MITIGATION MEASURES TO REDUCE CO_2 EMISSIONS AS A GREENHOUSE GAS AND ENHANCE ITS UTILISATION IN PETROCHEMICAL INDUSTRIES

A Thesis Presented to the Department of
Petroleum Engineering

African University of Science and Technology, Abuja

In Partial Fulfilment of The Requirements for the Degree of

Master of Science

By

ISMAIL USMAN

Abuja-Nigeria

July, 2023

CERTIFICATION

This is to certify that the thesis titled “Mitigation Measures to Reduce CO_2 Emissions as a Greenhouse Gas and Enhance its Utilisation in Petrochemical Industries” submitted to the School of Postgraduate Studies, African University of Science and Technology (AUST), Abuja, Nigeria for the award of the Master's degree, is a record of original research carried out by Ismail Usman in the Department of Petroleum Engineering.

MITIGATION MEASURES TO REDUCE CO_2 EMISSIONS AS A GREENHOUSE GAS AND ENHANCE ITS UTILISATION IN PETROCHEMICAL INDUSTRIES

By

ISMAIL USMAN

A THESIS APPROVED BY THE PETROLEUM ENGINEERING DEPARTMENT

RECOMMEDED:

AOI July 10, 2023
Dr. Alpheus O. Igbokoyi (Supervisor)

MA (11/07/2023)
Prof. Mukhtar Abdulkadir (Committee member)

AOI July 10, 2023
Head, Department of Petroleum Engineering

APPROVED:

....
Chief Academic Officer

....
Date

ABSTRACT

The removal and use of the greenhouse gas, carbon dioxide (CO_2), which contributes significantly to global warming, from flue gas was investigated using the absorption method in this study. To investigate its utilisation, the captured CO_2 was used as a feedstock for an urea synthesis process. The absorption model was simulated using the ASPEN HYSYS software and the urea synthesis section was modelled using the ASPEN Plus. For the CO_2 absorption, Methydiethanolamine (MDEA) was used as the solvent serving to be the absorbent medium. The effect of operating parameters such as flue gas inlet temperature, absorber column number of stages, and absorbent circulation rate on absorption capacity were examined. A flue gas stream containing about 128.2ton/h fractional mass rate of CO_2 was treated to capture 109.8ton/h of CO_2 which means 85.67% of CO_2 recovered. The outlet clean flue gas stream was concluded to be relatively safe to be vented to the atmosphere with about 8.7ton/h (6.8%) of CO_2 in it and the remnant was recircled in the loop as slippage into the absorbent solution. Captured CO_2 was used as a feed to urea synthesis where 32.9ton/h of CO_2 was used to give a wet urea flow of 42.6ton/h. The two models simulated showed that global warming could be greatly reduced by curtailing CO_2 emissions from industrial activities. It also shows that the ASPENTECH software is a promising software for simulating carbon capture for utilisation in urea production.

Keywords: Global warming, Carbon capture, Carbon dioxide (CO_2*) recovery, Flue gas, Simulation, Urea synthesis, Aspen Hysys, Aspen Plus.*

DEDICATION

This research work is dedicated to Allah (S.W.T.) for making all things possible and easy for me when they appear to be impossible. Alhamdulillah!

ACKNOWLEDGEMENT

I am very grateful to the African University of Science and Technology (AUST) who gave me a scholarship to study at this prestigious University.

I am deeply grateful to my supervisor, Dr. Alpheus Igbokoyi for his relentless efforts, fatherly concerns, patience and immense supports. I highly appreciate your efforts Sir for being with me throughout my thesis work to see that the right things are done in the right ways. I would also like to give special thanks to Dr. Mukhtar Abdulkadir, one of my committee members, for his unending supports.

I will not forget to mention the contributions from the AUST faculties especially the Petroleum Engineering stream and my fellow colleagues during my stay at the university, you have been so helpful to me from different angles. God bless you all.

Finally, I would like to thank my family and friends for their unwavering support, understanding, and encouragement throughout this journey. Their love and belief in me kept me motivated during challenging times. At this juncture, I have to mention the supports, contributions and guidance of Dr. Sagir Adamu, my brother and my mentor. Thank you so much Sir.

I am deeply grateful to everyone mentioned above and to all those who have indirectly contributed to this project. Your support and collaboration have made this endeavour a success.

Thank you all.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

ABBREVIATION	DEFINITION
AIChE	American Institute of Chemical Engineers
ASU	air separation unit
CCS	CO_2 capture and storage
DRI	direct-reduced iron
EJ	Exajoules (an SI unit of energy equal to 10^{18} joules)
EOR	Enhanced Oil Recovery
GHG	Greenhouse gases
GtC	Gigatonnes of carbon
$GtCO_2$	Gigatonnes of CO_2
GWe	Gigawatt-electric
IEA	International Energy Agency
IGCC	Integrated Gasification Combined Cycle
IPCC	Intergovernmental Panel on Climate Change report
OLS	Ordinary least square (a method of regression analysis)
MDEA	Methydiethanolamine
MEA	Monoethanolamine
$MtCO_2$	Million metric tonnes of CO_2
$MtCO_2e$	Million metric tonnes of carbon dioxide equivalent
NGCC	Natural gas combined cycle
OECD	Organization for Economic Cooperation and Development
PC	Pulverized coal
PFD	Process flow diagram
RCY-1	Recycle stream
SEP	Separator in ASPEN Plus
STG	Steam turbine generators
UNEP	United Nations Environment Programme
USA	United state of America
USAID	The United States Agency for International Development
USURA	User Subroutine in ASPEN Plus
VLE	Vapour-Liquid Equilibrium
WEO	World Environment Organisation

CHAPTER 1

1.0 STUDY OVERVIEW

1.1 Background

The main cause of the environmental crisis in the twenty-first century is generally known to be global warming. The release of greenhouse gases (GHG) connected to human activities, which might have catastrophic effects if not controlled and mitigated, has been demonstrated in many studies to be the primary driver of global warming. GHG emission increment is driven by economic and population growth which are getting higher. This has led to the increase of atmospheric concentration of the six greenhouse gases which are carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), hydrofluorocarbon (HFC's), perfluorocarbons (PFC's) and sulphur hexafluoride (SF_6) (IPCC, 2014). The major contributor of GHG is CO_2 and almost 30 billion ton of CO_2 that enters atmosphere was due to human activities each year (IPCC, 2014). The increase in CO_2 has contributed about 76% of the global greenhouse gases up to 2010. (Rudin et al., 2017).

The industry sector emits around 8 Gt CO_2 equivalent (CO_2e) per year, contributing 23% of global greenhouse gas (GHG) emissions (IEA, 2016). The GHG emissions of the industry sector could be reduced by substituting fossil energy with renewable energy. However, energy substitution is not sufficient, as part of the industry sector's GHG emissions is process-inherent since CO_2 is produced as a by-product. This part of the industry sector's GHG emissions is particularly difficult to eliminate (Davis et al., 2018).

Given their significant contribution to rising atmospheric greenhouse gas concentrations, accounting for emissions of CO_2, N_2O and CH_4 from agricultural practices has become increasingly important. Emissions of these gases may occur either directly during agricultural activities (e.g., cultivation and harvesting), or indirectly during the production and transport of required inputs (e.g., herbicides, pesticides and fertilisers).

Emission of CO_2 can be divided into two categories: stationaries or non-stationary. Stationary sources are a point of large CO_2 emission which provides significant and realistic chances for reduction of CO_2 emission. The large stationary sources are mostly from heavy industries such as power plants, cement production, iron and steel industries, refineries, petrochemicals and gas processing plants which contribute to more than 60 % of the total stationary emission. Without further initiative on the emission reduction, the total CO_2 emission from industrial may project up to 90% by 2050 compared to 2007 (IEA, 2010).

There are both natural and human sources of carbon dioxide emissions. Natural sources include decomposition, ocean release and respiration. Human sources come from activities like cement production, deforestation as well as the burning of fossil fuels like coal, oil and natural gas.

Due to human activities, the atmospheric concentration of carbon dioxide has been rising extensively since the Industrial Revolution and has now reached dangerous levels not seen in the last 3 million years. Human sources of carbon dioxide emissions are much smaller than natural emissions but they have upset the natural balance that existed for many thousands of years before the influence of humans.

Carbon dioxide separation and purification have long been practised for a variety of causes and applications, including the food business, the metal industry, welding, and injection into oil fields during the enhanced oil recovery process (EOR). However, due to environmental concerns and the effects of greenhouse gases on climate change (Iliuta et al., 2015), the CO_2 capture and storage (CCS) process has been developed in recent years to reduce this pollutant from its primary sources, such as power plants, petrochemical plants, cement factories, oil refineries, and so on (Iliuta et al., 2015). Because power plants emit the majority of this pollutant, numerous studies have concentrated on removing it from power plant flue emissions (Wall et al., 2013).

Urea accounts for almost 50% of world nitrogen fertiliser production. The synthesis of urea is based on the combination of ammonia and carbon dioxide at high pressure to form ammonium carbonate, which is subsequently dehydrated by the application of heat to form urea and water. Liquid Urea-Ammonium Nitrate (UAN) is formed by mixing and cooling concentrated urea and ammonium nitrate solutions. Being a stable compound, urea can also be used as a fertilizer, which can sequester carbon in the soil and reduce greenhouse gas emissions (Sun et al., 2018).

The major GHG emissions associated with nitrogen-containing fertiliser production are carbon dioxide (CO_2) emitted when flue gas is generated, when natural gas is combusted as part of ammonia synthesis, power generation for use around the plant and nitrous oxide (N_2O) emitted during nitric acid production (Wood & Cowie, 2004).

With the recent concern of climate change and the world target to achieve a net zero emissions climate change mitigation, many researches are done to estimate and mitigate GHG emissions from different sources and to capture these gases especially CO_2. In this work, ASPENTech software was used in simulating a model that will capture this CO_2 from industrial processes and analyse its utilisation in urea production. ASPEN HYSYS is employed in the CO_2 capture simulation and ASPEN Plus is used for the urea synthesis to demonstrate the utilisation of the captured CO_2 into something useful.

1.2 Problem Statement

The petrochemical industry contributes significantly to carbon dioxide (CO_2) emissions, a primary greenhouse gas responsible for climate change. Mitigating CO_2 emissions from petrochemical businesses and developing effective ways to use the captured CO_2 are critical. This study intends to find and investigate mitigation techniques that can minimise CO_2 emissions from petrochemical companies while also increasing their use in urea synthesis.

Key challenges:

- High CO_2 Emissions: The petrochemical industry emits a significant amount of CO_2 during various operations such as cracking, reforming, and burning. These emissions considerably contribute to the overall greenhouse gas footprint.
- Limited CO_2 Utilization: At the moment, captured CO_2 from the petrochemical industry is frequently vented or sequestered, resulting in inefficient utilisation and wasted potential for value-added applications.
- Urea Production: Urea is a common nitrogen fertiliser that is heavily reliant on natural gas and energy-intensive processes. Finding strategies to include CO_2 utilisation into the urea manufacturing process will assist reduce carbon intensity and increase fertiliser sustainability.

Energy models and simulations are therefore necessary to handle these issues and for effective energy management systems. These models will give an idea of the possible emissions quantification, aid in policy decision making and mitigate these emissions significantly. The simulations will also aid in predicting possible solutions of converting these emissions into something valuable.

1.3 Research Aim and Objectives

- Present a comprehensive framework for the implementation of CO_2 mitigation measures in petrochemical industries.

- Develop a model using ASPEN HYSIS for the separation and capture CO_2 from flue gas streams from power plants.
- Develop a model using ASPEN PLUS software to analyse utilising the captured CO_2 in producing urea.

1.4 Research Scope

This study focuses on the use of the ASPENTech software comprising of ASPEN HYSYS and ASPEN PLUS software using available data from a producing fertilizer industry to analyse the feasibility of capturing CO_2 from auxiliary boilers and reformer flue gas streams and utilising it at the urea plant for urea production.

1.5 Research Organization

This work is organized into five chapters as follows; Chapter one (Introduction) comprises of background, problem statement, aims and objectives of the research, scope of the research, and how the research is organized. Chapter two (Literature review) describes reviewed relevant literatures on the subject matter. Chapter three (methodology) outlines the procedure and methodology carried out in the course of the research in achieving the stated aims and objectives. It also describes the sources of data and information used in the course of the work. Chapter four (Results and Discussion) gives and discusses the results obtained based on the methodology followed. Lastly, Chapter five (Conclusion and Recommendation) presents the conclusions derived and the given recommendations, based on the results obtained.

CHAPTER 2

2.0 LITERATURE REVIEW

2.1 INTRODUCTION

The international community is becoming increasingly concerned about global warming. The rise in atmospheric temperature is most likely linked to an increase in anthropogenic greenhouse gas emissions. Carbon dioxide is the most significant contributor to the greenhouse gas effect; according to the most current Intergovernmental Panel on Climate Change report (IPCC), CO_2 emissions accounted for 76% of total emissions in 2010, with CH_4 accounting for 16%, N_2O accounting for roughly 6%, and mixed fluorinated gases accounting for around 2%. The combustion of fossil fuels and natural gas are the principal sources of CO_2 emissions (Gray, 2015).

Furthermore, many industrial activities such as oil refineries, cement, steel, and aluminium manufacture emit massive volumes of CO_2 into the atmosphere on a yearly basis. In this context, CO_2 capture has recently sparked significant interest in reducing industrial CO_2 emissions by separating CO_2 from various gaseous mixes to produce a concentrated stream ready for sequestration or further use (Bennett et al., 2014).

Greenhouse gases (GHG) are gases that trap heat or infrared radiation emitted from the Earth’s surface, and then reradiate back to the surface of the earth, hence adding up to the greenhouse gas effect. Greenhouse gases emission comprises primarily of carbon dioxide (CO_2), methane, nitrous oxide, and water vapor (Wood & Cowie, 2004).

CO_2 emissions are mostly caused by the usage of fossil fuels. CO_2 can also be emitted as a result of direct human-induced consequences on forestry and other land use, such as deforestation, land clearing for agriculture, and soil degradation. Similarly, land may absorb CO_2 from the atmosphere through reforestation, soil restoration, and other activities.

Meanwhile, the major source of increasing GHG emissions is the petrochemical and oil and gas sectors. About 89% of carbon dioxide emissions are from the use of fossil fuels, especially for generation of electricity and heat, transportation, and manufacturing and consumption. As a matter of fact, the United States Agency International Development (USAID) revealed that the GHG emissions in Nigeria increased by 25% (98.22 $MtCO_2e$) between 1990 and 2014, with average annual change in total emissions of 1% as reported by Climtelinks. Climatelinks article revealed that the total GHG emissions in 2014 were 492.44 million metric tons of carbon dioxide equivalent ($MtCO_2e$), of which 38.2% came from the land-use change and forestry sector, followed by the energy (32.6%), waste (14%), agriculture (13%) and the industrial processes sector contributing 2.1%. (Greenhouse Gas Emissions Factsheet: Nigeria, 2018).

To remove CO_2 from flue gases, three approaches have been proposed: pre-combustion, post-combustion, and oxy-fuel combustion. Pre-combustion converts fossil fuel to syngas, which consists of CO and H_2, and after converting CO to CO_2, the hydrogen is removed from the CO_2. The high purity oxygen obtained from the air separation unit (ASU) is utilised in the combustion process instead of air in the oxy-fuel combustion. As a result, the concentration of CO_2 in the flue gases rises, making it easier to separate following dehydration via cooling and compression. Furthermore, because nitrogen is eliminated in oxy-fuel combustion, the flame temperature rises, resulting in decreased fuel usage. Though greater flame temperatures, particularly above 1700K (Koohestanian et al., 2018), increase the formation of nitrogen oxides (NO_x), the major pollutant of concern will not be the primary issue in oxy-fuel combustion due to the low nitrogen concentration of the flue gas stream. However, in the oxyfuel approach, some of the CO_2 gas is recycled to the combustion chamber to control the flame temperature and compensate for the removed N_2 from the fuel gas mixture (Koohestanian et al., 2018). The CO_2 separation post-combustion causes only minor adjustments to the basic configuration of the current power plant.

Carbon dioxide can be separated and stored underground in empty gas reservoirs or utilised in the EOR process. However, from an economic standpoint, storing CO_2 in empty reservoirs is not justified. Furthermore, it can be emitted during natural disasters such as earthquakes, causing the CO_2 pollution level to skyrocket. Injecting CO_2 into oil fields can reduce crude oil viscosity and extraction costs, but it does not result in its removal, and the cost of the sweetening process increases as well.

In recent years, the separation of CO_2 as a useful raw resource rather than a waste, and its conversion to valuable products, has received a lot of attention (Koohestanian et al., 2018). Many petrochemical compounds, particularly urea and methanol, employ carbon dioxide as a raw material. To use CO_2 in each of the petrochemical plants, full assessments of market demand, other raw materials, and CO_2 delivery methods are necessary.

CO_2 can be converted into methane and methanol using the following reactions (Sabatier reaction):

$$1)\ CO_2 + 4H_2 \rightleftarrows CH_4 + 2H_2O, \Delta \mathrm{H}_{298\mathrm{K}} = -\frac{165.00KJ}{Mol} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots 2.1$$

$$2)\ CO_2 + 3H_2 \rightleftarrows CH_3OH + H_2O, \Delta \mathrm{H}_{298\mathrm{K}} = -49.4.00KJ/Mol \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots 2.2$$

If the conversion of CO_2 into methanol is carefully analysed from an environmental standpoint while hydrogen is supplied through water electrolysis, the manufacture of methanol from CO_2 would be justifiable. However, in order to avoid the reproduction of CO_2, the electricity required for plant operation should be delivered by renewable energy sources such as wind and solar energy. However, rather than removing CO_2 from the cycle, using it to synthesize these chemicals just delays their entry into the environment (Koohestanian et al., 2018).

Urea is another chemical derived from carbon dioxide. Urea is a rich source of nitrogen that is frequently utilised in the fertiliser industry. Urea is non-toxic and has the lowest nitrogen nutrition shipping cost per unit. Furthermore, urea is used as a raw ingredient in the synthesis of a wide range of significant chemical compounds, including polymers, resins, and adhesives. Urea-formaldehyde, urea-melamine-formaldehyde, and urea-nitrate explosives material are some of its derivatives. According to reports, the world today produces roughly 180Mt/y of urea (Koohestanian et al., 2018). It takes 132Mt/y of CO_2 to make this quantity of urea. The most popular technique of creating urea is to reform natural gas, which produces carbon dioxide and ammonia. Then urea is formed based on the reaction (3):

3) $2NH_3 + CO_2 \rightleftarrows NH_2CONH_2 + H_2O$ … 2.3

The above reaction, in fact, consists of two phases. First, ammonium carbamate (NH_2OCONH_4) is formed via the heterogeneous reaction of ammonia and carbon dioxide, as shown in reaction (4). Then, following the creation of ammonium carbamate in liquid form, urea is generated by dehydration of ammonium carbamate by reaction (5):

4) $2NH_3 + CO_2 \rightleftarrows NH_2COONH_4$ … 2.4

Ammonium carbamate formation

5) $NH_2COONH_4 \rightleftarrows NH_2CONH_2 + H_2O$ … 2.5

Urea formation

Combustion can also produce carbon dioxide. Given that CO_2, nitrogen, and water are the primary byproducts of the combustion process, capturing CO_2 and eliminating water from the combustion gas can result in nearly pure N_2. The latter product of the hydrogen reaction provides ammonia by the reaction (6):

6) $N_2 + 3H_2 \rightleftarrows 2NH_3$ ……………………………………………………………………….2.6

2.2 CO_2 Capture Technology Options and Applications

The goal of CO_2 capture is to create a concentrated stream of CO_2 at high pressure that can be easily transported to a storage location. Although, in theory, the entire gas stream carrying low amounts of CO_2 might be carried and injected underground, energy costs and other associated factors often make this strategy impracticable. As a result, it is important to produce a practically pure CO_2 stream for transit and storage. Applications for separating CO_2 in big industrial operations, such as natural gas treatment plants and ammonia production facilities, are already in use. Currently, CO_2 is typically removed to purify other industrial gas streams. Removal has been used for storage purposes in only a few cases; in most cases, the CO_2 is emitted to the atmosphere. Capture processes also have been used to obtain commercially useful amounts of CO_2 from flue gas streams generated by the combustion of coal or natural gas. To date, however, there have been no applications of CO_2 capture at large power plants (e.g., 500 MW) (CARBON DIOXIDE CAPTURE AND STORAGE, n.d.).

