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LAZREG Wissale

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Deprotonation of an imine bases by differents strong bases; CO2 treatment Application

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Dr.	ADAIKA Kaltoum	MCA	University of Biskra	President
Dr.	ALMI Sana	MCA	University of Biskra	Reporter
Dr.	ADAIKA Kaltoum	MCB	University of Biskra	Examiner

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ABSTRACT

To reduce the impact on the climate caused by CO2 emissions, primary options have been considered such as Capture, utilization or storage of CO2 as the. Several technological approaches have been proposed depending on the point of actuation (pre-combustion, post-combustion, or oxyfuel combustion), but absorption processes are still the most extended solution implemented in the industry. Alkanolamines, Amino acids and their salts, ionic liquids show very good performance in CO_2 capture. In this study, the use of hydroxide imine and their salts in CO_2 capture was investigated. We report the synthesis of N-(2-hydroxybenzylidene)-o-nitroaniline HNSA and three bases (NaOH, Na_2CO_3 and $NaNO_3$) have been used to forming the imine salts NSA^-Na^+. The obtained salts were characterized by IR and UV-Vis spectra.

Keywords: CO_2 capture, imine salts, IR pectra, UV-Vis spectra.

مـــلـــخـــص

لتقليل التأثير على المناخ الناجم عن انبعاثات ثاني أكسيد الكربون ، تم النظر في الخيارات الأولية مثل التقاط أو استخدام أو تخزين ثاني أكسيد الكربون. تم اقتراح العديد من الأساليب التكنولوجية اعتمادًا على نقطة التشغيل (ما قبل الاحتراق ، أو ما بعد الاحتراق ، أو احتراق الوقود بالأكسجين) ، ولكن لا تزال عمليات الامتصاص هي الحل الأكثر امتدادًا الذي يتم تنفيذه في الصناعة. يظهر الكانولامين والأحماض الأمينية وأملاحها والسوائل الأيونية أداءً جيدًا للغاية في التقاط ثاني أكسيد الكربون المتحقق فيه. في هذه الدراسة ، تم التحقق في استخدام هيدروكسيد أمين وأملاحهم في التقاط ثاني أكسيد الكربون المتحقق فيه . أبلغنا عن تخليق 2-N (هيدروكسي بنزيليدين o-) نيتروانيلين HNSA وثلاث قواعد (هيدروكسيد الصوديوم و كربونات الصوديوم ونيترات الصوديوم) تم استخدامها لتشكيل أملاح الإيمين NSA-Na +. تميزت الأملاح التي تم الحصول عليها بأطياف الأشعة تحت الحمراء والأشعة المرئية وفوق البنفسجية.

الــكــلــمــات الــمــفــتــاحــيــة : التقاط ثاني أكسيد الكربون ، ملح الأمين ، أطياف الأشعة تحت الحمراء ، أطياف الأشعة المرئية وفوق البنفسجية.

Table of Contents

CHAPTER I: Reactive absorption process used in the treatment of CO2 containing industrial gas streams (CO2 capture processes)

List of Figures

Chapter I: Reactive absorption process used in the treatment of CO2 containing industrial gas streams (CO2 capture processes)

Chapter II: Experimental Section: CO2- HNSA -H2O absorption system

Chapiter III: Results And Discussion

List of Tables

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Symbols & Acronyms

CO_2	Carbone Dioxide
H_2S	Hydrogen Sulfide
SO_2	Sulfur Dioxide
HCN	Hydrogen Cyanide
NH3	Ammonia
NOx	Nitrogen Oxides
SOx	Sulfur Oxides
NO_2	Nitrogen Dioxide
N_2	Nitrogen
O_2	Oxygen
H_2S	Hydrogen Sulfide
HCl	Hydrochloric Acid
MEA	Mono Ethanol Amine
CCS	Carbon Capture and Storage
PCC	Post-Combustion Capture
CPU	Carbon dioxide Purification Unit
SC	Stirling Coolers
CCC	Cryogenic Carbon Capture
ECL	External Cooling Loop
IGCC	Integrated Gasifier Combined Cycle
FGD	Flue Gas Desulfurization
ASU	Air Separation Unit
GHGs	Green House Gases

IEA	International Energy Agency
LNG	Liquefied Natural Gas
ILs	Ionic Liquid
PH	Potential Hydrogen
ORP	Oxidation Reduction Potential
LCD	Designed with a Large Display
FTIR	Fourier Transform Infrared Spectroscopy
IR	Infra Red
DMF	Diméthyl Form amide
DMSO	Diméthyl Sulfoxyde

