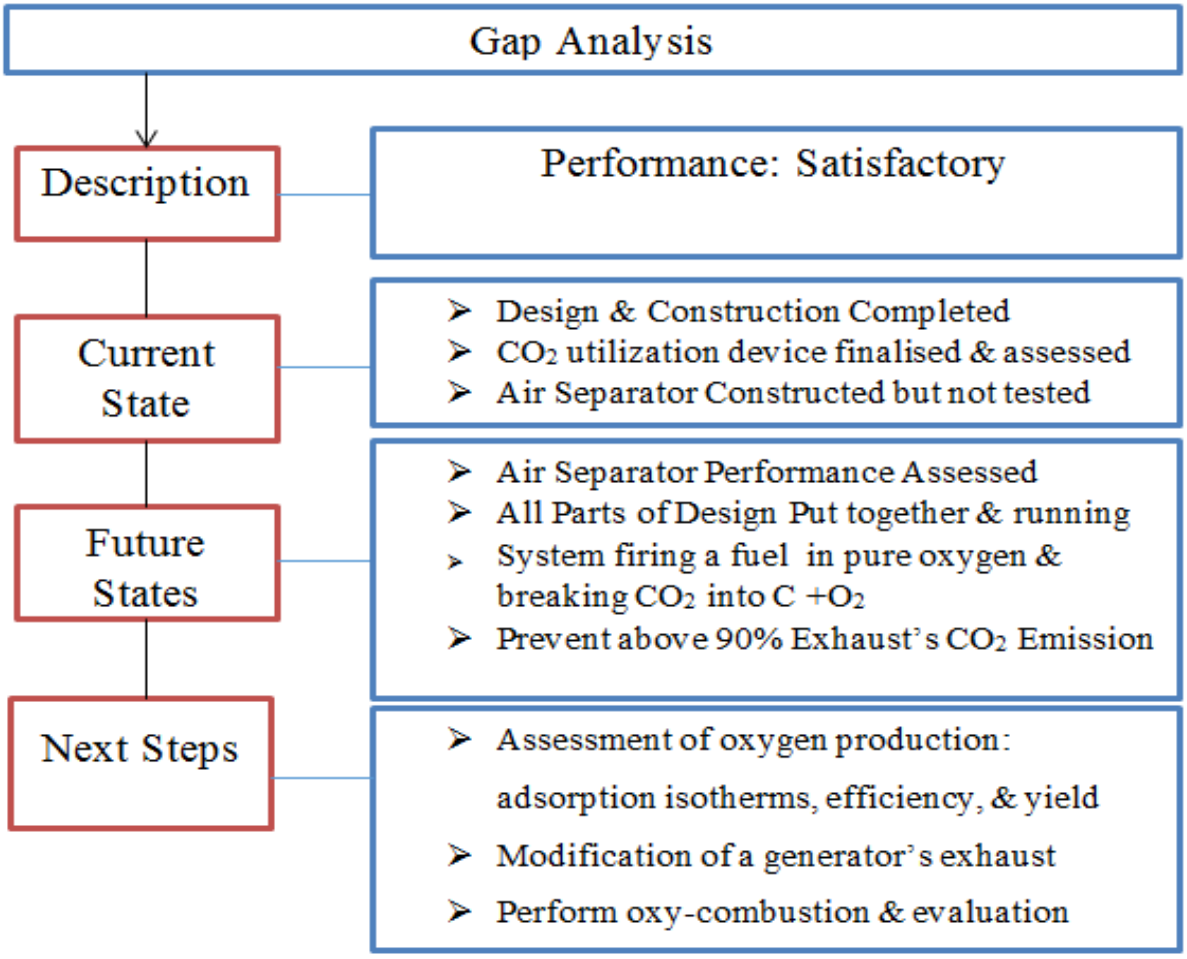


Figure 5.1: Gap Analysis

### 5.1.1 Gap Description

The current performance of the design is satisfactory as for the target goals set forth in the objectives of this study. Nonetheless, the entire process can draw up a comprehensive plan that outlines the specific steps needed for the reaching of its future target objectives as outlined in the following sections;

### 5.1.2 The Current State

The design and construction process is complete. The air separator was constructed and pressure tested (See table 3.2, p28), even though most thermodynamic and kinetic parameters for oxygen production were not yet assessed at this stage. The $CO_2$ utilization component was

finalized, set up and running which permitted the collection of useful information on $CO_2$ breaking into C + $O_2$. Thus, the entire process was only partly assessed through the experimental data obtained on $CO_2$ utilization component. This sets forth the future steps.