There are three basic techniques to capturing CO_2 generated by a primary fossil fuel (coal, natural gas, or oil), biomass, or mixes of these fuels, depending on the process or power plant application in question:

Post-combustion systems separate CO_2 from the flue gases produced by the combustion of the primary fuel in air. These systems normally use a liquid solvent to capture the small fraction of CO_2 (typically 3–15% by volume) present in a flue gas stream in which the main constituent is nitrogen (from air). For a modern pulverized coal (PC) power plant or a natural gas combined cycle (NGCC) power plant, current post-combustion capture systems would typically employ an organic solvent such as monoethanolamine (MEA) (CARBON DIOXIDE CAPTURE AND STORAGE, n.d.).

Pre-combustion systems process the primary fuel in a reactor with steam and air or oxygen to produce a mixture consisting mainly of carbon monoxide and hydrogen ("synthesis gas"). Additional hydrogen, together with CO_2, is produced by reacting the carbon monoxide with steam in a second reactor (a "shift reactor"). The resulting mixture of hydrogen and CO_2 can then be separated into a CO_2 gas stream, and a stream of hydrogen. If the CO_2 is stored, the hydrogen is a carbon-free energy carrier that can be combusted to generate power and/or heat. Although the initial fuel conversion steps are more elaborate and costly than in post-combustion systems, the high concentrations of CO_2 produced by the shift reactor (typically 15 to 60% by volume on a dry basis) and the high pressures often encountered in these applications are more favourable for CO_2 separation. Pre-combustion would be used at power plants that employ integrated gasification combined cycle (IGCC) technology. (CARBON DIOXIDE CAPTURE AND STORAGE, n.d.).

Oxyfuel combustion systems use oxygen instead of air for combustion of the primary fuel to produce a flue gas that is mainly water vapour and CO_2. This results in a flue gas with high CO_2 concentrations (greater than 80% by volume). The water vapour is then removed by cooling and compressing the gas stream. Oxyfuel combustion requires the upstream separation of oxygen from air, with a purity of 95–99% oxygen assumed in most current designs. Further treatment of the flue gas may be needed to remove air pollutants and non-condensed gases (such as nitrogen) from the flue gas before the CO_2 is sent to storage. As a method of CO_2 capture in boilers, oxyfuel combustion systems are in the demonstration phase. Oxyfuel systems are also being studied in gas turbine systems, but conceptual designs for such applications are still in the research phase.

Figure 2.1 shows a schematic diagram of the main capture processes and systems. All require a step involving the separation of CO_2, H_2 or O_2 from a bulk gas stream (such as flue gas, synthesis gas, air or raw natural gas). These separation steps can be accomplished by means of physical or chemical solvents, membranes, solid sorbents, or by cryogenic separation. The choice of a specific capture technology is determined largely by the process conditions under which it must operate. Current post-combustion and pre-combustion systems for power plants could capture 85–95% of the CO_2 that is produced. Higher capture efficiencies are possible, although separation devices become considerably larger, more energy intensive and more costly. Capture and compression need roughly 10–40% more energy than the equivalent plant without capture, depending on the type of system. Due to the associated CO_2 emissions, the net amount of CO_2 captured is approximately 80–90%. Oxyfuel combustion systems are, in principle, able to capture nearly all of the CO_2 produced. However, the need for additional gas treatment systems to remove pollutants such as sulphur and nitrogen oxides lowers the level of CO_2 captured to slightly more than 90% (CARBON DIOXIDE CAPTURE AND STORAGE, n.d.).

As stated previously, CO_2 capture is already used in several industrial applications. The same technologies as would be used for pre-combustion capture are employed for the large-scale production of hydrogen (which is used mainly for ammonia and fertilizer manufacture, and for petroleum refinery operations). The separation of CO_2 from raw natural gas (which typically contains significant amounts of CO_2) is also practised on a large scale, using technologies similar to those used for post-combustion capture. Although commercial systems are also available for large-scale oxygen separation, oxyfuel combustion for CO_2

capture is currently in the demonstration phase. In addition, research is being conducted to achieve higher levels of system integration, increased efficiency and reduced cost for all types of capture systems.

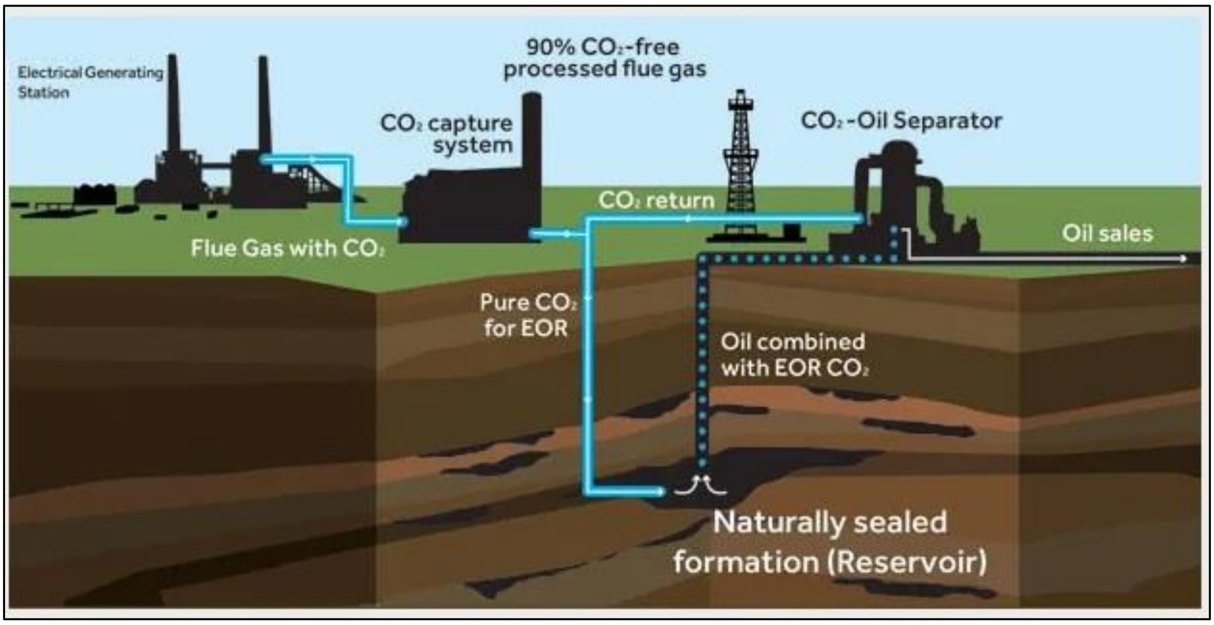


Figure 2.1: Use of CO_2 *in Enhanced Oil Recovery (EOR) Source: https://spectrum.ieee.org/*

2.3 CO_2 Emissions and Energy Consumption

Fossil fuels are the dominant form of energy utilized in the world (86%), and account for about 75% of current anthropogenic CO_2 emissions (IPCC, 2001c). In 2002, 149 Exajoules (EJ) of oil, 91 EJ of natural gas, and 101 EJ of coal were consumed by the world's economies (IEA, 2004). Global primary energy consumption grew at an average rate of 1.4% annually between 1990 and 1995 (1.6% per year between 1995 and 2001); the growth rates were 0.3% per year (0.9%) in the industrial sector, 2.1% per year (2.2%) in the transportation sector, 2.7% per year (2.1%) in the buildings sector, and –2.4% per year (–0.8%) in the agricultural/other sector (IEA, 2003). Average global CO_2 emissions increased by 1.0% per year between 1990 and 1995 (1.4% between 1995 and 2001), a rate slightly below that of energy consumption in both periods. In individual sectors, there was no increase in emissions from industry between 1990 and

1995 (0.9% per year from 1995 to 2001); there was an increase of 1.7% per year (2.0%) in the transport sector, 2.3% per year (2.0%) in the buildings sector, and a fall of 2.8% per year (1.0%) in the agricultural/other sector (IEA, 2003). Total emissions from fossil fuel consumption and flaring of natural gas were 24Gt CO_2 per year (6.6 GtC per year) in 2001 – industrialized countries were responsible for 47% of energy-related CO_2 emissions (not including international bunkers). The Economies in Transition accounted for 13% of 2001 emissions; emissions from those countries have been declining at an annual rate of 3.3% per year since 1990. Developing countries in the Asia-Pacific region emitted 25% of the global total of CO_2; the rest of the developing countries accounted for 13% of the total (IEA, 2003).

2.4 Other Greenhouse Gas Emissions

Anthropogenic climate change is mainly driven by emissions of CO_2 but other greenhouse gases (GHGs) also play a part. Since some of the anthropogenic CO_2 comes from industrial processes and some from land use changes (mainly deforestation), the contribution from fossil fuel combustion alone is about half of the total from all GHGs.

In terms of impact on radiative forcing, methane is the next most important anthropogenic greenhouse gas after CO_2 (currently accounting for 20% of the total impact) (IPCC, 2001b). The energy sector is an important source of methane but agriculture and domestic waste disposal contribute more to the global total (IPCC, 2001c). Nitrous oxide contributes directly to climate change (currently 6% of the total impact of all GHGs); the main source is agriculture but another is the industrial production of some chemicals; other oxides of nitrogen have an indirect effect. A number of other gases make significant contributions (IPCC, 2001c).

2.5 Overview of the CO_2 Capture and Storage Concept and its Development

Capturing CO_2 typically involves separating it from a gas stream. Suitable techniques were developed 60 years ago in connection with the production of town gas; these involved scrubbing the gas stream with a chemical solvent (Siddique, 1990). Subsequently they were adapted for related purposes, such as capturing CO_2 from the flue gas streams of coal- or gas-burning plant for the carbonation of drinks and brine, and for enhancing oil recovery. These developments required improvements to the process so as to inhibit the oxidation of the solvent in the flue gas stream. Other types of solvent and other methods of separation have been developed more recently. This technique is widely used today for separating CO_2 and other acid gases from natural gas streams. Horn and Steinberg (1982) and Hendriks *et al.* (1989) were among the first to discuss the application of this type of technology to mitigation of climate change, focusing initially on electricity generation. CO_2 removal is already used in the production of hydrogen from fossil fuels; Audus *et al.* (1996) discussed the application of capture and storage in this process as a climate protection measure.

In order to transport CO_2 to possible storage sites, it is compressed to reduce its volume; in its 'dense phase', CO_2 occupies around 0.2% of the volume of the gas at standard temperature and pressure. Several million tonnes per year of CO_2 are transported today by pipeline (Skovholt, 1993), by ship and by road tanker.

In principle, there are many options available for the storage of CO_2. The first proposal of such a concept (Marchetti, 1977) envisaged injection of CO_2 into the ocean so that it was carried into deep water where, it was thought, it would remain for hundreds of years. In order to make a significant difference to the atmospheric loading of greenhouse gases, the amount of CO_2 that would need to be stored in this way would have to be significant compared to the amounts of CO_2 currently emitted to the atmosphere – in other words gigatonnes of CO_2 per year. The only potential storage sites with capacity for such quantities are natural reservoirs, such as geological formations (the capacity of European formations was first assessed by

Holloway *et al.*, 1996) or the deep ocean (Cole *et al.*, 1993). Other storage options have also been proposed, as discussed below.

Injection of CO_2 underground would involve similar technology to that employed by the oil and gas industry for the exploration and production of hydrocarbons, and for the underground injection of waste as practised in the USA. Wells would be drilled into geological formations and CO_2 would be injected in the same way as CO_2 has been injected for enhanced oil recovery since the 1970s (Blunt *et al.*, 1993; Stevens and Gale, 2000). In some cases, this could lead to the enhanced production of hydrocarbons, which would help to offset the cost. An extension of this idea involves injection into saline formations or into unminable coal seams (Stevens and Gale, 2000); in the latter case, such injection may sometimes result in the displacement of methane, which could be used as a fuel. The world's first commercial-scale CO_2 storage facility, which began operation in 1996, makes use of a deep saline formation under the North Sea (Cole *et al.*, 1993).

Monitoring will be required both for purposes of managing the storage site and verifying the extent of CO_2 emissions reduction which has been achieved. Techniques such as seismic surveys, which have developed by the oil and gas industry, have been shown to be adequate for observing CO_2 underground (Stevens and Gale *et al.*, 2001) and may form the basis for monitoring CO_2 stored in such reservoirs.

Many alternatives to the storage of dense phase CO_2 have been proposed: for example, using the CO_2 to make chemicals or other products, fixing it in mineral carbonates for storage in a solid form, storing it as solid CO_2 ('dry ice'), as CO_2 hydrate, or as solid carbon (Steinberg, 1996). Another proposal is to capture the CO_2 from flue gases using micro-algae to make a product which can be turned into a biofuel (Benemann, 1993).

The potential role of CO_2 capture and storage as a mitigation option has to be examined using integrated energy system models. An assessment of the environmental impact of the technology through life cycle analysis was reported by Audus (1997) and other studies also.

The concept of CO_2 capture and storage is therefore based on a combination of known technologies applied to the new purpose of mitigating climate change. The economic potential of this technique to enable deep reductions in emissions was examined by Edmonds *et al.* (2001).

2.5.1 The Basis of CO_2 Capture

The main application of CO_2 capture is likely to be at large point sources: fossil fuel power plants, fuel processing plants and other industrial plants, particularly for the manufacture of iron, steel, cement and bulk chemicals.

Capturing CO_2 directly from small and mobile sources in the transportation and residential & commercial building sectors is expected to be more difficult and expensive than from large point sources. An alternative way of avoiding emissions of CO_2 from these sources would be by use of energy carriers such as hydrogen or electricity produced in large fossil fuel-based plants with CO_2 capture or by using renewable energy sources.

In an analysis of possible future scenarios for anthropogenic greenhouse-gas emissions it is implicit that technological innovations will be one of the key factors which determines our future path. Therefore, this chapter deals not only with application of existing technology for CO_2 capture, but describes many new processes under development which may result in lower CO_2 capture costs in future.

2.5.2 CO_2 Capture Systems

There are four basic systems for capturing CO_2 from use of fossil fuels and/or biomass:

- Capture from industrial process streams;
- Post-combustion capture;
- Oxy-fuel combustion capture;
- Pre-combustion capture.

These systems are shown in simplified form in Figure 2.2.

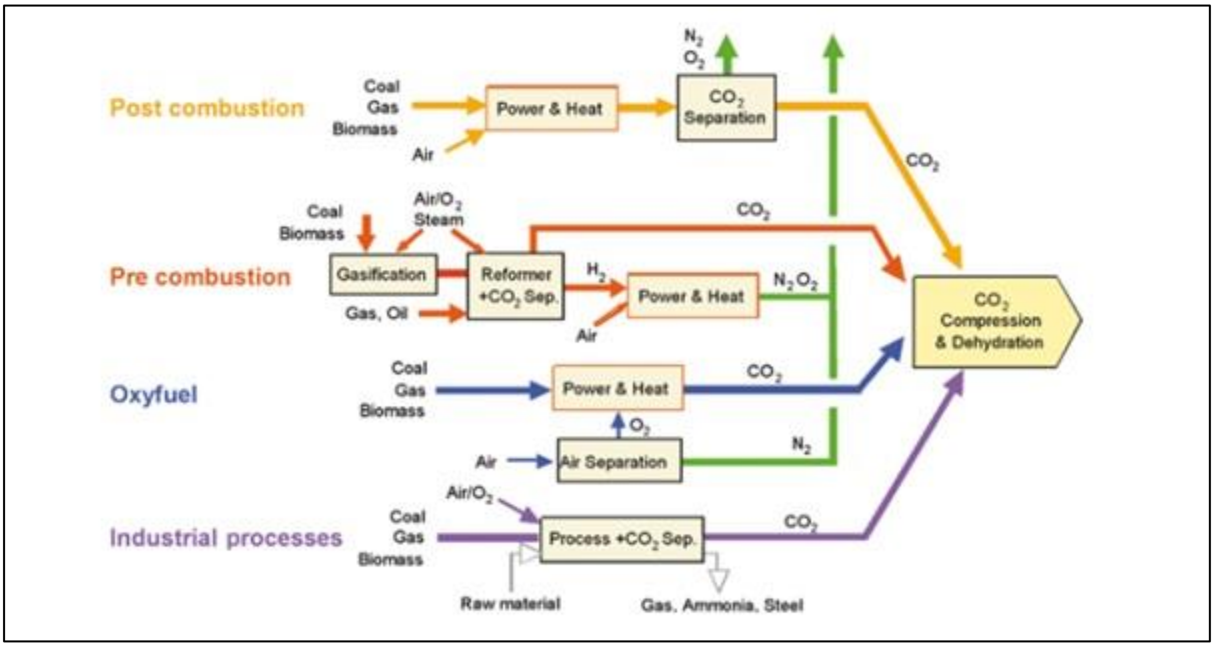


Figure 2.2: Overview of CO_2 *capture processes and systems*

2.5.2.1 CO_2 Capture from Industrial Process Streams

CO_2 has been captured from industrial process streams for 80 years (Kohl and Nielsen, 1997), although most of the CO_2 that is captured is vented to the atmosphere because there is no incentive or requirement to store it. Current examples of CO_2 capture from process streams are purification of natural gas and production of hydrogen-containing synthesis gas for the manufacture of ammonia, alcohols and synthetic liquid fuels. Most of the techniques employed for CO_2 capture in the examples mentioned are also similar to those used in precombustion capture. Other industrial process streams which are a source of CO_2 that is not captured include cement and steel production, and fermentation processes for food and drink production. CO_2 could be captured from these streams using techniques that are common to post-combustion capture, oxyfuel combustion capture and pre-combustion capture.

2.5.2.2 Post-Combustion CO_2 Capture

Capture of CO_2 from flue gases produced by combustion of fossil fuels and biomass in air is referred to as post-combustion capture. Instead of being discharged directly to the atmosphere, flue gas is passed through equipment which separates most of the CO_2. The CO_2 is fed to a storage reservoir and the remaining flue gas is discharged to the atmosphere. A chemical sorbent process as described below (Section 2.7.2) would normally be used for CO_2 separation.

Apart from industrial applications, the main systems of reference for post-combustion capture are the current installed capacity of 2261 GWe of oil, coal, and natural gas power plants (IEA WEO, 2004), with 155 GWe of supercritical pulverised coal fired plants (IEA CCC, 2005) and 339 GWe of natural gas combined cycle (NGCC) plants representing the types of high efficiency power plant technology where CO_2 capture can be best applied.

2.5.2.3 Oxy-Fuel Combustion CO_2 Capture

In oxy-fuel combustion, virtually pure oxygen is utilised for combustion instead of air, resulting in a flue gas primarily composed of carbon dioxide and water vapour. The flame temperature is extremely high when fuel is burnt in pure oxygen, however CO_2 and/or H_2O-rich flue gas can be returned to the combustor to mitigate this. Oxygen is typically created through low temperature (cryogenic) air separation, and novel strategies for supplying oxygen to the fuel, including as membranes and chemical looping cycles, are being researched. The power plant systems of reference for oxy-fuel combustion capture systems are the same as those mentioned above for post-combustion capture systems.

2.5.2.4 Pre-Combustion Capture

Pre-combustion capture is the process of reacting a fuel with oxygen, air, and/or steam to produce primarily a 'synthesis gas (syngas)' or 'fuel gas' comprised of carbon monoxide and hydrogen. In a catalytic reactor known as a shift converter, carbon monoxide reacts with steam to produce CO_2 and additional hydrogen. CO_2 is subsequently separated, typically through physical or chemical absorption, yielding a hydrogen-rich fuel that can be utilised in a variety of applications such as boilers, furnaces, gas turbines, engines and fuel cells. These systems are considered to be strategically important but the power plant systems of reference today are 4 GWe of both oil and coal-based, integrated gasification combined cycles (IGCC) which are around 0.1% of total installed capacity worldwide (3719 GWe; IEA WEO, 2004).