General

Introduction

General Introduction

Human activities have contributed to increase drastically the atmospheric concentration of greenhouse gases. Carbon dioxide, even though it is not the more armfuls of them, is by far the most problematic of these gases. Indeed, its concentration is so high and it is predicted to rise to above 750 ppmv by 2100 if no action is taken to address the current situation [1]. In order to mitigate the CO_2 atmospheric concentration, the focus is made on the flue gas at the exit of the power plants. [2]

Industries have already reacted to help decrease their carbon dioxide release. The number of CO_2 capture technologies has increased significantly due to their flexibility and design, efficacious cost, and proficient application [3,4]. The currently most developed method to capture CO_2 from flue gas is the use of absorption column. [5], where CO_2 in the flue gas is chemically bond by a solvent, resulting in a cleaned gas being released to the atmosphere. Heating of the solution, desorbs the CO2 and regenerates the solvent, which is then ready for a new round of absorption. The captured CO_2 can then be compressed and sent to storage [6].

Aqueous solutions of alkanolamines are typical solvents used in captured CO_2 process, but they degrade as a result of long exposure or repeated use, because of side reactions with carbon dioxide, oxygen and other contaminants. Amino acid salt solutions, ionic liquid have emerged as an alternative to the alkanolamines.

In this study we use the imines as CO_2 capture because they have the same functional groups as alkanolamines, and can be expected to behave similarly towards carbon dioxide. This investigation focuses on phase equilibrium experiments of the systems of CO_2 + imino salt + H_2O

The structure of this study subdivided into three Chapters:

Chapter I: The first part is devoted to a review of the processes of carbon dioxide depletion and its chemical and structural properties of the matched state.

Chapter II: As brief description of all the experimental techniques used in this study and the experimental conditions used and adopted.

Chapter III: Is dedicated to the deprotonation of the imine and its comportment study in two phases system in order to use it as solvents in CO_2 capture.

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Chapter I:

Reactive absorption process used in the treatment of CO2 containing industrial gas streams (CO2 capture processes)

I. Introduction

A considerable amount of attention has been focused on our planet due to the conceivable outcomes of climate change, which is a result of the energy generated from fossil fuel emissions and greenhouse gases such as CO_2. Therefore, the number of CO_2 capture technologies has increased significantly due to their flexibility and design, efficacious cost, and proficient application [1, 2]. Currently, chemical solvents using absorption process consider use the technology of the post-combustion CO_2 capture technologies, considered one of the best technologies for capturing CO_2, in addition to pre-combustion capture that has been used to remove CO_2 and H_2S from natural gas components in a refinery [3, 4].

Figure (I.1): Carbon dioxide gas emissions[4].

I.1.Carbon dioxide

It is a chemical compound of oxygen and carbon with the chemical formula CO_2, a colorless and a mild pungent taste. Carbon dioxide in the atmosphere is the source of carbon for plants.

- Carbon dioxide is heavier than air and does not aid in combustion.
- Carbon dioxide is used in fire extinguishing equipment.
- Carbon dioxide is a natural component of the atmosphere, and is relatively harmless in itself.

- Carbon dioxide plays an important role in the global warming effect.
- It is formed during the combustion of fossil fuels when the carbon content of the fuel reacts with oxygen during combustion.
- Carbon dioxide is formed when living things breathe.
- Carbon dioxide is an essential component of plant nutrition, but in the oceans, phytoplankton can absorb and release large amounts of this gas [5].
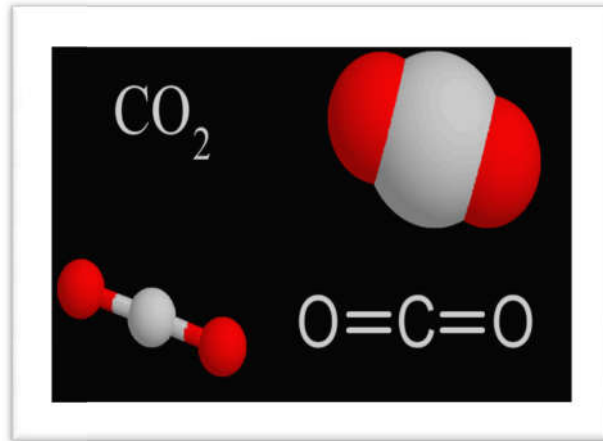
Figure (I.2): Carbon Dioxide [5].