### 5.1.3 The Future State

The future state is the expected end of the design characterized by an optimized combustion system comprising an air separator unit connected to a small generator with a modified exhaust. Precisely the future state will comprise three main components interconnected namely; the air separator unit, a generator (for combustion), and a modified exhaust with ultraviolet light for $CO_2$ utilization. The final outcome is firing a fuel in an oxygen-enriched air avoiding nitrogen impurities such as NOx (NO, $NO_2$), and breaking $CO_2$ into C +$O_2$ along the exhaust pipe.

### 5.1.3 The Next Steps

More work lies ahead to meet the future targets; the air separator performance on oxygen production together with all mandatory parameters such as pressure isotherms, the adsorption capacity and efficiency, purge time, and the oxygen yield will be assessed. As well, the overall effects of oxy-combustion on engine performance like temperature, fuel efficiency, and the final exhaust composition will unmistakably be evaluated. Only then, will the system be judged weather or not fit for the purpose of exhausts clean-up and $CO_2$ utilization for reduction of atmospheric emissions.

## 5.2 Conclusions

The results above confirm that, $CO_2$ breaking is possible under the effect of UV-rays. The reaction was subject to a different set of conditions such as time, temperature, and pressure which allowed the indication of what the optimal reaction conditions could be. The chromatographic data subsequently displayed two peaks characteristic of carbon dioxide and oxygen. As the reaction proceeded over time, carbon dioxide became smaller in composition whilst oxygen was being produced. This, in fact, confirmed that oxygen was being produced as $CO_2$ was consumed. Carbon dioxide declined dismally from 69.25% (reaction at 0 min) to less than 1% after 10 mins whilst oxygen was produced from 0% to 100% in composition. The concentration of products changed with time. The observed rise in temperature over time

was possibly due to the incident UV-rays inside the sealed tube rather than the reaction itself, because $CO_2$ breaking is believed to be an endothermic process which cannot produce heat.

The reaction did not seem to depend on temperature because it occurred perfectly at 25°C and 30°C, where the amount of $CO_2$ was reduced to less than 1% with $O_2$ reaching above 99% in composition. Further changes in temperature did not bring significant changes on reaction performance as it did with variation in time. Based on the parameters tested, the reaction did not seem to occur perfectly at pressures above 1 bar or did not occur at all. However, more data might be necessary with variation in analytical method to arrive to a more convincing conclusion.

The oxygen and carbon produced are considered eco-friendlier than $CO_2$ and could offer some commercial benefits. In fact, the benefits are far greater than just environmental; whilst emissions are avoided, energy and materials could be recovered for other utilities or industrial applications. For example, oxygen is an important molecule that has a wide medical application in intensive care unit (ICU), theaters and surgery, whilst carbon is a starting material for most synthetic fuels (oil, methane), construction materials, and fluids that have a large industrial and commercial application.

Purifying oxygen using catalysts like Zeolite materials and UV-energy offers a cost benefit besides being technically feasible and efficient to adapt to most combustions systems such as power plants, aviation, navigation, road, and railways. This study will be carried out at PhD level for better conclusions.

## 5.3 Recommendations

This technological innovation holds a great potential to solve the problem of air emissions. The utilization of $CO_2$ is the best way to curb the environmental effects of carbon emissions because; utilizing $CO_2$, rather than capturing, eliminates the constraints associated with the energy penalties of $CO_2$ capture, transportation, and storage. Further, the utilization of $CO_2$ is a useful way to recover carbon and energy whilst mitigating the impacts of atmospheric emissions. The technology is simple, flexible, and escalating; it can be applied in mining, manufacturing, and transportation-related applications.

The divestment of fossils like oil and natural gas must not be emotional given that more than 90% of the world's fuels are still sourced from fossils. Whilst pollution of the environment cannot be justified, the solutions to the problem should be sustainably and wisely evaluated. The economy dependence on energy is incontestable and should become an important aspect of decision-making on energy landscape. As such, when considering energy alternatives, the technology should evenly be deployed to making fossils more economically viable but environmentally friendly. The idea that renewable sources of energy would replace fossils still cannot materialize; with the ever growing world's population, the idea of renewables has become a supplement rather than a replacement.

A careful review on what has been done in the field of atmospheric emissions, clearly demonstrated that more focus and efforts were placed on $CO_2$ capture and storage rather than on $CO_2$ utilization. Whilst it could be possible to make the process of CCS viable, the findings of this study offer another opportunity to exit the problems of atmospheric emissions.

The climate crisis is not a problem without a solution; it is a problem with many solutions that requires actors from different perspectives like technological, societal, political, and economical to come together with courage and determination for an immediate but effective action to reset and redesign the way people interact and react with the planet. The structure for exhausts clean-up and $CO_2$ utilization is one of those technologies that proposes a solution to the problem of atmospheric emissions, climate change and global warming.

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Appendix: Pictures of Experiment

Photography 1: UV-Photoreactor System

Photography 2: Air Separator Unit