2.5.3 Classes of CO_2 Capture Technologies

Many of the known gas separation technologies are used in CO_2 capture systems, which are integrated into the fundamental CO_2 capture systems outlined in the previous section. A synopsis of these separation procedures is provided below, with additional information available in other vast literatures.

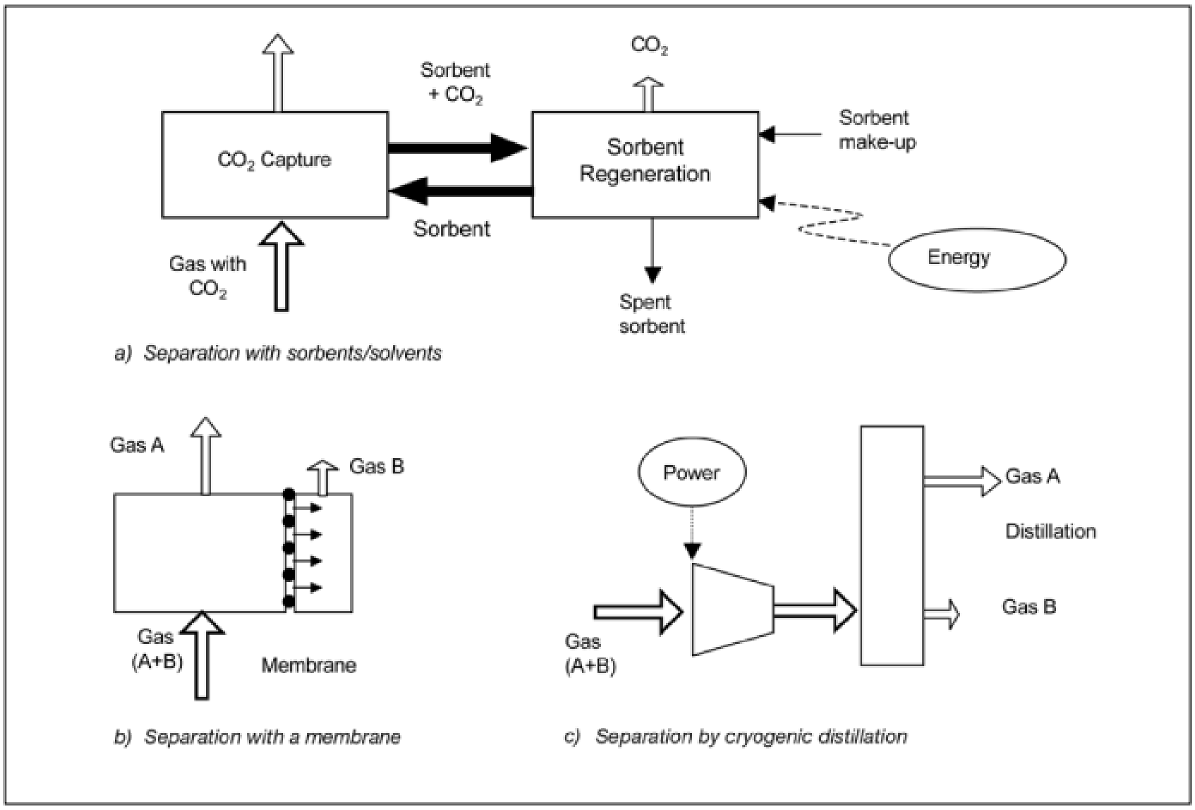


Figure 2.3: General schemes of the main separation processes relevant for CO_2 *capture.*

The gas eliminated during the separation process could be CO_2, H_2, or O_2. One of the separated gas streams (A and B) in Figures 2.3b and 2.3c is a concentrated stream of CO_2, H_2 or O_2, and the other is a gas stream containing all of the remaining gases in the original gas (A+B).

2.5.3.1 Separation Using Sorbents/solvents

The separation is accomplished by bringing the CO_2-containing gas into close contact with a liquid absorbent or solid sorbent capable of retaining the CO_2. The sorbent loaded with captured CO_2 is moved to a separate vessel in Figure 2.3a, where it releases the CO_2 (regeneration) after being heated, after a pressure decrease, or after any other change in the conditions around the sorbent. In a cyclic process, the sorbent formed after regeneration is returned to capture more CO_2. In other forms of this scheme, the sorbent is solid and does not circulate between vessels since sorption and regeneration are accomplished through cyclic changes (in pressure or temperature) in the vessel where the sorbent is contained. A make-up flow of fresh sorbent is always required to compensate for the natural decay of activity and/or sorbent losses. In some situations, the sorbent may be a solid oxide which reacts in a vessel with fossil fuel or biomass producing heat and mainly CO_2. The spent sorbent is then circulated to a second vessel where it is re-oxidized in air for reuse with some loss and make up of fresh sorbent.

Figure 2.3 depicts the overall architecture that regulates several key CO_2 capture systems, including prominent commercial choices such as chemical absorption and physical absorption and adsorption. Other innovative processes are being developed to overcome the limits of existing systems, such as those based on new liquid sorbents or new solid regenerable sorbents. One typical issue with these CO_2 capture systems is that the sorbent flow between the vessels in Figure 2.3a is high since it must match the massive flow of CO_2 handled in the power plant. As a result, the equipment sizes and energy required for sorbent regeneration are high, resulting in a significant efficiency penalty and additional expense. Also, in systems using expensive sorbent materials there is always a danger of escalating cost related to the purchase of the sorbent and the disposal of sorbent residues. Good sorbent performance under high CO_2 loading in many repetitive cycles is obviously a necessary condition in these CO_2 capture systems.

2.5.3.2 Separation Using Membranes

Membranes (Figure 2.3b) are specially designed materials that allow a gas to pass through them selectively. The nature of the material influences the membrane's selectivity to different gases, however the flow of gas through the membrane is usually driven by the pressure difference across the membrane. As a result, high-pressure streams are commonly used for membrane separation. Many different types of membrane materials (polymeric, metallic, ceramic) may be used in CO_2 capture systems to preferentially separate H_2 from a fuel gas stream, CO_2 from a variety of process streams, or O_2 from air, with the separated O_2 assisting in the production of a highly concentrated CO_2 stream. Despite the fact that membrane separation has numerous current commercial applications in industry (some on a huge scale, such as CO_2 separation from natural gas), it has not yet been deployed for the large scale and demanding requirements in terms of reliability and cheap cost required for CO_2 capture systems. A substantial global R&D effort is underway to develop more acceptable membrane materials for CO_2 capture in large-scale applications.

2.5.3.3 Distillation of a Liquefied Gas Stream and Refrigerated Separation

A series of compression, cooling, and expansion stages can be used to convert a gas to a liquid. Once in liquid form, the components of the gas can be separated in a distillation column. In the case of air, this technique is currently carried out commercially on a big scale. Oxygen can be extracted from air using the strategy shown in Figure 2.3c and used in a variety of CO_2 capture systems (oxy-fuel combustion and pre-combustion capture). The primary challenge with these systems, as stated in earlier paragraphs, is the huge amount of oxygen required. Refrigerated separation can also be used to separate CO_2 from other gases. It can be used to separate impurities from relatively high purity CO_2 streams, for example, from oxy-fuel combustion and for CO_2 removal from natural gas or synthesis gas that has undergone a shift conversion of CO to CO_2.

2.6 Industrial Process Capture Systems

There are various industrial applications involving process streams where huge amounts of CO_2 can be captured at lower prices than the methods discussed in the rest of this chapter. Capture from these sources will not be a complete solution to climate change needs because the amounts of combustion-generated CO_2 are substantially higher, but it may be the first capture and storage location.

2.6.1 Natural Gas Sweetening

Natural gas contains different concentration levels of CO_2, depending on its source, which must be removed. Often pipeline specifications require that the CO_2 concentration be lowered to around 2% by volume (although this amount varies in different places) to prevent pipeline corrosion, to avoid excess energy for transport and to increase the heating value of the gas.

Depending on the level of CO_2 in natural gas, different processes for natural gas sweetening (i.e., H_2S and CO_2 removal) are available (Kohl and Nielsen, 1997):

- Chemical solvents
- Physical solvents
- Membranes

Natural gas sweetening using various alkanolamines (MEA, DEA, MDEA, etc.), or a mixture of them, is the most commonly used method.

2.6.2 Steel Production

The iron and steel industry are the world's most energy-intensive manufacturing sector, requiring 10-15% of total industrial energy consumption (IEA GHG, 2000a). In 1995, associated CO_2 emissions were expected to be 1442 $MtCO_2$. There are two types of iron and steel-making technology in use today. The integrated steel plant has a typical capacity of 3-5 Mtonnes per year of steel and uses coal as its basic fuel with, in many cases, additional natural gas and oil. The mini-mill uses electric arc furnaces to melt scrap with a typical output of 1

Mtonnes per year of steel and an electrical consumption of 300-350 kWh per ton of steel. Mini-mills are increasingly blending direct-reduced iron (DRI) with scrap to improve steel grade. Direct-reduced iron is created by reacting high oxygen content iron ore with H_2 and CO to yield reduced iron plus H_2O and CO_2. As a result, several direct reduction iron processes are capable of capturing a pure CO_2 stream.

2.6.3 Cement Production

CO_2 emissions from the cement industry account for 6% of the total CO_2 emissions from stationary sources. Large amounts of fuel are required to power the high temperature, energy-intensive reactions connected with the calcination of the limestone, which is calcium carbonate being transformed to calcium oxide with the development of CO_2. For every 1000 kg of cement produced, the industry generates about 900 kg of CO_2 (MAHASENAN et al., 2003).

CO_2 concentrations in flue gases range from 15% to 30% by volume, which is greater than that of flue gases from power and heat generation (3%-15% by volume). In theory, the stated post-combustion CO_2 capture methods might be applied to cement manufacturing plants, but would necessitate the additional generation of steam in a cement plant to regenerate the solvent used to capture CO_2. Oxy-fuel combustion capture technology may also be a promising method for recovering CO_2 (IEA GHG, 1999).

2.6.4 Ammonia Production

CO_2 is a byproduct of ammonia (NH_3) synthesis. Two main groups of processes are used:

- Steam reforming of light hydrocarbons (natural gas, liquefied petroleum gas, naphtha)

- Partial oxidation or gasification of heavy hydrocarbons (coal, heavy fuel oil, vacuum residue)

Because processes within the steam methane reforming group produce around 85% of ammonia, a description of the process is useful. This technique of producing ammonia consists of three major process steps: high pressure catalytic reforming of natural gas, gas purification, and ammonia synthesis. The first two phases entail the production of hydrogen gas, the addition of nitrogen in a stoichiometric proportion, and the removing of catalyst poisons: carbon dioxide, carbon monoxide, and water. Ammonia synthesis entails the catalytic fixation of nitrogen at high temperatures and pressures, followed by the recovery of ammonia.

In a more expanded form, the ammonia production comprises of the following steps:

1. Purification of the feed;

2. Primary steam methane reforming;

3. Secondary reforming, with the addition of air, commonly called auto thermal reforming;

4. Shift conversion of CO and H_2O to CO_2 and H_2;

5. Removal of CO_2;

6. Methanation (a process that reacts and removes trace CO

and CO_2);

7. Ammonia synthesis.

2.7 Post-Combustion CO_2 Capture Systems

The majority of current anthropogenic CO_2 emissions from stationary sources occur from combustion systems such as power plants, cement kilns, industrial furnaces, and iron and steel production plants. In these large-scale processes, direct firing of fuel with air in a combustion chamber has been (and continues to be) the most cost-effective method of extracting and utilising the energy contained in the fuel for centuries. When confronted with the realities of today's CO_2 emission sources, the strategic necessity of post-combustion capture technologies becomes unambiguous. All of the CO_2 capture systems described in this section are designed to separate CO_2 from the flue gases produced by a large-scale combustion process that uses fossil fuels. Similar capture systems can also be applied to biomass fired combustion processes that tend to be used on a much smaller scale compared to those for fossil fuels.

Flue gases or stack gases found in combustion systems are usually at atmospheric pressure. Because of the low pressure, the large presence of nitrogen from air and the large scale of the units, huge flows of gases are generated. In principle, post-combustion capture systems can be applied to flue gases produced from the combustion of any type of fuel. However, the impurities in the fuel are very important for the design and costing of the complete plant. Flue gases coming from coal combustion will contain not only CO_2, N_2, O_2 and H_2O, but also air pollutants such as SOx, NOx, particulates, HCl, HF, mercury, other metals and other trace organic and inorganic contaminants. Figure 2.4 shows a general schematic of a coal-fired power plant in which additional unit operations are deployed to remove the air pollutants prior to CO_2 capture in an absorption-based process. Since these processes are highly cost intensive, large R&D effort is being undertaken worldwide to develop more efficient and lower cost post-combustion systems, following all possible approaches for the CO_2 separation step (using sorbents, membranes or cryogenics) (Rao and Rubin, 2002).

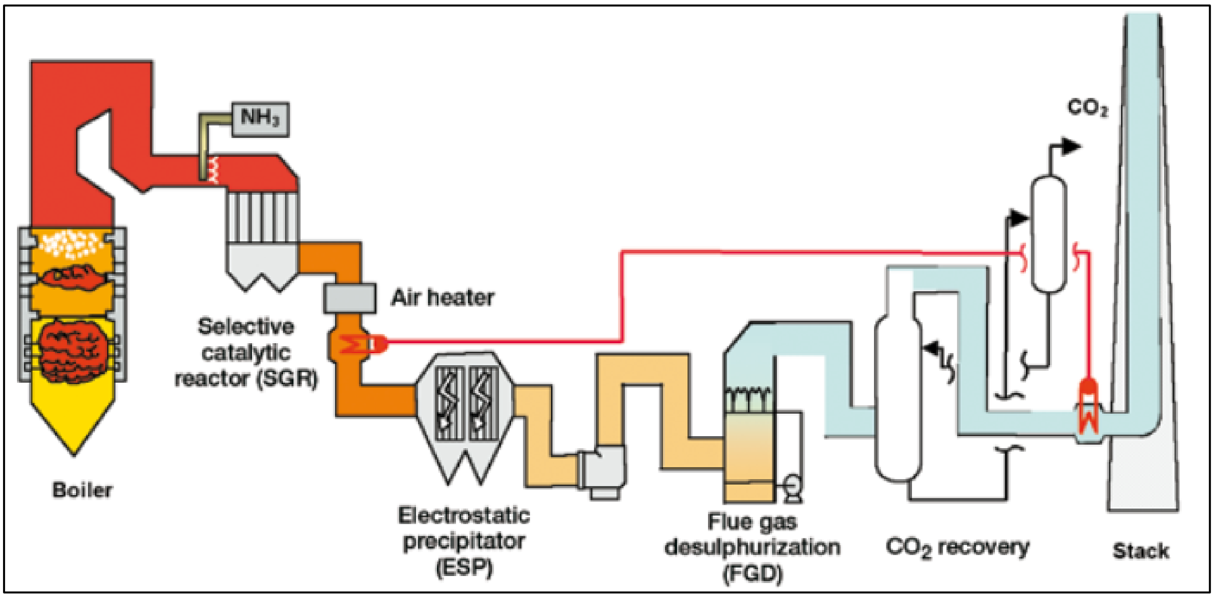


Figure 2.4: Schematic of a pulverized coal-fired power plant with an amine-based CO_2 *capture system and other emission controls.*

2.7.1 Current CO_2 Capture Technologies

There are various commercially available process technologies that can be utilised to extract CO_2 from exhaust gases in theory. However, comparative evaluation studies (Hendriks, 1994; Riemer and Ormerod, 1995; IEA GHG, 2000b) have revealed that chemical solvent absorption methods are currently the preferable alternative for post-combustion CO_2 capture. When compared to other existing post-combustion capture techniques, they now offer excellent capture efficiency and selectivity, as well as the lowest energy use and costs. For post-combustion CO_2 capture systems, absorption technologies have reached the commercial level of operation, albeit not on the scale necessary for power plant flue gases. The fundamentals of the CO_2 separation step using commercial chemical absorption processes are discussed in the subsequent section.

2.7.2 Absorption Processes

The reversible nature of the chemical reaction of an aqueous alkaline solvent, usually an amine, with an acid or sour gas is used in post-combustion capture absorption procedures.

Figure 2.5 shows the process flow diagram of a commercial absorption system. The flue gas is brought into contact with the solvent in the absorber after it has been cooled. To offset the pressure decrease through the absorber, a blower is necessary. CO_2 is bound by the chemical solvent in the absorber at absorber temperatures ranging from 40 to 60°C. The flue gas is then washed to balance the water in the system and get rid of any solvent droplets or solvent vapour carried over before leaving the absorber. As a result of the chemical reaction in the solvent, it is feasible to reduce the CO_2 concentration in the exit gas to very low values; however, lower exit concentrations typically increase the height of the absorption vessel. The 'rich' solvent, which contains the chemically bonded CO_2, is then pumped via a heat exchanger to the top of a stripper (or regeneration tank). The regeneration of the chemical solvent is carried out in the stripper at elevated temperatures (100°C–140°C) and pressures not very much higher than atmospheric pressure. Heat is supplied to the reboiler to maintain the regeneration conditions. This leads to a thermal energy penalty as a result of heating up the solvent, providing the required desorption heat for removing the chemically bound CO_2 and for steam production which acts as a stripping gas. Steam is recovered in the condenser and fed back to the stripper, whereas the CO_2 product gas leaves the stripper. The ‘lean’ solvent, containing far less CO_2 is then pumped back to the absorber via the lean-rich heat exchanger and a cooler to bring it down to the absorber temperature level.

The following are the key factors that determine the technical and economic operation of a CO_2 absorption system:

- Flue gas flow rate - The flue gas flow rate determines the size of the absorber, and the absorber contributes significantly to the overall cost.

- CO_2 content in flue gas - Because flue gas is typically at atmospheric pressure, the partial pressure of CO_2 can range from 3 to 15 kPa. Aqueous amines (chemical solvents) are the best absorption solvents under these low CO_2 partial pressure conditions (Kohl and Nielsen, 1997).

- CO_2 removal - In practise, CO_2 recoveries typically range between 80% and 95%. The actual recovery option is an economic trade-off; a higher recovery will result in a taller absorption column, larger energy penalties, and hence higher costs.

- Solvent flow rate - Aside from the absorber, the solvent flow rate determines the size of the majority of the equipment. The flow rate of a specific solvent is determined by the previous parameters as well as the CO_2 concentrations chosen within the lean and rich solutions.

- Energy consumption - The process's energy consumption is the sum of the thermal energy required to regenerate the solvents and the electrical energy required to operate the liquid pumps and the flue gas blower or fan. It requires additional energy to compress the recovered CO_2 to the final pressure required for transportation and storage.

The Process flow diagram for CO_2 recovery from flue gas by chemical absorption is shown in figure 2.5 below.

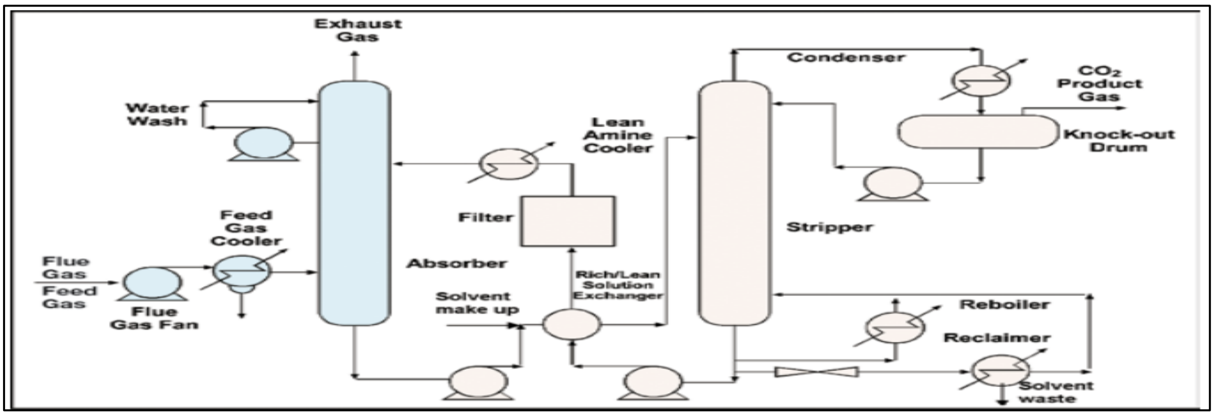


Figure 2.5: Process flow diagram for CO_2 *recovery from flue gas by chemical absorption.*

In this work, the chemical absorption methodology is employed to capture CO_2 from a process plant flue gas stream. Captured CO_2 is utilised as a feedstock for other industrial activities.