I.2.Chemestry of carbon dioxide

Carbon dioxide (CO_2) is a stable and relatively inert triatomic molecule that exists as a gas at ambient temperature and pressure. A CO_2 molecule exhibits a linear structure in which the carbon is bonded to each oxygen atom via a σ and π bond forming two C=O bonds. Each C=O bond has a length of 116.3 pm and 750 kJ.mol^{-1} bonding energy, considerably higher than the bonding energy of C=C, C–O, and C–H bonds [5].

Carbon dioxide is generated naturally from various sources such as forest fires, volcanic eruptions, and respiration of living organisms. The photosyntheses of plants and other autotrophs play an indispensable role in balancing the carbon/oxygen cycle and consequently in maintaining the earth life [6].

I.2.1. Physical and chemical properties of carbon dioxide

The table, shows some chemical and physical properties of carbon dioxide.

Table(I.1): Physical and chemical properties of carbon dioxide.

Physical	Chemical
•Gaseous substance	• Does not support combustion, only active metals burn in it
• Has no color and smell	• Enters into interaction reactions with simple substances such as hydrogen and carbon
• Heavier than air	• When heated, carbon dioxide decomposes into carbon monoxide and oxygen $(2CO_2 \leftrightarrow 2CO + O_2)$(eq (I.1))
• Thrmally stable, when compressed and cooled, it easily transforms into solid (dry ice) and liquid states	• When carbon dioxide interacts with peroxides of active metals, carbonates are formed and oxygen is released
• Poorly soluble in water, partially reacts with it	• A qualitative reaction to carbon dioxide is the reaction of its interaction with lime water, with calcium hydroxide, in which a white precipitate is formed- calcium carbonate
•Carbon dioxide is used in food (carbonation of lemonade), chemical (temperature control in the production of synthetic fibers), metallurgical (environmental protection, such as brown gas precipitation) and other industries.	• Carbon dioxide belongs to the class of acidic oxides, when interacting with water, it forms an acid - it is called carbonic acid (it is chemically unstable and immediately decomposes into components at the time of formation, the reaction of interaction of carbon dioxide with water is reversible)
•Most of the planet's carbon dioxide is of natural origin (decomposition of organic elements, volcanic eruptions).	•The specific reaction of carbon dioxide is a reaction with lime water, with calcium hydroxide, in which a white precipitate is formed - calcium carbonate.

I.3. Carbon Capture and Storage

CCS refers to many technologies that capture CO_2 at some stage of a combustion Process or an industrial process that produces CO_2 as waste [7,8]. In the first case, the CO_2 capture can be carried out after the combustion process (post-combustion, oxy-combustion and chemical looping combustion) or before the combustion process (pre-combustion), as represented in Figure (I.3) [9]. The higher the partial pressure of CO_2 in the gas, the better the efficiency of adsorption or absorption of CO_2 [10,11,12].
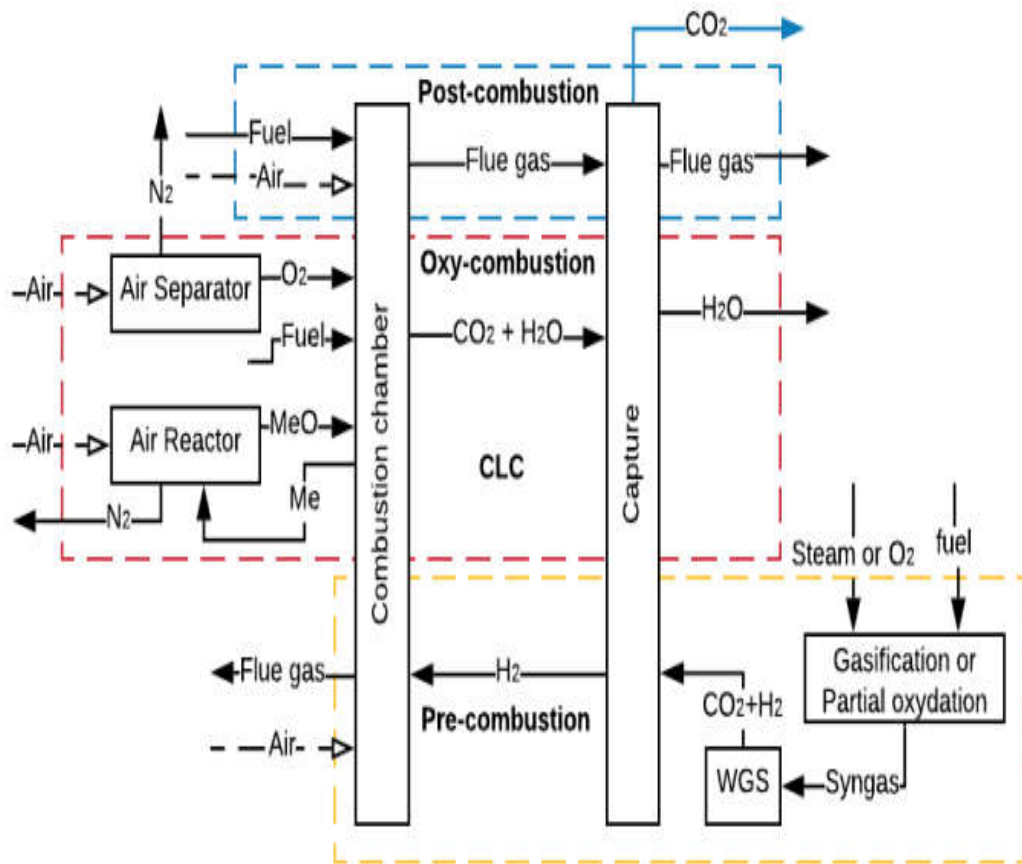
Figure (I.3): CCS methods [12].