2.8 Overview of Urea Production

Urea, which is known to be an important petrochemical product, is mainly used as fertilizer. Urea (NH_2CONH_2) is produced commercially by reaction of ammonia (NH_3) and carbon dioxide (CO_2), under conditions depending on each particular plant technology. Urea accounts for almost 50% of world nitrogen fertiliser production (Wood & Cowie, 2004).

There are a lot of urea synthesis technologies available such as Snamprogetti process, Stamicarbon process and etc. In most operating processes, the synthesis reaction is carried out in the liquid phase, at pressure from 140 to 150atm and at temperature between 170°C and 200°C. In this study, a simulation using an ASPENTech software, the ASPEN Plus, is developed specifically for the high-pressure urea synthesis section using a stream of CO_2 captured from a power plant flue gas stream (simulation included in this work). We adopted the Stamicarbon process because of its simplicity and industrial benefits. In this study, the formation of ammonium carbamate is considered to occur through the heterogeneous reaction of carbon dioxide and ammonia in the Stamicarbon procedures.

The principal raw materials required for this purpose are NH_3 & CO_2. Urea production consists of two main reactions. In the first reaction, ammonia and carbon dioxide reacts to form ammonium carbamate which decomposes to urea and water in the next step. These two reactions are expressed as follows:

1) $2NH_3 + CO_2 \rightleftarrows NH_2COONH_4$

Ammonium carbamate formation

2) $NH_2COONH_4 \rightleftarrows NH_2CONH_2 + H_2O$

Urea formation

2.8.1 Properties of Urea

The physical property of urea is that it is a white, odourless, hygroscopic solid. It is non-corrosive in itself. It is a very stable compound and hence its ability to sequester CO_2 in the earth for a very long time.

2.8.2 Chemical Properties of Urea

The chemical properties of urea are summarised in table 2.1 below.

Table 2.1: Chemical Properties of Urea

Molecular weight	60 °C
Relative humidity	60 %
Maximum nitrogen content	46.6%
Specific gravity	1.335
Heat of fusion	60 Cal/g
Heat of solution in water	58 Cal/g
Bulk density	0.74g/cm^3

2.8.3 Process Description

Ammonia & CO_2 are compressed separately and fed to a high-pressure reactor (140-150 atm) as shown in which must be water cooled due to the highly exothermic nature of the reaction. A mixture of urea, ammonium carbamate, H_2O and unreacted (NH_3+CO_2) is produced.

This liquid effluent is let down to lower pressure and fed to a special flash-evaporator containing a gas-liquid separator and condenser. Unreacted NH_3, CO_2 & H_2O are thus removed & recycled. An aqueous solution of carbamate-urea is passed to the atmospheric flash drum where further decomposition of carbamate takes place. The off gases from this step can either be recycled or sent to NH_3 processes for making chemical fertilizer. The 80% aqueous urea solution can be used as it is, or sent to a vacuum evaporator to obtain molten urea containing less than 1 % water.

2.8.4 Urea Process Technologies

There are many types of processes to produce urea using NH_3 and CO_2 in the modern industrial scale. Common one of the processes include:

- Stamicarbon CO_2 stripping process
- Snamprogetti ammonia and self-stripping urea process
- Toatsu Chemicals technology
- Etc.

In this work, the urea synthesis section is modelled using the conventional Starmicarbon process technology with ASPEN Plus software.

2.8.4.1 Starmicarbon Process Technology

The Starmicarbon process technology is also known as CO_2-stripping process as it uses carbon dioxide as the stripping agent. The main characteristic of this process is the recycling of nonconverted material from the high-pressure stripper in gas phase rather than aqueous phase.

NH_3 and CO_2 are converted to urea via ammonium carbamate at a pressure of approximately 140 bars and a temperature of 180-185°C. The molar NH_3/CO_2 ratio applied in the reactor is about 2.95. This results in a CO_2 conversion of about 60% and an NH_3 conversion of 41%. The reactor effluent, containing unconverted NH_3 and CO_2 is subjected to a stripping operation at essentially reactor pressure, using CO_2 as stripping agent. The stripped-off NH_3 and CO_2 are then partially condensed and recycled to the reactor. The heat evolving from this condensation is utilized to produce 4.5 bar steam, some of which can be used for heating purposes in the downstream sections of the plant. Surplus steam is sent to the turbine of the CO_2 compressor. The NH_3 and CO_2 in the stripper effluent are vaporized in a low-pressure decomposition stage and subsequently condensed to form a carbamate solution, which is recycled to the 140 bar synthesis section. Further concentration of the urea solution leaving the decomposition stage takes place in the evaporation section, where a 99.7% molten urea is produced.

A typical schematic of a process flow diagram for the Starmicarbon urea process technology is shown in figure 2.6 below.

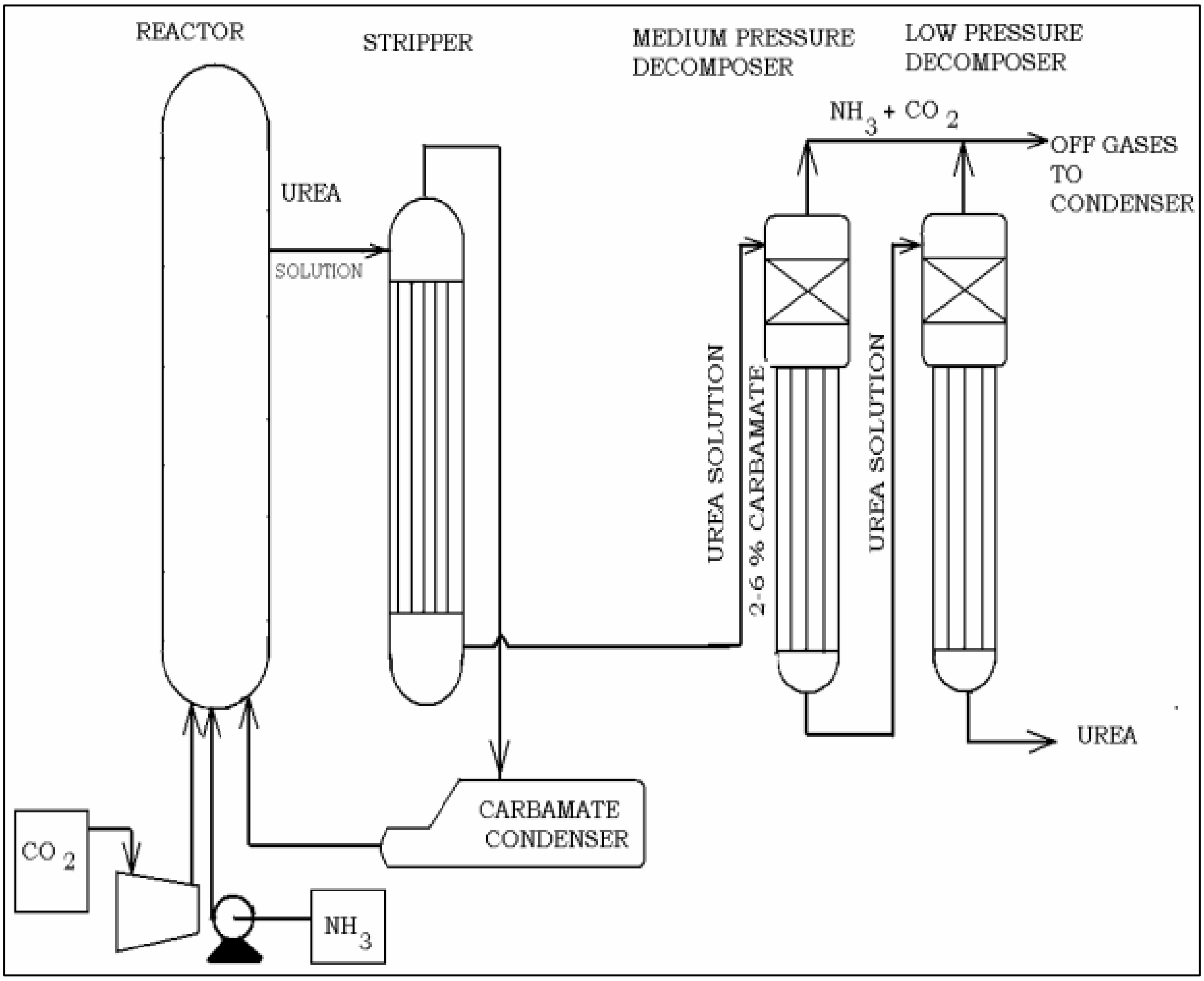


Figure 2.6: Starmicarbon Urea process technology

CHAPTER 3

3.0 RESEARCH METHODOLOGY

This chapter discusses the methodology used in this work. In Section 3.1, data about the flue gases streams is presented. The specifications of the flue gases data are obtained from a 120MW power plant involving three steam turbine generators (STG) of about 40MW capacity. Each of the turbine shaft is driven by steam generated from the auxiliary boilers of about 200 ton/hour steam production capacity. Flue gas is generated in the course of producing the steam in the auxiliary boilers and during the steam methane reforming of natural gas at the primary reformer.

In section 3.3, ASPEN HYSIS simulation was carried out to capture CO_2 from both streams of auxiliary boilers and primary reformer exhaust flue gases streams.

This work shows how obtained stream of CO_2 separated from flue gas streams can be gainfully used to produce Urea. For that, ASPEN HYSIS was used to capture CO_2 which in turn was used as a feedstock for urea production using ASPEN PLUS software to rigorously model the urea synthesis process using the Stamicarbon Technology.

3.1 Modelling Approach

The modelling of the two processes for this research was achieved by the use of **ASPENTech** package which is a leading provider of engineering software solutions, and their process simulation software, ASPEN PLUS and ASPEN HYSYS, are widely used in the industry for various applications. ASPEN PLUS and ASPEN HYSYS are considered industry standards and are widely adopted by process engineers and researchers across various sectors. The software is continuously updated to meet the evolving needs of the industry, ensuring that users have access to the latest modelling techniques and optimization tools. It is a very user-friendly software with lots of process integration for modelling purposes to meet up real industrial requirements.

3.2 Data Gathering and Model Structure

The flue gases leave the boiler and the primary reformer furnaces at exceptionally high temperatures (about 1000 ^{0}C). This flue gas is used for heat exchange for boiler feed water preheating and some other process gases preheating for requirements in various parts of the plant. It leaves to the stack at a temperature of about 60 ^{0}C. From the stack after filtering to remove ash and other particulates and after the initial cooling and dehydration, the flue gas is fed to the CO_2 capture unit at a temperature of about 45 ^{0}C.

3.2.1 Flue Gas Laboratory Analyses

Flue gases from auxiliary boilers and reformer were analysed by the central laboratory and the average mole fraction compositions over a month period are obtained as follows:

CO_2: 10%

N_2: 70%

H_2O: 15%

O_2: 4.95%

Others: ~0.05%

The constituent "others" above refer to compositions of particulate matter, soot and unburnt hydrocarbons.

For the sake of the simulation presented in this work, we did not take this component as its percentage is very much negligible in the entire stream and oxygen percentage was approximated to be 5%.

3.3 Separation and Capture of CO_2 from the Flue Gas Stream

ASPEN HYSIS simulation is carried out to separate the CO_2 from the flue gas using ASPEN HYSIS version V11(37.0.0.395). The selected ASPEN HYSIS property package is *Acid Gas-Chemical Solvents* as it perfectly matches our flue gas composition.

The feed stream composition is as presented as follows:

3.3.1 Flue Gas Specifications

Temperature: 40 ^{0}C

Pressure: 150 kPa

Molar flow: 29138 Kgmole/h

Mass flow: 825 Ton/h

CO_2: 10%

N_2: 70%

H_2O: 15%

O_2: 5%

3.3.2 MDEA solution specifications

The absorbent, an ammonia solution in the form of Methyl Diethanolamine (MDEA) is used in an absorber for the absorption of the CO_2 from the flue gas. Simulation results give the mass and molar flows of the CO_2 absorbed. These values are directly used as CO_2 feed in the urea plant for the production of urea.

It is to be noted that the total flow of both flue gas streams (from auxiliary boilers and ammonia plant primary reformer) is considered. An alternative to this is to analyse the 2 streams separately and finally add the CO_2 flows for use as feedstock to urea plant. For this, two identical simulations with different flue gas flows would have to be developed.

The following data specifications is used for the MDEA solution feed:

Temperature: 65 ^{0}C

Pressure: 120 kPa

Molar flow: 58560 Kgmole/h

Mass flow: 1336 Ton/h

MDEA: 30%

Water: 70%

3.3.3 Unit Operations used

The following unit operations are used for the simulation:

A) **Absorber**: This is the first column used in the simulation. In it, the flue gas and the absorbent flow counter-currently and the absorption takes place by the 2 fluid contact. It is specified with 18 number of stages and an efficiency of 75% for optimal absorption. CO_2 capturing efficiency is studied by performing a sensitivity analysis in varying the number of stages and studying the corresponding effects on the percentage CO_2 recovery.

B) **Lean cooler:** The amine cooler is typically an air cooler which lowers the lean amine temperature before it enters the absorber. It is installed on the recycle stream coming from the bottom of the stripper. Typically, it drops the recycle stream temperature with a temperature drop of about 20^{0}C and also matches the specifications of the main MDEA feed into the absorber. This way, the recycle stream will be able to converge with the absorbent at equal stream specifications.

C) **Lean pump and Rich MDEA pump:** These pumps of centrifugal type are used to boost the pressures of their corresponding streams to meet downstream equipment requirement in the simulation. The driving mechanism for both is an electric motor attached to the pumps. The corresponding utility specification for the 2 pumps is presented in chapter 4.

D) **Mixer:** The purpose of the mixer in the model is to blend, emulsify or mix the recycled lean MDEA and the makeup MDEA in order for the recycle stream parameter specifications to meet the MDEA feedstock specifications to form a final single product.

E) **Rich/lean MDEA heat exchanger:** The rich/lean MDEA heat exchanger has the task of preheating the rich amine prior to it entering the stripper, thus reducing the reboiler workload, and also precooling the lean amine prior to its re-entry into the absorber as a recycle.

F) **Stripper:** Here the stripping phase or liquid absorbent regeneration takes place, it is the step in the process where the CO_2 captured in the absorption step is then stripped from the liquid absorbent. A distillation column is used for the simulation which is equipped with an overhead condenser for condensing the stripped CO_2 and a reboiler for heating part of the bottom product for recycling back to the column to maintain the column temperature.

The stripper is equipped with 18 number of stages just like the absorber with an efficiency of 75% for efficient CO_2 recovery.

3.3.4 Main equipment simulation specifications

A) The absorber has the following parameter specifications:

Top pressure: 120 kPa

Bottom pressure: 150 kPa

Number of stages: 18

Efficiency: 75%

B) The stripper has the following parameter specifications:

Condenser pressure: 160 kPa

Reboiler pressure: 180 kPa

Number of stages: 18

Efficiency: 75%

C) The rich pump has the following specifications:

Pump pressure drop: 50 kPa

Type: centrifugal pump driven by electric motor

D) The lean pump has the following specifications:

Pump pressure drop: 65 kPa

Type: centrifugal pump driven by electric motor

3.3.5 Simulation Environment

Steady-state condition was assumed to simulate the CO_2 capture model in ASPEN HYSIS. No pressure fluctuations in the system were considered. All the reactions were assumed to be taken place under equilibrium. The feed stream consists of the flue gas and the MDEA solution. The MDEA feedstock is later joined by a recycle stream with similar components property and compositions.

The product stream is made up of the overhead product which is the lean gas and the bottom product which is the rich solvent.

In defining the component in the ASPEN HYSIS for this particular type of simulation, Hydrogen peroxide (H_2O_2) and Hydrogen Sulphide (H_2S) are added in order to conform to the property package selection of the category *Acid Gas-Chemical Solvents* Absorption. This package is suitable for the component feed. An inappropriate package will cause deviation and lack of convergence of the model. Specifications for the calculation are listed in table 3.1.

Table 3.1: Specifications for Base Case CO_2 removal

Inlet gas temperature	40 ^{0}C
Inlet gas pressure	150 kPa
Inlet gas flow	29138 kgmole/h
CO_2 in inlet gas	10%
Water in inlet gas	15%
Lean MDEA temperature	65 ^{0}C
Lean MDEA pressure	120 kPa
Lean MDEA rate	98070 Kgmole/h
MDEA content in lean stream	27.7%
CO_2 in lean MDEA	0.11% mole frac.
Number of stages in absorber	18
Efficiency in absorber	75%
Rich MDEA pump pressure	10 kPa
Heated rich MDEA temperature	70 ^{0}C
Number of stages in stripper	18
Reflux ratio in stripper	0.3
Lean MDEA pump pressure	15 kPa
Minimum deltaT in heat exchanger	10 ^{0}C

The model simulation interface can be seen from figure 3.1 below.

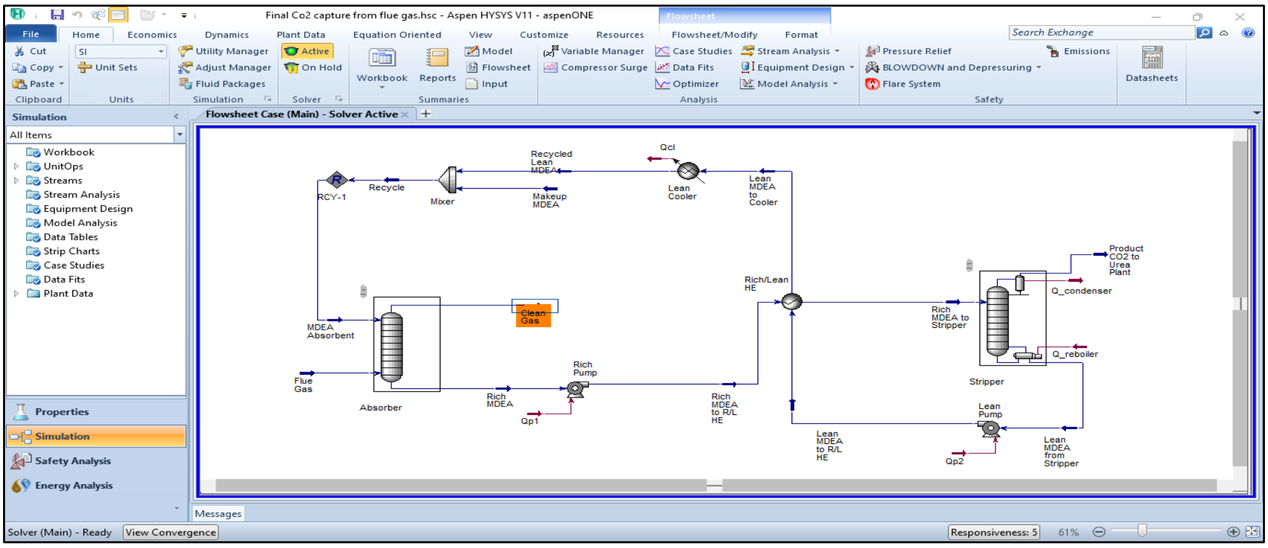


Figure 3.1: The CO₂ *Capture Model Simulation Interface.*

3.4 Urea Synthesis from Captured CO_2

Urea synthesis model development is described in this section. Even though the modelling is complicated due to the formation of ammonium carbamate, an intermediate product but it was finally achieved by employing a special property package (the SR-POLAR Property method). This kind of model is helpful for analysing plant performance and for enhancing plant performance through energy-saving research to boost plant's profitability, research on specific pieces of equipment with the goal of boosting their performance or throughput, modification of flowcharts for improved plant performance, locating chokepoints and as a foundation for an optimisation study and the creation of an online plant control system.

Although the simulation of the Stamicarbon urea production process is described in this work, the accurate results show that ASPEN PLUS and the data package may be applied to other urea processes.

3.4.1 Feed description

Two main feedstocks for the urea production are carbon dioxide (CO_2) and ammonia (NH_3). After the separation and capture from the previous processes, the exhaust flue gas stream enters into the urea unit as the carbon dioxide feed stream. The specification of this stream is given as:

Molar flow:	17076 kmol/day
Temperature:	100 ^{0}C
Pressure:	141 Kg/cm^2

It should be noted that the temperature of the CO_2 feed stream is obtained after passing different stages of heat exchange in the CO_2 stripping sections. As for the pressure, the CO_2 arrives urea plant at a very low pressure (about 1-2 kg/cm^2). For our case, the CO_2 leaves the capture unit at a pressure of 160 kPa (1.63kg/cm^2). It gets pressurised with a CO_2 compressor in order to meet up the urea reactor design conditions. In this work, the compression section is not included but rather the final typical plant values are fed in for simulation purposes.

The ammonia is obtained from the ammonia plant (not included in this work). Typical specification for daily production and for the purpose of our simulations is given below:

Molar flow:	34038 kmol/day
Temperature:	34 ^{0}C
Pressure:	160 Kg/cm^2

3.4.2 Model Development

The process flow diagram (PFD) of the urea unit was setup based on the Stamicarbon process. This process is a common procedure in urea production based on the full recycle of unreacted materials. The urea process was modelled in ASPEN PLUS version V11(37.0.0.395) environment using Schwartzentruber-Renon (SR-POLAR) thermodynamic equation of state

(Soave, 1972; Schwartzentruber and Renon, 1989). The SR-POLAR is well recommended for the highly non-ideal processes at high temperatures and pressures, such as urea, methanol, and supercritical extraction applications by ASPENTech company (ASPEN PLUS, 2011). Furthermore, the model contains extensions that enable an accurate description of the phase and chemical equilibria, the density and the other thermodynamic properties (e.g., enthalpy) of this system.

Figure 3.2 shows the model simulation interface in ASPEN PLUS.

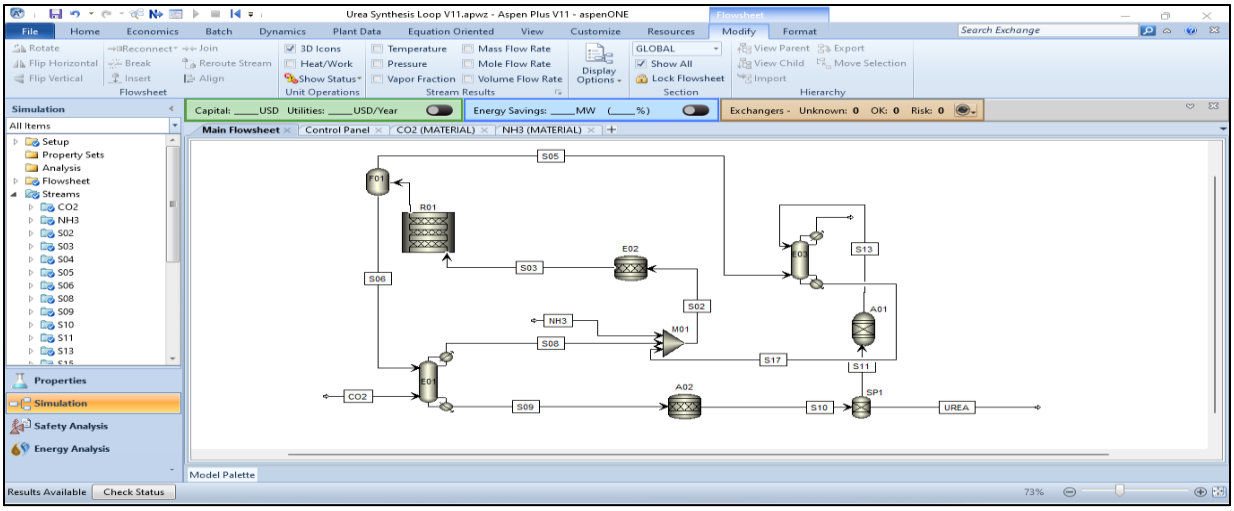


Figure 3.2: User Interface of the Urea Simulation Environment

3.4.3 Chemical Reactions Kinetics

Two main reactions take place in the urea synthesis process. These can be seen from the reactions represented by equations 3.1 and 3.2 below:

$$2NH_3 + CO_2 \rightleftarrows NH_2COONH_4(CARB) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.1$$

Ammonium carbamate formation

$$NH_2COONH_4 \rightleftarrows NH_2CONH_2 + H_2O \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.2$$

Urea formation

Overall reaction is as follows:

$$2NH_3 + CO_2 \rightleftarrows NH_2CONH_2 + H_2O \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.3$$

In the liquid phase, the first reaction converts ammonia and carbon dioxide into ammonium carbamate. This is a very exothermic and rapid reaction. Chemical equilibrium is easily attained in the reactor under normal operating circumstances. The second reaction, which also occurs in the liquid phase, is endothermic. It moves slowly, and equilibrium is rarely established in the reactor.

Kinetics of Reaction 3.1 has been set to be rapid so that equilibrium is effectively reached. Limited literature data were used for the kinetics of Reaction 3.2. The reaction kinetics has been formulated to approach the equilibrium composition for large residence times. The equilibrium has been described in terms of the fugacity coefficients since an equation of state is used as the thermodynamic model. The equilibrium constant for Reaction 3.1, in terms of mole fractions, is written as follows:

$$K_1 = \exp\left\{\frac{-\left(G^0_{CARB} - 2G^0_{NH_3} - G^0_{CO_2}\right)}{RT}\right\}\left(\frac{P}{P^0}\right)\left[\frac{\varphi^2_{NH_3}\varphi_{CO_2}}{\varphi_{CARB}}\right] \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.4$$

Where;

T stands for temperature, ^{0}C

$\mathrm{P} =$ pressure, bar

$\mathrm{x} =$ mole fraction (represented with the subscript)

$\mathrm{R} =$ Gas constant, J/mol·K

$\mathrm{P^0} =$ reference pressure $(= 1\ \mathrm{atm})$, atm

$\mathrm{G^0_i} =$ ideal gas Gibb's free energy constant (in Joules, J) of component i at T, $\mathrm{P^0}$

$\varphi_{\mathrm{CARB}} =$ furgacity of compoent at T, P and x, (in bar)

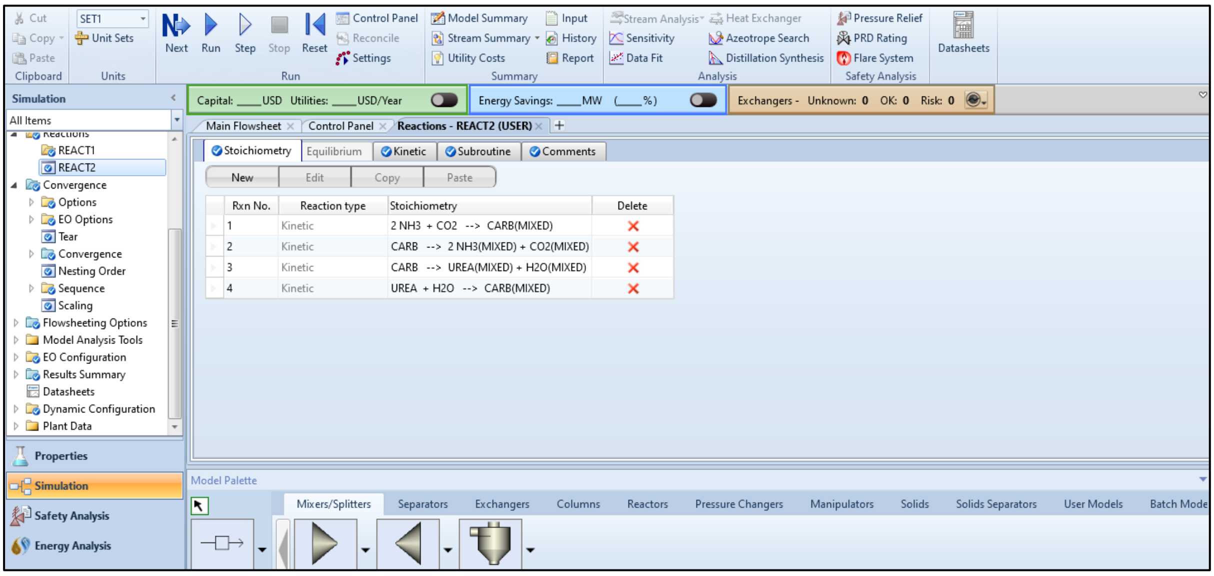
The equilibrium constant for Reaction 1 in terms of mole fractions is as follows:

$$K_1 = \frac{X_{CARB}}{X^2_{NH_3}X_{CO_2}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.5$$

Similar equilibrium equations can be written for Reaction 3.2. The rates for Reactions 3.1 and 3.2, in units of kmol/s/m^3, are as follows:

$$Rate_1 = k_1 \left\{ X_{NH_3}^2 X_{CO_2} - \frac{X_{CARB}}{K_1} \right\} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.6$$

$$Rate_2 = k_2 \left\{ x_{CARB} - \frac{x_{CARB}}{K_1} \right\} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.7$$



Rxn No.	Reaction type	Stoichiometry	Delete
1	Kinetic	2 NH3 + CO2 --> CARB(MIXED)	✗
2	Kinetic	CARB --> 2 NH3(MIXED) + CO2(MIXED)	✗
3	Kinetic	CARB --> UREA(MIXED) + H2O(MIXED)	✗
4	Kinetic	UREA + H2O --> CARB(MIXED)	✗

Figure 3.3: Model Reaction Specification Interface

3.4.4 Urea Synthesis Simulation Environment

The CO_2 Stripper, E01, is a falling film type that was approximated by a 10-stage RADFRAC (multistage distillation) block. To simulate the transfer of heat from the tubes, heat is supplied to stages 2-9. The descending urea solution on the tube walls is stripped of volatile NH_3 by the entering CO_2 gas. The model analyses the equilibrium of carbamate in the liquid as well as the VLE of the mixture at each stage. It should be noted that the carbamate formation kinetics are significant enough to ensure that chemical equilibrium for the carbamate reaction is reached in each stage of the RADFRAC block. An RPLUG block is used to model the R01 Urea Reactor. The kinetics are provided by the user subroutine USURA in the RPLUG block. The exothermic carbamate reaction and the endothermic urea production reaction are both taking place in the reactor. The reactor is intended to have a large enough volume to produce the necessary amount of urea. A 5-stage RADFRAC block is used to model the HP Scrubber. Heat is removed from the bottom stage. Similar to the Stripper, E01, the model examines the equilibrium of carbamate in the liquid as well as the VLE of the mixture at each stage.

The E02 high pressure CO_2 Condenser is modelled by a RSTOIC block. A Design Specification paragraph is given to monitor the required reactor outlet temperature of 183^oC by modifying the extent of the carbamate reaction in E02. This simulation is based on a closed-loop flowsheet. The downstream part is approximated by employing a SEP block to connect the Stripper bottom urea solution to the recycled carbamate solution. The Aspen Plus run was made using Version v11.

CHAPTER 4

4.0 RESULTS AND DISCUSSIONS

Based on the simulations carried out, results obtained from this study are presented in this chapter. Section 4.1 discusses about the CO_2 capturing process. Urea synthesis from the captured CO_2 is discussed in section 4.2.

4.1 CO_2 Capture Model

A model for the absorption and stripping process for CO_2 removal with an aqueous MDEA solution has been simulated. Flue gas from utility boilers and reformer (not simulated here) is used as the feed to this model. The absorption column is specified with 18 stages each with a column efficiency of 0.75. Traditional concentrations, temperatures and pressures are used in the simulation. The thermodynamics for this mixture is described by an Acid Gas-Chemical Solvents available in Aspen HYSYS. Specifications for the calculation are listed in table 3.1. The Aspen HYSYS CO_2 removal model is presented in figure 4.1. The CO_2 capture simulation is carried out using ASPEN HYSIS as shown in the previous chapter. The simulation model is shown in the figure 4.1 below.

4.1.1 CO_2 Capture Model Description

The flue gas is fed in to the unit with an absorbent, an ammonia solution in the form of methyldiethylineamine (MDEA). To increase the efficiency of the CO_2 recovery, the flue gas stream enters directly to the absorber where CO_2 will be absorbed by ammonium solvent (MDEA) in recycle stream (RCY-1). At the outlet of the absorber, clean gas is sent to vent as “Clean Gas to Vent” and the bottom product contains the absorbed CO_2 which will be further stripped off. This rich MDEA stream is sent to pump (Rich MDEA Pump) and is slightly heated in the Rich/Lean heat exchanger for pressure and temperature boost respectively to meet up with downstream requirements. According to this advantage, the ammonium solution regeneration within the process reduces the concerns about the solvent supply. unabsorbed CO_2 in the flue gas stream (Flue Gas), was removed by the MDEA solvent in the absorber column (ABSORBER), subsequently, in order for the desorption of CO_2 from the enriched ammonia, this stream enters into the stripping column (STRIPPER). As one knows, the absorption and desorption processes are exothermic and endothermic processes, respectively. Therefore, some of the required energy for the endothermic stripping process is provided by the Rich/Lean heat exchanger. In the stripping column, CO_2 is released as the top product. The lean absorbent stream is pumped to increase its pressure as requirement for downstream specifications and it exchanges its energy with a rich absorbent stream (RICH-MDEA). This gets cooled in the Lean Cooler and mixed with makeup ammonium solution (Makeup MDEA) stream before entering into the ABSORBER as recycle stream (RCY-1).

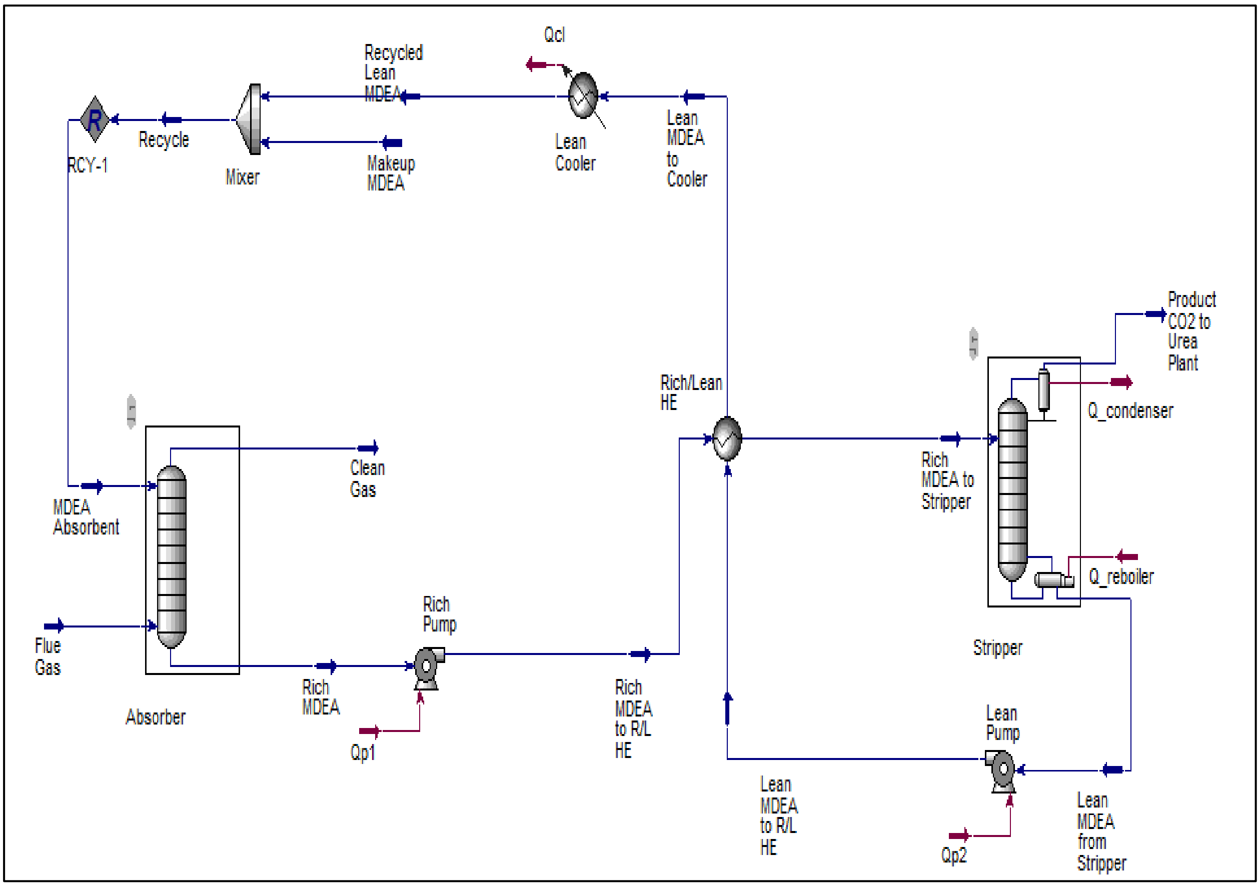


Figure 4.1: ASPEN HYSIS Model of the CO_2 *Capture from flue gas streams.*

4.1.2 Model Convergence

There are numerous convergence issues while making the simulations. The issues usually arise in the absorption or stripping column. The convergence was finally achieved for the absorber column with a solving method of *Hysim Inside-out method* with fixed damping. As for the stripper, Modified HYSIM Inside-out solving method with adaptive damping provides the best convergence. If there are too many stages specified in the columns, they tend to diverge. That is traditional for column stage calculations in typical process simulation tools.

The fixed damping factor was set to a value of 0.1 to give numerous iterations for faster and best convergence. Schematics for the solver pages for both the absorber and stripper columns can be found in the Appendix A as figure A1 and figure A2.

4.1.3 Absorption Efficiency Investigation

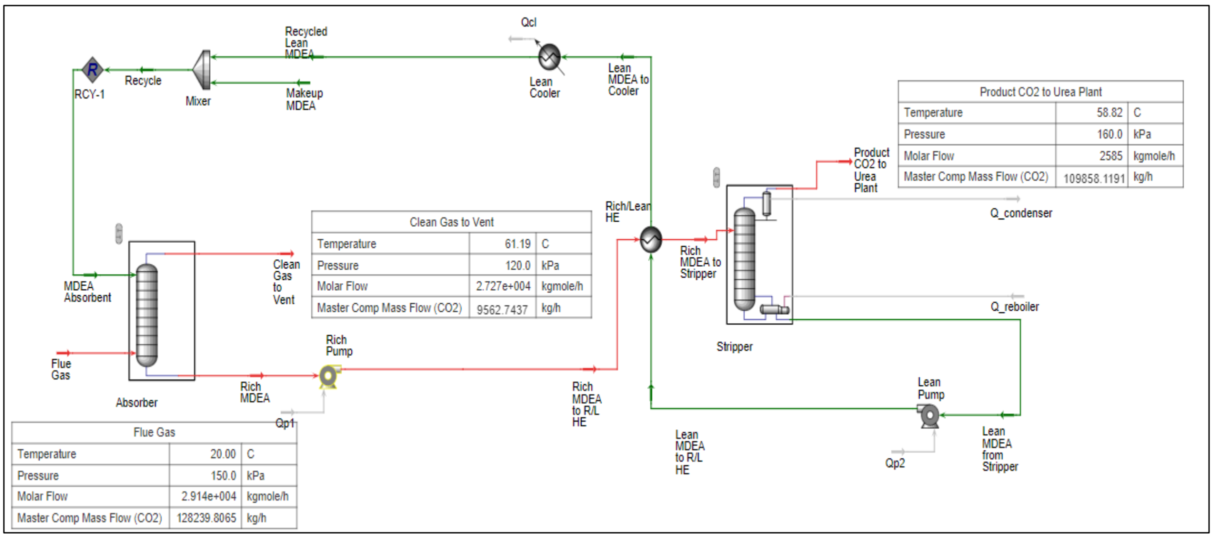
The CO_2 capturing efficiency of the model is presented by the schematics below in figure 4.2. The red lines indicate streams where CO_2 is present. The green lines represent streams with negligible amount of CO_2. Each stream is summarised by property table which gives the master component for the CO_2 mass flow in Kg/h.