CCS is a process consisting of the separation of CO_2 from industrial and energy-related sources, transport to a storage location and long-term isolation from the atmosphere [13]. According to this definition, there is three steps: CO_2 capture at the point of generation, compressing it to a supercritical fluid to transport it and finally storing it [14]. The capture is achieved by different methods such as absorption,

adsorption, membrane separation or cryogenic separation [15-17]. The transport of the compressed gas is done by pipeline or ship and the carbon dioxide is then stored by geological or ocean storage or via mineralization [18, 22].

A diagram explaining various carbon-utilization pathways figure (I.4).
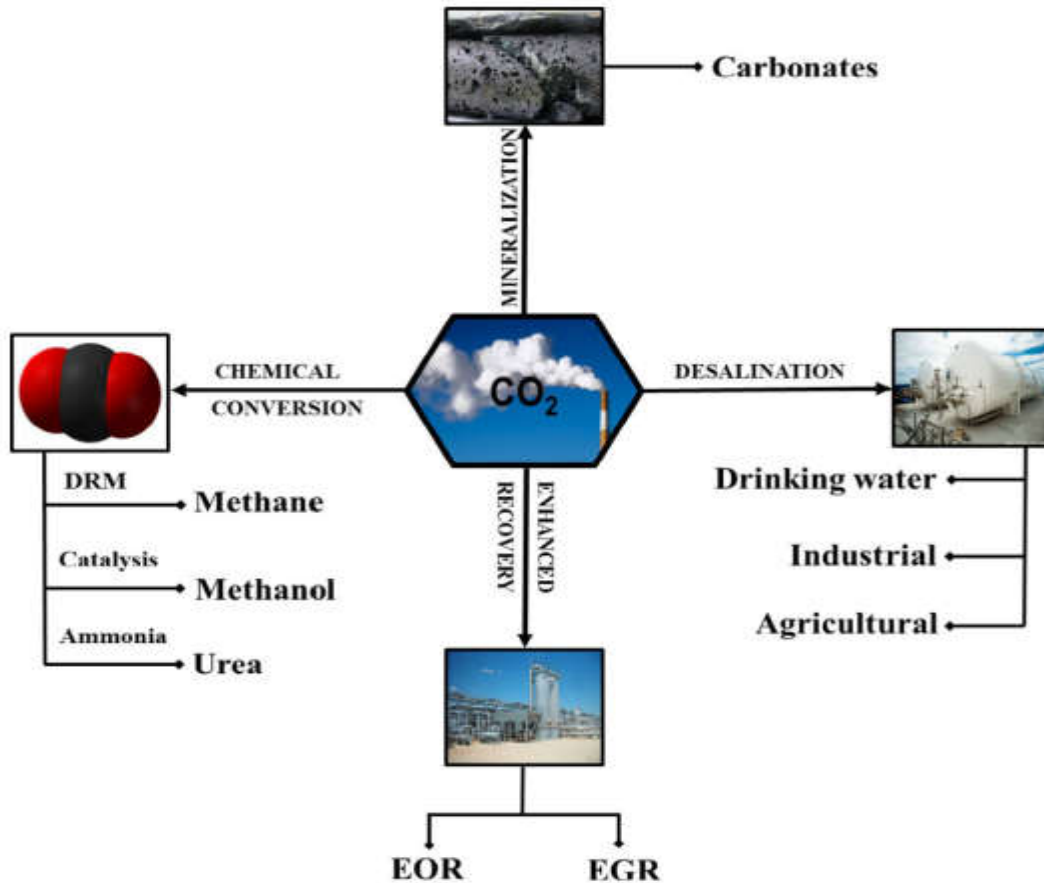
Figure (I.4): Various carbon-utilization pathways [19].