Starting from the feed stream, there is 128239 Kg/h (~128.2 ton/h) of CO_2 which is meant to be absorbed by the MDEA solution and subsequently stripped off as CO_2 gas. At the outlet of the absorber, the top product contains the clean gas with a CO_2 mass flow of 8764 Kg/h (~8.7 ton/h). The final CO_2 stripped off contains a CO_2 of about 109 ton/h (109,858 kg/h). This gives an efficiency of 85.67% of the CO_2 separated.

Based on the outlet compositions of the clean gas, it can be said that it is relatively safer to the environment to release the exhaust flue gas stream into the atmosphere with just about 6.8% of CO_2 in it compared to the raw flue gas that is vented into the atmosphere by most power plants.

The most abundant and of course the most disturbing greenhouse gas will be greatly reduced by this method. Cleaner environment will result and captured CO_2 would be economically useful.

Captured CO_2 (top product of the CO_2 stripper) is sent to urea plant for use as feedstock component for producing urea.



Product CO2 to Urea Plant		
Temperature	58.82	C
Pressure	160.0	kPa
Molar Flow	2585	kgmole/h
Master Comp Mass Flow (CO2)	109858.1191	kg/h

Clean Gas to Vent		
Temperature	61.19	C
Pressure	120.0	kPa
Molar Flow	2.727e+004	kgmole/h
Master Comp Mass Flow (CO2)	9562.7437	kg/h

Flue Gas		
Temperature	20.00	C
Pressure	150.0	kPa
Molar Flow	2.914e+004	kgmole/h
Master Comp Mass Flow (CO2)	128239.8065	kg/h

Figure 4.2: Simulated model with CO_2 *stream displayed*

4.1.4 Parameter variations

Different parameters have been varied to identified the effects and to make a tool for optimizing the process. The effects of inlet flue gas temperature, absorber number of stages and MDEA solution circulation rates were studied.

4.1.4.1 Effect of Inlet Gas Temperature Variation

An increase in gas and liquid inlet temperature leads to reduced absorption at equilibrium. Simulation results based on a constant stage efficiency are shown in figure 4.3 below. In practice, the absorption capacity increases as the temperature decreases and this is clearly depicted in the variation below. In the base case, we selected a temperature of 40 ^{0}C for the simulation as it is the closest value to the flue gas temperature from the stack. Lower temperatures of the feed flue gas are used for the purpose of simulation only.

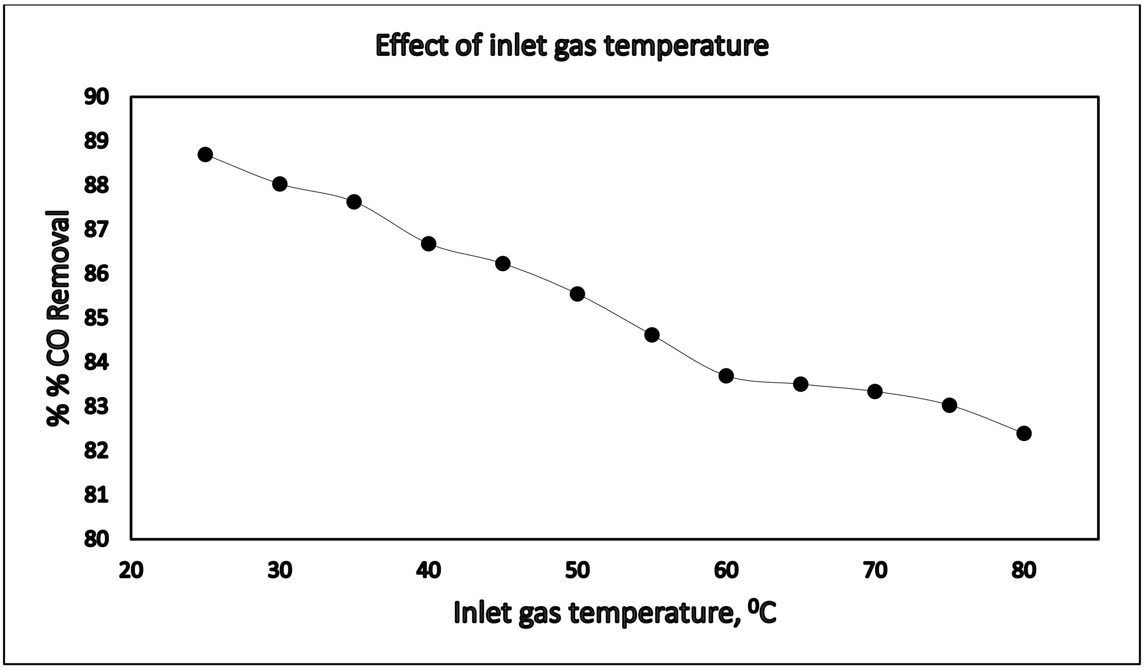


Figure 4.3: Effect of inlet gas temperature variation

4.1.4.2 Effect of Absorber Number of Stages

The effect of number of stages variation can be seen from the figure 4.4 below. The height of the absorption column is adjusted by varying the number of absorber stages. The CO_2 absorber stage efficiency is kept constant at 0.75. The height can also be changed by varying the stage efficiency. As expected, increasing column height enhances removal grade. Figure 4.4 shows the end result. The calculation diverges when more than 25 stages are used in the column.

The disadvantage of increasing the number of stages is that a bigger absorber is required which means more cost of equipment purchase and also more equipment installation space is required. Hence our choice of 18 as a moderate number of stages.

Another disadvantage with higher number of stages is that the model will hardly converge or gets to converge after a very long time of iterations which of course will be very unfavourable for sensitivity analysis of the said model.

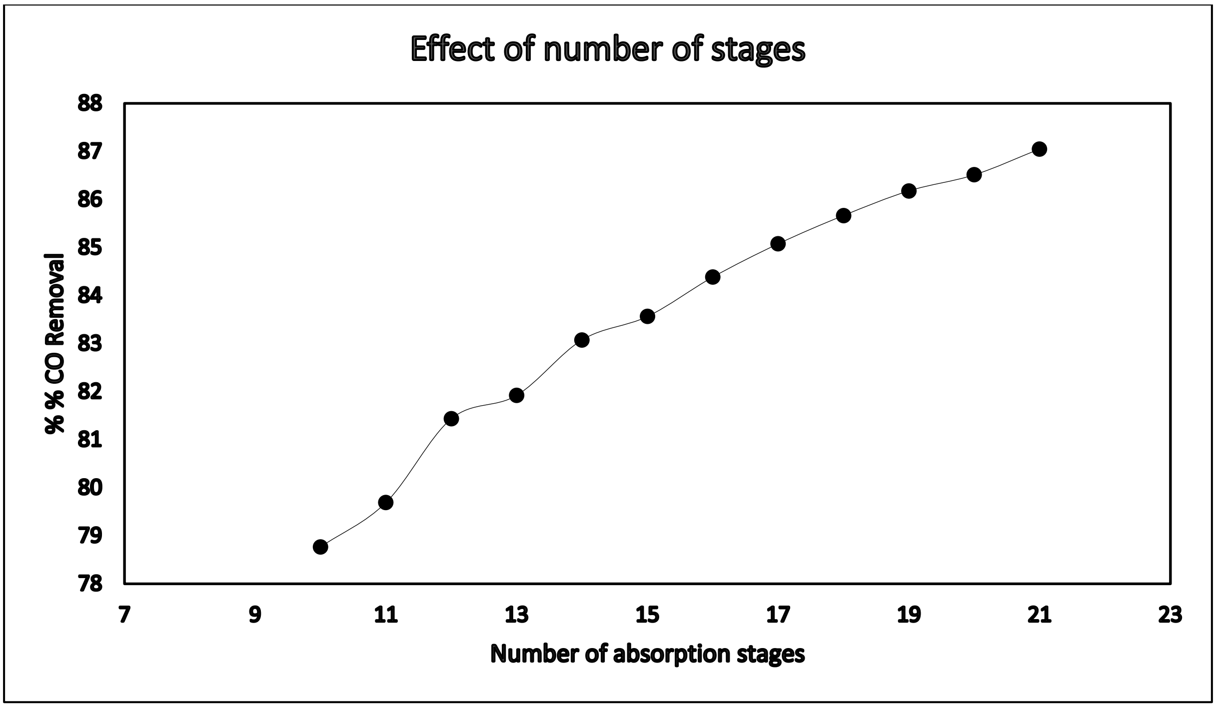


Figure 4.4: Effect of absorber number of stages variation

4.1.4.3 Effect of Absorbent Circulation Rate

The effect of increased circulation rate, is that the removal grade increases. The results of the simulations are shown in figure 4.5. This figure shows a minimum circulation rate (18x10^5 ton per hour) above which carbon-dioxide continue to improve.

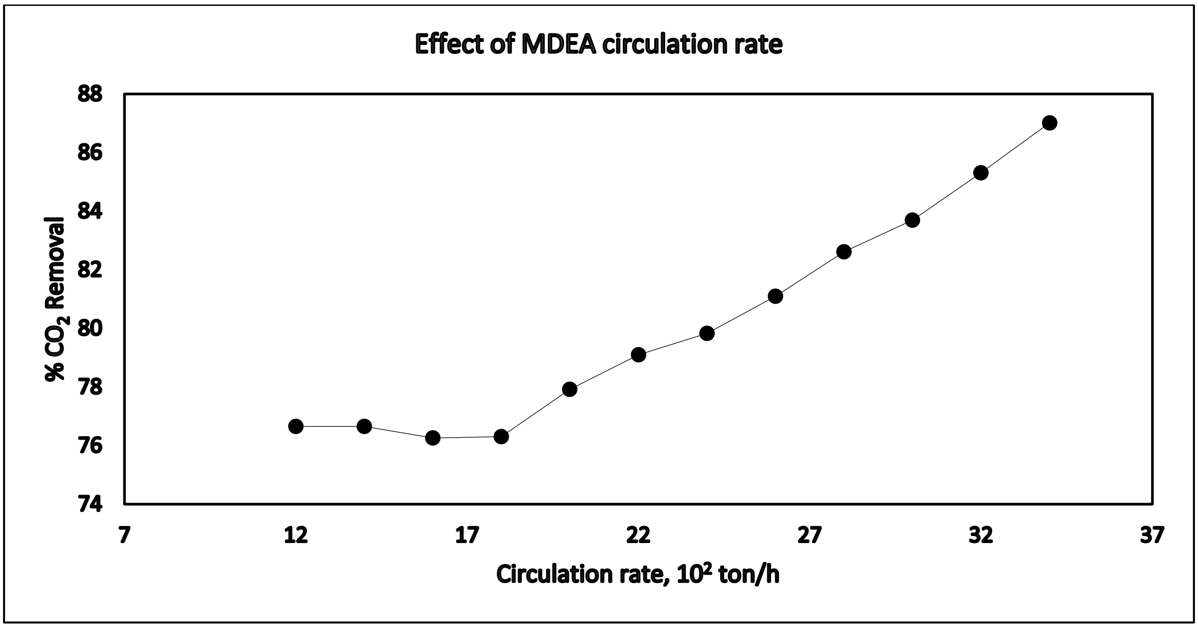


Figure 4.5: Effect of flue gas circulation rate

4.1.5 Regression Analyses of CO_2 Capture Model Parameters

In this section, predictive analysis using regression is carried out for the CO_2 capture model parameters to study more the relationship of the accompanying variables on the CO_2 recovery. Excel is used to perform ordinary least squares (OLS) regression on the parameters of interest. The OLS is a method for constructing predictive models when the factors are not many and linear. Independent Parameters of inlet flue gas temperature, number of absorber stages and absorbent circulation rates are each related to the percentage CO_2 recovery serving as the dependent variable in a single regression analysis. Same was repeated to check for the dependence of the CO_2 recovery on the 3 key parameters in a multivariate regression analysis. No reasonable result was obtained with the multivariate analysis, hence graphical method was used as shown in figure 4.6.

The single regressed model is given by:

$$Y = a + bX \qquad (4.1)$$

- Y – is the dependent variable
- X – is the independent (explanatory) variable
- a – is the intercept
- b – is the slope

The Multivariate regression model is given by the equation below:

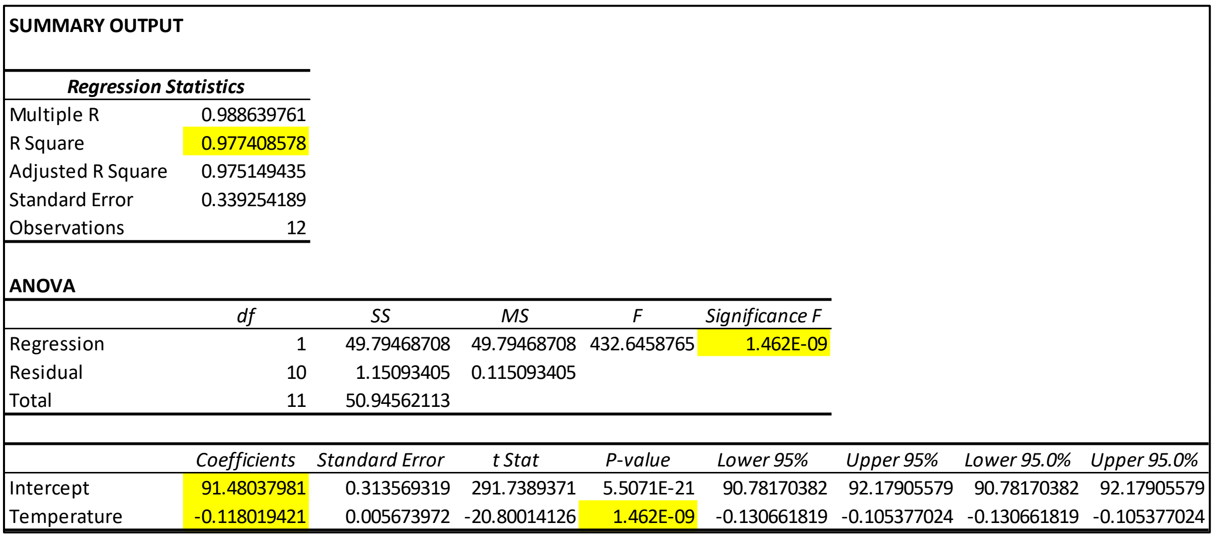
$$Y = a + b_1X_1 + b_2X_2 + b_3X_3 + \cdots b_nX_n \qquad (4.2)$$

where:

- Y – is the dependent variable
- X_1, X_2….X_n – are the independent (explanatory) variables
- a – is the intercept
- b_1, b_2…b_n – are the slopes

4.1.5.1 Temperature Dependence of the CO_2 Recovery

Table 4.1: Regression Analysis on Temperature Dependence



SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.988639761
R Square	0.977408578
Adjusted R Square	0.975149435
Standard Error	0.339254189
Observations	12

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	49.79468708	49.79468708	432.6458765	1.462E-09
Residual	10	1.15093405	0.115093405		
Total	11	50.94562113			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	91.48037981	0.313569319	291.7389371	5.5071E-21	90.78170382	92.17905579	90.78170382	92.17905579
Temperature	-0.118019421	0.005673972	-20.80014126	1.462E-09	-0.130661819	-0.105377024	-0.130661819	-0.105377024

From the regression summary output, it can be seen that the model is well explained by the available data. This can be seen from the R^2 value which gives 0.9774 meaning that the CO_2 recovery dependence on temperature. The relationship between the 2 parameters is a negative one. This can be seen from the temperature coefficient with a value of -0.118. By this, it means that the higher the temperature, the lower the percentage CO_2 to be recovered and vice versa. Furthermore, from the result of the regression carried out, a model can be fitted to define the relationship between the two parameters by the equation 4.3 below:

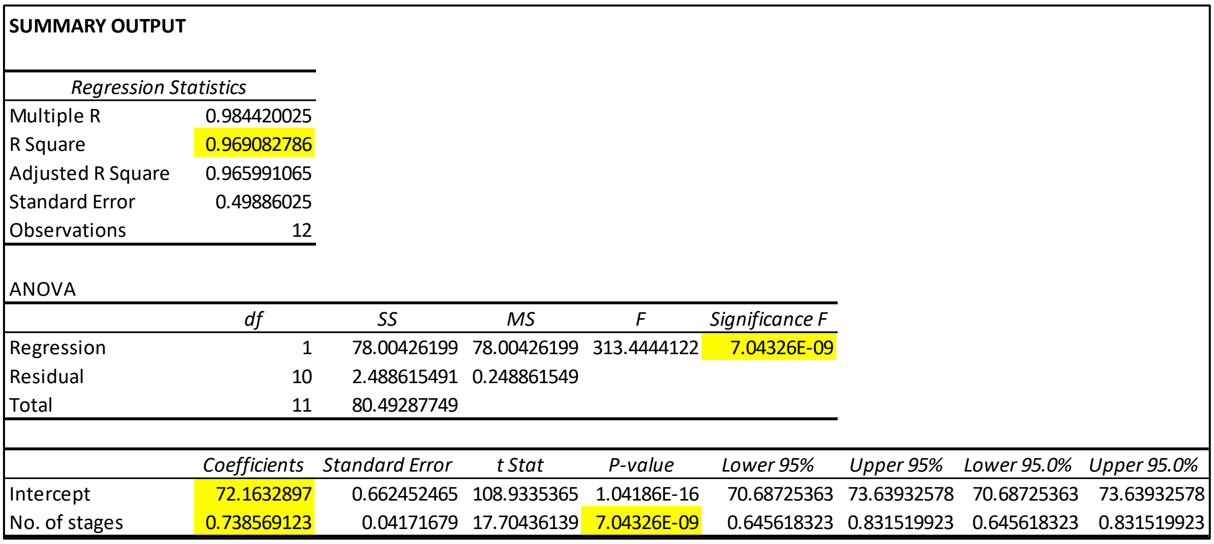
$$\%CO_2 = 91.48 - 0.118T \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 4.3$$

where, T stands for the Inlet Flue Gas Temperature, ^0C.

4.1.5.2 Number of Stages Dependence of the CO_2 Recovery

The effect of the absorber number of stages on the CO_2 recovered is summarized in table 4.2 below from the regression carried out.

Table 4.2: Regression Analysis on Number of Stages Dependence



SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.984420025
R Square	0.969082786
Adjusted R Square	0.965991065
Standard Error	0.49886025
Observations	12

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	78.00426199	78.00426199	313.4444122	7.04326E-09
Residual	10	2.488615491	0.248861549		
Total	11	80.49287749			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	72.1632897	0.662452465	108.9335365	1.04186E-16	70.68725363	73.63932578	70.68725363	73.63932578
No. of stages	0.738569123	0.04171679	17.70436139	7.04326E-09	0.645618323	0.831519923	0.645618323	0.831519923

For the absorber number of stages, the relationship is a positive one. This means that the more the number of stages in the absorber, the more the efficiency to capture more CO_2. It can also be inferred that the two parameters are well explained by the available data with 96.9%, this can be seen from the R^2 result. Furthermore, from the result of the regression carried out, a model can be fitted to define the relationship between the two parameters by the equation 4.4 below:

$$\%CO_2 = 72.16 + 0.738N \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 4.4$$

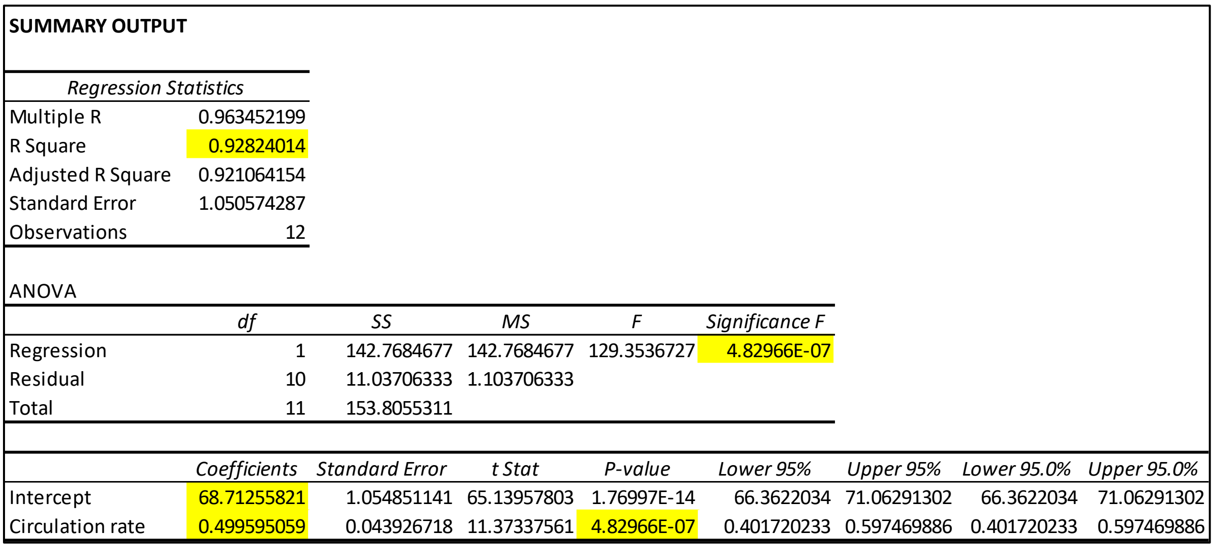
Where N stands for number of stages in the absorber.

4.1.5.3 Circulation Rate Dependence of the CO_2 Recovery

From the regression analysis carried out, the effect of the absorbent rate of circulation on the CO_2 recovered is summarized in table 4.3 below.

It can be seen that the regression analysis carried out between the absorbent circulation rate and the CO_2 recovery reveals that the higher the absorbent flow that is fed into the absorber the higher the CO_2 to be recovered as can be depicted from the positive relationship between the coefficients. The relationship is defined by about 92.8% and it is strongly significant.

Table 4.3: Regression Analysis on Circulation rate Dependence



SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.963452199
R Square	0.92824014
Adjusted R Square	0.921064154
Standard Error	1.050574287
Observations	12

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	142.7684677	142.7684677	129.3536727	4.82966E-07
Residual	10	11.03706333	1.103706333		
Total	11	153.8055311			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	68.71255821	1.054851141	65.13957803	1.76997E-14	66.3622034	71.06291302	66.3622034	71.06291302
Circulation rate	0.499595059	0.043926718	11.37337561	4.82966E-07	0.401720233	0.597469886	0.401720233	0.597469886

The equation governing this relationship as can be inferred from the regression summary output is:

$$\%CO_2 = 68.71 + 0.499R \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 4.5$$

Where R stands for absorbent circulation rate in the absorber.

Figure 4.6 shows the multivariate analysis using a graphical method. By solving the equations for the intersection points, the optimum number of stages is 21 while the feed velocity should not be lower than 31 ton/hr. The optimum temperature range of the feed is estimated to be between 21°C and 31°C. Economics constraint must have justified the 18 number of stages being used in this plant.

4.1.5.4 Multivariate Regression Analyses

Another regression was carried out to check for the dependence of the CO_2 recovery on the 3 key parameters in a multivariate regression analysis. No reasonable result was obtained with the multivariate analysis, hence graphical method was used to define the relationship among the parameters of interest as shown in figure 4.6.

Table 4.4: Multivariate Regression Data

% CO_2 Recovery	Inlet Temperature of Flue Gas ^OC	Circulation rate of Absorbent Ton/hr	Number of Stages in Absorber Tower
76.650	80	12	10
76.650	75	14	11
76.259	70	16	12
76.308	65	18	13
77.921	60	20	14
79.095	55	22	15
79.828	50	24	16
81.100	45	26	17
82.616	40	28	18
83.691	35	30	19
85.305	30	32	20
87.017	25	34	21

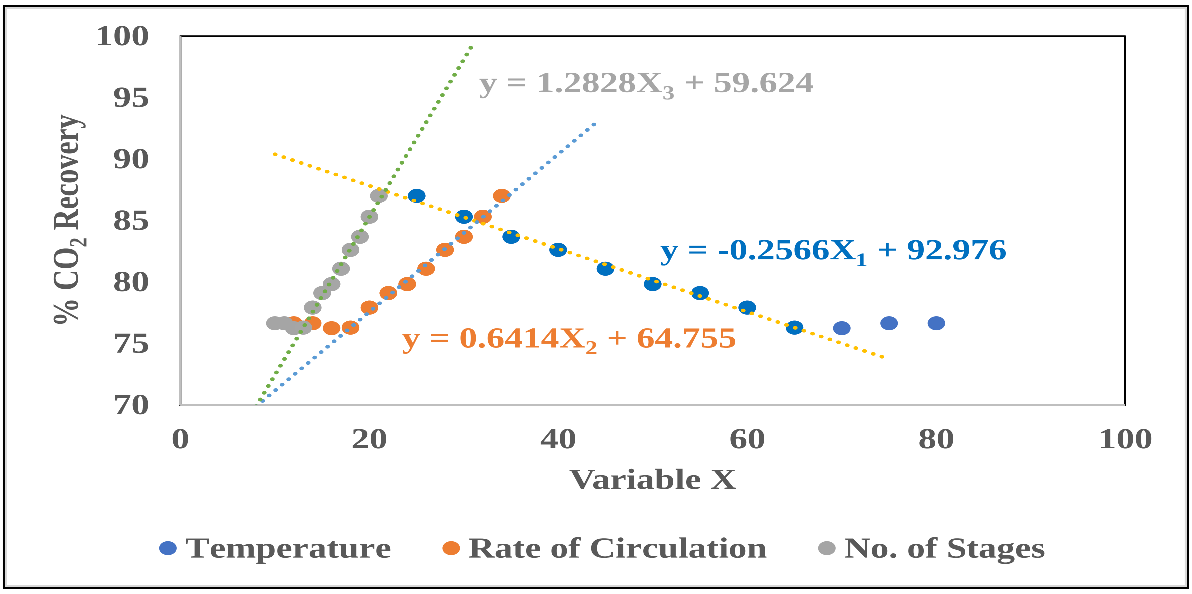


Figure 4.6: Multivariate analysis using graphical method

4.1.6 Captured CO_2 to urea plant

Captured CO_2 leaving the CO_2 removal section is sent to urea plant as one of the feedstocks for the urea production processes. Simulation from ASPEN HYSYIS calculated the outlet specifications of the captured CO_2 as follows:

Table 4.5: Simulated CO_2 modelled parameters

Parameter	Value	Unit
Temperature	58.82	^{0}C
Pressure	160	Kpa
Molar flow	2585	Kgmole/h
CO_2 Mass flow	109858.1191	Kg/h
CO_2 recovered	85.67	%

4.2 Urea synthesis

In this section, urea production process using CO_2 and ammonia is explained in more details. The developed process flow diagram (PFD) of the urea production is shown in figure 4.7. Compressed CO_2 and ammonia were made to react in a urea synthesis reactor and subsequently passed through a flash evaporator, flash drum, and a vacuum evaporator to obtain 99% pure molten urea which can be sent to granulation plant to obtain granulated urea accordingly. Recyclable separated materials from flash evaporator and drum are recycled back to the urea synthesis reactor with necessary pressure rise. Heat recovered from exothermic urea synthesis reaction to obtain hot water is used for subsequent heating in other parts of the plant.

Other plants use a different technology on getting the final dried urea. While granulation marks the last stage of the urea processing of getting granulated urea prior to bagging and final stages of distribution and consumption, other plant use prilling towers to obtain prilled urea. This discussion is beyond the scope of this work.

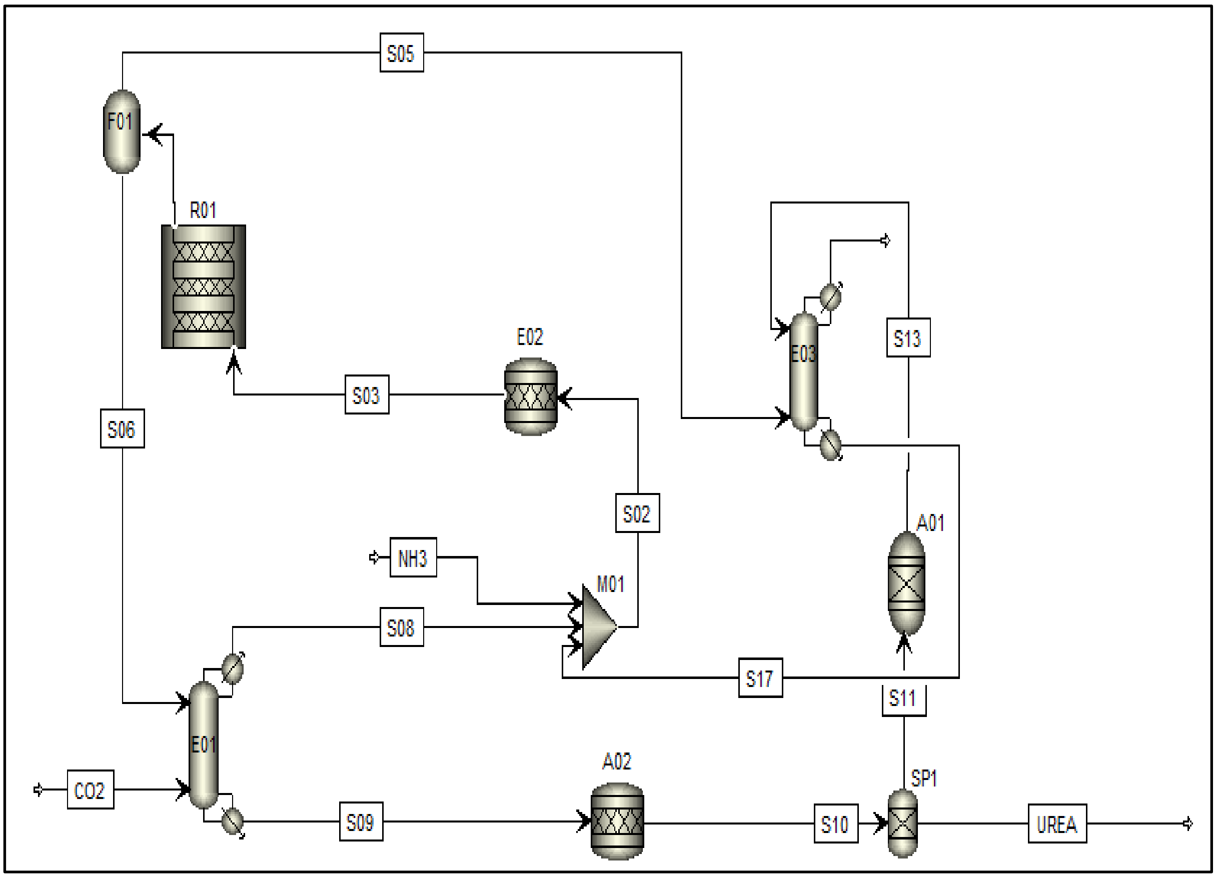


Figure 4.7:ASPEN Plus simulation Model for urea synthesis

Figure 4.7 shows the urea synthesis section of the high-pressure loop which is operated at around 141 kg/cm^2 and consists of the following key equipment. Simulated blocks (unit operations) description is summarised in table 4.6 below.

Table 4.6: simulated CO_2 main modelled blocks

Unit Operation	**Function**
E01	High pressure CO_2 Stripper: this is where the bulk of the unreacted carbamate from the reactor effluent is decomposed by stripping with CO_2 gas and with heat input.
E02	High pressure Condenser: where the gaseous CO_2 and NH_3 condense and react to form ammonium carbamate.
E03	High pressure Scrubber: where the recycled carbamate solution from the downstream low pressure section is used to absorb unreacted gases from the reactor.
R01	Urea Reactor: this is where ammonium carbamate is dehydrated to urea.

4.2.1 Process Description of the Developed Urea Model

The process from the converged simulated process flow diagram is described as follows.

The feed CO_2 gas is sent to the CO_2 stripper, E01, which removes the urea solution from the reactor. Ammonium carbamate decomposes in the stripper, releasing more NH_3 and CO_2 to be stripped away. Condensing steam provides heat to the shell side of the tubes, while the urea solution falls inside the tubes counter-currently down past the rising CO_2 stripping gas. The stripper's outlet liquid solution is high in urea and is routed to the downstream portion for urea purification.

An aqueous solution of NH_3 and CO_2 (much in the form of ammonium carbamate) and vapours move upward through 8 stages of reactor volume in the adiabatic urea reactor, R01, to minimise back-mixing and give ample residence time for urea production. Remaining gases condense and carbamate breaks down in the reactor, providing heat for the slightly endothermic carbamate-to-urea reaction. The urea solution (S06) overflows from the reactor's top to the Stripper E01, while the unreacted gases (S05) exit the reactor's top.

Unreacted gases are routed to the Scrubber, E03, where recycled carbamate solution from the Evaporation/Recirculation section (S13) is passed over the top of a packed bed and fills the tube side section of the vertical tubes. The gases rise via the tubes and pass through the packed area before exiting the tank at the top. The unreacted NH_3 and CO_2 are absorbed by the carbamate solution, while the inert gases O_2, N_2, and others (S15) are vented from the top. Recirculated cooling water flowing inside tubes at the bottom eliminates the heat of absorption from the carbamate solution.

The carbamate solution overflows out of the vessel. The carbamate solution, along with the Stripper's top vapour stream, is sent to the Carbamate Condenser, E02, through an ejector, with the ammonia feed (S01) serving as the pumping fluid. This condenser produces ammonium carbamate. The vapour-liquid mixture (S03) flows via tubes, and the heat of reaction is removed on the shell side by the formation of steam. The mixture flows to the reactor's bottom for urea synthesis. The bottom stream (S09) from the Stripper E01 is sent to the downstream section to recover urea. After recovering the urea (S13), the recycled stream is returned to the H.P. Scrubber to complete the loop.

4.2.2 Model Physical Property Selection

The thermodynamic properties of the system (NH_3-CO_2-H_2O-UREA-CARB-N_2-O_2) are modelled using the SR-POLAR model in Aspen Plus (Soave, 1972; Schwartzentruber and Renon, 1989). Because the model employs an equation of state, it is appropriate for the high-pressure, high-temperature circumstances of urea production. Furthermore, the model includes extensions that allow for an accurate representation of the system's phase and chemical equilibria, density, and other thermodynamic parameters (e.g., enthalpy).

This physical property selection was concluded after reviewing some previous works in an attempt to simulate the urea production. Bernadis et al. (1989) developed improved theoretical models by including ionic species and describing the nonideality of the liquid phase by a modified UNIQUAC model. We assume that the extent of ionisation will be minimal due to the high temperatures (160 to 200°C) and relatively low water concentrations of urea production. Furthermore, current equations of state, such as the SR-POLAR model, are well suited to the representation of nonideal systems' thermodynamic properties at high pressures and temperatures. As a result, we chose the SR-POLAR model as the physical-property alternative.

4.2.3 Simulated Model Analyses

The output streams results and the mass balance as obtained from the urea synthesis model simulation are summarized in table 4.7 below. Also, the simulated model showing the three key process parameters of temperature, pressure and mass flow for each stream is shown in figure 4.8 below. The feeds into the urea plant are the CO_2 and NH_3 each corresponding to mass flows of 32,940Kg/h and 24,154Kg/h respectively. The urea outlet stream has a total mass flow of 55,487Kg/h. From the ASPEN Plus stream results, this outlet stream is consisting of 42,571.52kg/h of molten urea, 12,909.4Kg/h of water and about 6Kg/h of N_2 and O_2 traces. These results based on 825,000Kg/h flue gas in the CO_2 recovery section, reveal that feeding in 32,940Kg/h CO_2 will produce 42,571.52Kg/h molten urea with corresponding flow of 24,153.59Kg/h of ammonia (not simulated in this work).

These processes involve a lot of power requirement which is expected to be supplied by the power plant. The excess heat generated from exothermic reactions occurring in the top of the urea reactor can be utilised in heat exchange and low-pressure steam generation.

The result of this study highlighted that if the appropriate process is designed for the utilisation of CO_2 in flue gases, not only it would reduce the environmental risk, but also more than 1.29 tons of urea per ton of CO_2 would be produced.

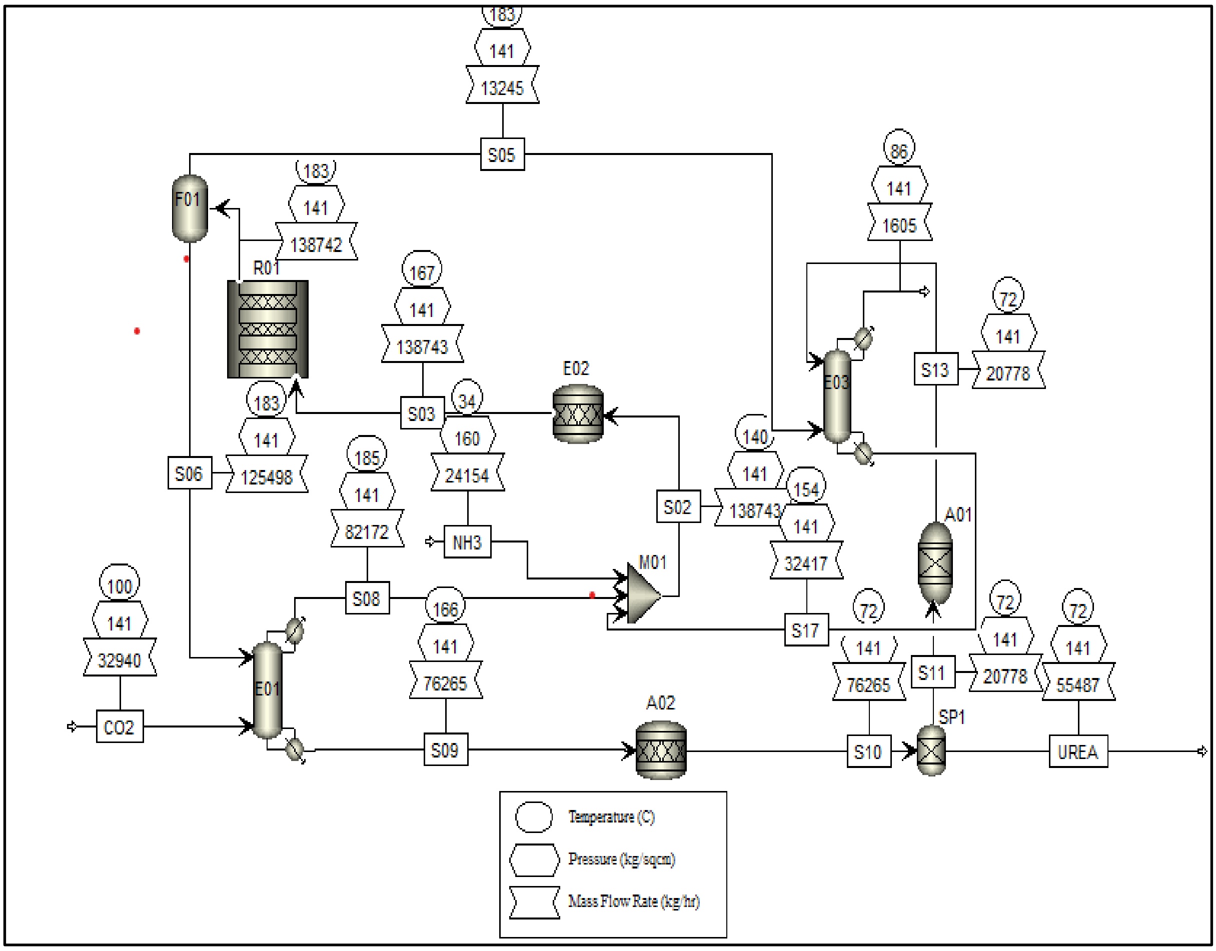


Figure 4.8:Parameter embedded Simulation Flowsheet of the Urea Synthesis Loop

From the simulation result pane on ASPEN Plus, key variables governing the operations of major equipment in the urea synthesis section are presented in table 4.7 below.

Table 4.7: Simulation results of measure equipment and streams

Unit Equipment	Variable	Value	Unit
E01 - CO$_2$ Stripper	Heat duty	0	MMkcal/hr
	Top temperature	185.16	^{0}C
	Bottom temperature	166.00	^{0}C
	Top stream	82172.42	Kg/h
	Bottom stream	76264.73	Kg/h
	Urea production	42636.62	Kg/h
E02 - CO$_2$ Condenser	Heat duty	-17.97	MMkcal/h
	Outlet temperature	167.00	^{0}C
E03 - Scrubber	Heat duty	-69.52	MMkcal/h
	Top temperature	86.20	^{0}C
	Bottom temperature	154.24	^{0}C
	Top stream	1604.98	Kg/h
	Bottom stream	32417.34	Kg/h
R01 – Reactor	Heat duty	0	MMKcal/h
	Top temperature	183.00	^{0}C
	Urea	42746.67	Kg/h

The mass balance around the specific streams is shown in table 4.8 below. All these are obtained from the ASPEN Plus result of the simulated model.

Table 4.8: Mass balance around the urea plant

Stream name	Raw materials		Product streams		Other simulated output streams				
	CO_2	NH_3	Product	Vent	S-02	S-03	S-04	S-05	S-06
Mole fraction									
Urea	0.00	0.00	0.50	0.00	0.00	0.00	0.16	0.00	0.19
Carbamate	0.00	0.00	0.00	0.00	0.05	0.24	0.11	0.00	0.12
CO_2	0.92	0.00	0.00	0.05	0.20	0.09	0.04	0.23	0.01
NH_3	0.00	1.00	0.00	0.01	0.64	0.51	0.38	0.63	0.35
H_2O	0.01	0.00	0.50	0.00	0.10	0.14	0.29	0.04	0.33
N_2	0.06	0.00	0.00	0.83	0.01	0.01	0.01	0.09	0.00
O_2	0.01	0.00	0.00	0.11	0.00	0.00	0.00	0.01	0.00
Total flow (Kmol/hr)	771.50	1418.25	1425.67	55.20	5387.59	4004.98	4316.50	541.95	3774.55
Total flow (Kg/hr)	32939.54	24153.59	55487.11	1604.98	138742.81	138742.87	138742.37	13244.72	125497.66
Temperature (^{0}C)	100.00	34.00	72.40	86.20	140.16	167.00	183.00	183.00	183.00
Pressure (kg/cm^2)	141.00	160.00	141.00	141.00	141.00	141.00	141.00	141.00	141.00

CHAPTER 5

5.0 CONCLUSION AND RECOMMENDATION

5.1 Conclusions

The simulation of CO_2 capture using the absorption technique was achieved using the ASPEN HYSYS. A percentage CO_2 recovery of about 85% is achieved. Captured CO_2 was utilised in producing urea which was modelled using ASPEN Plus. The results of this study highlighted that if the appropriate process is designed for the utilisation of CO_2 in flue gases, not only it would reduce the environmental risk, but also more than 1.29 tons of urea per ton of CO_2 would be produced. The following conclusions are drawn:

- A model for the absorption and stripping process for CO_2 removal with an aqueous MDEA solution has been simulated which gives about 85% CO_2 capture recovery.
- Another model has been built to demonstrate the utilisation of this captured CO_2 in producing urea and this can aid in predicting possible solutions for converting CO_2 emissions into something valuable like urea as in the case of this work.
- From the graphical multivariate analysis, the optimum number of stages in the absorber is 21 while the absorbent flowrate should not be lower than 31×10^2 ton/hr. The optimum temperature range of the feed is estimated to be between 21^oC and 31^oC. Economics constraint must have justified the 18 number of stages being used in this plant.
- These techniques convert CO_2 from unpleasant pollutant to valuable and useful compounds. In addition, urea is one of the most profitable products in the petrochemical industry.

- Since the oil and gas as well as other petrochemical industries emit a significant amount of CO_2 during their various operations, contributing to the overall greenhouse gas footprint, as can be seen from the emitted flue gas analyses in this work, it is therefore concluded that CO_2 capture is a promising mitigation technique to minimize CO_2 emissions from these companies and increase their use in beneficial processes like urea synthesis.
- Transporting and storing solid urea is more physically viable than storing CO_2 gas in underground storage reservoirs or other typical storage technologies. As a result, this technique may be more viable than storing in underground storage reservoirs or using EOR technology.
- Developed model can be applied to other companies within the oil and gas value chain to recover CO_2 thereby saving the environment and meeting up with regulatory requirements about environmental protection.

5.2 Recommendations

The following recommendations are drawn from this work:

- More research into detailed economics evaluation, detecting process weaknesses, computation of detailed design results, mass and energy integration, unit optimization, and determination of appropriate control parameters recommended.
- It is recommended to develop a comprehensive framework for the quantification of emissions and implementation of CO_2 emissions mitigation measures in petrochemical industries.

- Use energy models and simulations to address the challenges of CO_2 emissions in the oil and gas and the petrochemical industries, aid in policy decision making, and predict possible solutions for converting CO_2 emissions into something valuable.
- Other software should be considered for developing similar models with higher CO_2 recovery and more urea synthesis turnout.
- Since lower flue gas temperature shows a reasonable trend of producing more CO_2, viable cooling methodologies should be employed to lower the temperature of the flue gas without the formation of condensate in order to recover more CO_2.

REFERENCES

Audus, H., O. Kaarstad, and M. Kowal, 1996: Decarbonisation of fossil fuels: Hydrogen as an energy carrier. Proceedings of the 11th World Hydrogen Energy Conference

Aspen Plus Example Library- Urea Modelling, AspenTech | Asset Optimization Software - Asset Performance Management, Process Engineering for Chemicals, Energy and Engineering & Construction. https://www.aspentech.com

Benemann, J.R., 1993: Utilization of carbon dioxide from fossil fuel burning power plant with biological systems. Energy Conversion and Management, 34(9–11) pp. 999–1004

Bennett, S. J., Schroeder, D. J., & Mccoy, S. T. (2014). Towards a framework for discussing and assessing CO_2 utilisation in a climate context. Energy Procedia, 63, 7976–7992. https://doi.org/10.1016/j.egypro.2014.11.835

Blunt, M., F.J. Fayers, and F.M. Orr Jr. 1993: Carbon Dioxide in Enhanced Oil Recovery. Energy Conversion and Management, 34(9–11) pp. 1197–1204

CARBON DIOXIDE CAPTURE AND STORAGE. (n.d.).

Cole, K.H., G.R. Stegen, D. Spencer, 1993: Energy Conversion and Management, 34 (9–11), pp, 991–998.

Davis, S. J., Lewis, N. S., Shaner, M., Aggarwal, S., Arent, D., Azevedo, I. L., Benson, S. M., Bradley, T., Brouwer, J., Chiang, Y. M., Clack, C. T. M., Cohen, A., Doig, S., Edmonds, J., Fennell, P., Field, C. B., Hannegan, B., Hodge, B. M., Hoffert, M. I., … Caldeira, K. (2018). Net-zero emissions energy systems. In Science (Vol. 360, Issue 6396). American Association for the Advancement of Science. https://doi.org/10.1126/science.aas9793

Edmonds, J.A., P. Freund, J.J. Dooley, 2001: The role of carbon management technologies in addressing atmospheric stabilization of greenhouse gases. Proceedings of the 5th International Conference on Greenhouse Gas Control Technologies, D. Williams, B. Durie, P. McMullan, C. Paulson, A. Smith (eds). CSIRO, Australia, pp. 46–51.

Gale, J., N.P. Christensen, A. Cutler, and T.A. Torp, 2001: Demonstrating the Potential for Geological Storage of CO_2: The Sleipner and GESTCO Projects, Environmental Geosciences, 8(3), pp.160–165.

Gray, N. F. (2015). Measuring CO_2 Emissions. In Facing Up to Global Warming (pp. 103–133). Springer International Publishing. https://doi.org/10.1007/978-3-319-20146-7_5

Hendriks, C.A., K. Blok, and W.C. Turkenburg, 1989: The recovery of carbon dioxide from power plants. Proceedings of the Symposium on Climate and Energy, Utrecht, The Netherlands.

Holloway, S., J.P. Heederik, L.G.H. van der Meer, I. CzernichowskiLauriol, R. Harrison, E. Lindeberg, I.R. Summerfield, C. Rochelle, T. Schwarzkopf, O. Kaarstad, and B. Berger, 1996: The Underground Disposal of Carbon Dioxide, Final Report of JOULE II Project No. CT92-0031, British Geological Survey, Keyworth, Nottingham, UK

Horn, F.L. and M. Steinberg, 1982: Control of carbon dioxide emissions from a power plant (and use in enhanced oil recovery). Fuel, 61, May 1982

IEA WEO, 2004: IEA World Energy Outlook 2004, International Energy Agency, Paris France

IEA, 2003: CO_2 emissions from fuel combustion, 1971–2001, OECD/IEA, Paris

IEA, 2004: Energy Balances of Non-OECD Countries, 2001–2002. OECD/IEA, ParisIliuta, I., Bougie, F., & Iliuta, M. C. (2015). CO_2 removal by single and mixed amines in a hollow-fiber membrane module-investigation of contactor performance. AIChE Journal, 61(3), 955–971. https://doi.org/10.1002/aic.14678

International Energy Agency., & Organisation for Economic Co-operation and Development. (2010). World energy outlook. 2010. OECD/IEA.

IPCC, 2001c: Climate Change 2001: the Scientific Basis. Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change. J.T. Houghton, Y. Ding, D.J. Griggs, M. Noguer, P.J. van der Linden, X. Dai, K. Maskell, and C.A. Johnson, (eds.). Cambridge University Press, Cambridge, UK.

Kohl, A.O. and R.B. Nielsen, 1997: Gas purification, Gulf Publishing Co., Houston, TX, USA.

Koohestanian, E., Sadeghi, J., Mohebbi-Kalhori, D., Shahraki, F., & Samimi, A. (2018). A novel process for CO_2 capture from the flue gases to produce urea and ammonia. Energy, 144, 279–285. https://doi.org/10.1016/j.energy.2017.12.034

Marchetti, C., 1977: On Geo-engineering and the CO_2 problem. Climate Change, 1, pp. 59–68

Reference

Rao**,** A.B. and E.S. Rubin, 2002: A technical, economic, and environmental assessment of amine-based CO 2 capture technology for power plant greenhouse gas control. *Environmental Science and Technology,* 36**,** 4467-4475

Rudin, S. N. F. M., Muis, Z., Hashim, H., & Ho, W. S. (2017). Overview of carbon reduction, capture, utilization and storage: Development of new framework. In Chemical Engineering Transactions (Vol. 56, pp. 649–654). Italian Association of Chemical Engineering - AIDIC. https://doi.org/10.3303/CET1756109

Schwartzentruber, J.; Renon, H., “Extension of UNIFAC to High Pressures and Temperatures by the Use of a Cubic Equation of State,” I&EC Research, 28, 1049-1055 (1989).

Siddique, Q., 1990: Separation of Gases. Proceedings of 5th Priestley Conference, Roy. Soc. Chem., London, pp. 329

Skovholt, O., 1993: CO_2 transportation systems. Energy Conversion and Management, 34, 9–11, pp.1095–1103.

Soave, G., “Equilibrium Constants from a Modified Redlich-Kwong Equation of State,” Chem. Eng. Sci., 27, 1196-1203 (1972).

Stevens, S.H. and J. Gale, 2000: Geologic CO_2 Sequestration, *Oil and Gas Journal*, May 15th, 40-44

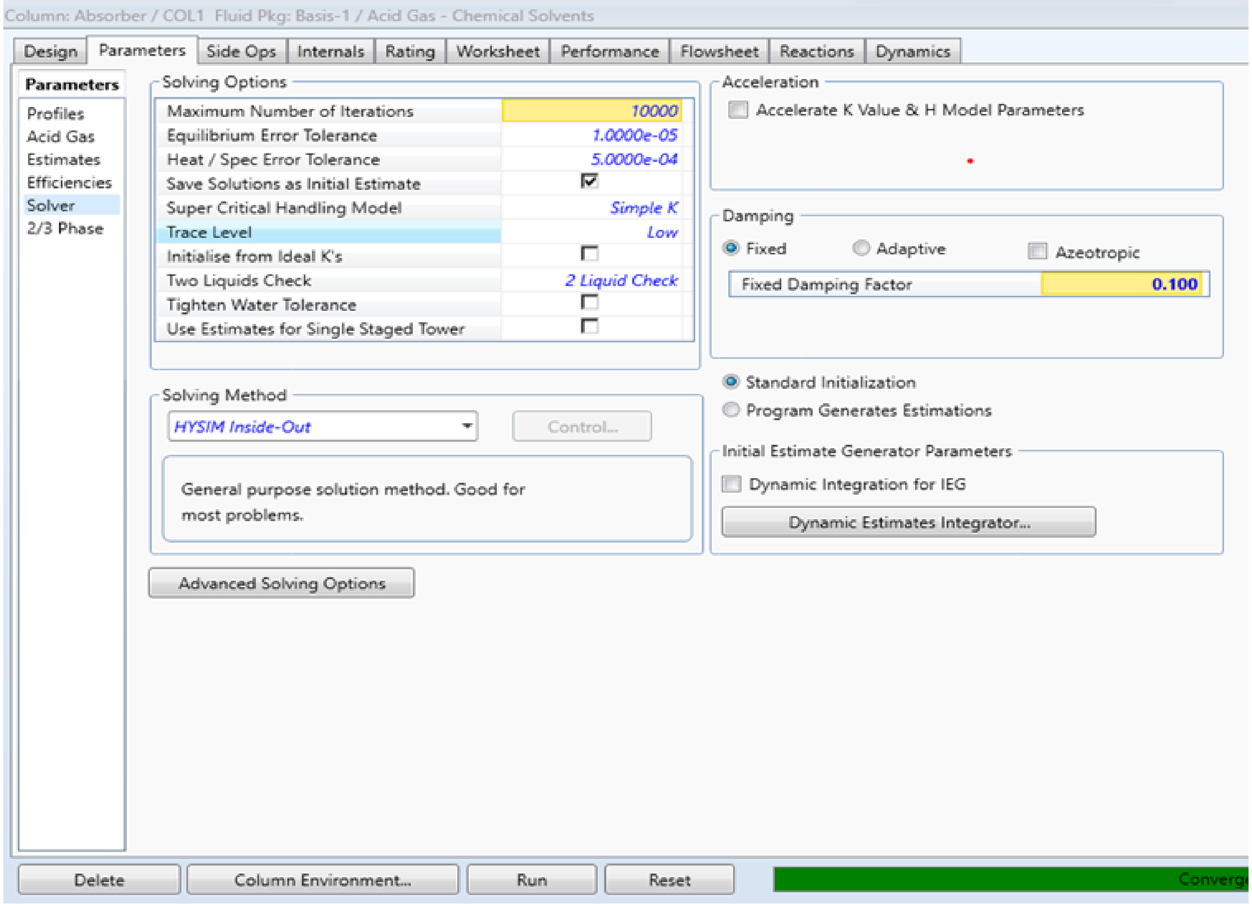
Sun, L., Ma, Y., Li, B., Xiao, C., Fan, L., & Xiong, Z. (2018). Nitrogen fertilizer in combination with an ameliorant mitigated yield-scaled greenhouse gas emissions from a coastal saline rice field in southeastern China. Environmental Science and Pollution Research, 25(16), 15896–15908. https://doi.org/10.1007/s11356-018-1808-6

Wall, T., Stanger, R., & Liu, Y. (2013). Gas cleaning challenges for coal-fired oxy-fuel technology with carbon capture and storage. Fuel, 108, 85–90. https://doi.org/10.1016/j.fuel.2011.03.037

Wood, S., & Cowie, A. (2004). A Review of Greenhouse Gas Emission Factors for Fertiliser Production.

APPENDIX A

Figure A1: CO$_2$ Absorber Solver Interface with HYSIM Inside-out solving method at fixed damping



Maximum Number of Iterations	10000
Equilibrium Error Tolerance	1.0000e-05
Heat / Spec Error Tolerance	5.0000e-04
Save Solutions as Initial Estimate	☑
Super Critical Handling Model	Simple K
Trace Level	Low
Initialise from Ideal K's	☐
Two Liquids Check	2 Liquid Check
Tighten Water Tolerance	☐
Use Estimates for Single Staged Tower	☐

☐ Accelerate K Value & H Model Parameters

● Fixed ○ Adaptive ☐ Azeotropic

Fixed Damping Factor: 0.100

HYSIM Inside-Out

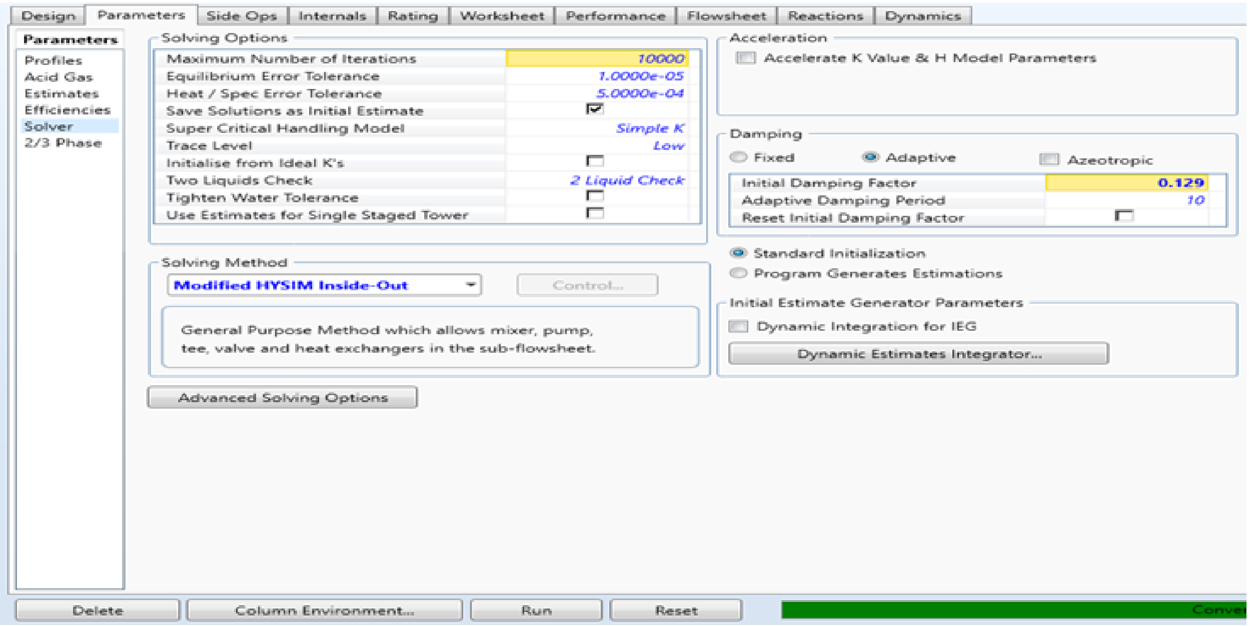
General purpose solution method. Good for most problems.

● Standard Initialization

○ Program Generates Estimations

☐ Dynamic Integration for IEG

Figure A2: CO_2 Stripper Solver Interface with Modified HYSIM Inside-out solving method with adaptive damping



Solving Options

Maximum Number of Iterations	10000
Equilibrium Error Tolerance	1.0000e-05
Heat / Spec Error Tolerance	5.0000e-04
Save Solutions as Initial Estimate	☑
Super Critical Handling Model	Simple K
Trace Level	Low
Initialise from Ideal K's	☐
Two Liquids Check	2 Liquid Check
Tighten Water Tolerance	☐
Use Estimates for Single Staged Tower	☐

Solving Method

Modified HYSIM Inside-Out

General Purpose Method which allows mixer, pump, tee, valve and heat exchangers in the sub-flowsheet.

Acceleration

☐ Accelerate K Value & H Model Parameters

Damping

○ Fixed ● Adaptive ☐ Azeotropic

Initial Damping Factor	0.129
Adaptive Damping Period	10
Reset Initial Damping Factor	☐

● Standard Initialization

○ Program Generates Estimations

Initial Estimate Generator Parameters

☐ Dynamic Integration for IEG