One of the major goal of CCS is to modify as less as possible the processes and carbon-based infrastructures and minimize the cost linked to the mitigation of CO_2 emissions [14]. The major contribution of the total cost of CCS is the capture of carbon dioxide which represents from 24 to 52 €/ton-CO_2. The transport costs that vary upon pipeline dimensions, pressure of CO_2 and landscape characteristics, are between 1 and 6 €/ton-CO_2 per 100 km of pipeline [14, 22]. All these additional requirements lead to an increase in power production costs from 75% up to 100% for plants integrating CCS technologies. However, this may be reduced to 30% to 50% in the long term [20] .

I .4. Carbon dioxide capture processes

Because power generation is the major in CO_2 emissions, the focus will be on the technologies dedicated to mitigate the emissions of this particular industrial sector. Figure (I.5) presents the three possible ways of CO_2 capture: post-combustion, pre-combustion and oxyfuel combustion. As previously stated, the capture of carbon dioxide represents the major cost of CCS and needs to become a more mature technology before the industrial sector heavily applies it. The choice of the capture technology depends on the concentration of the flue gas, the pressure of the gas stream and the fuel type [21, 22].
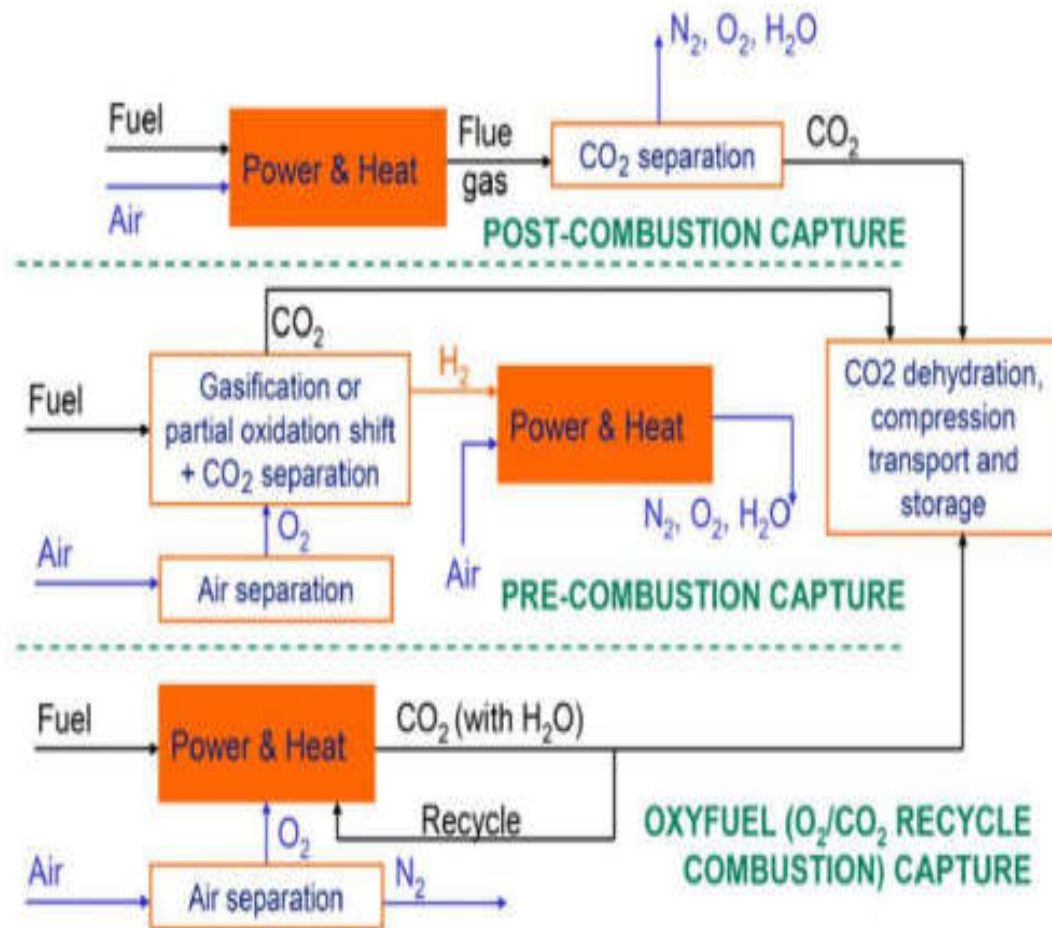
Figure (I.5): Carbon capture technologies [18].
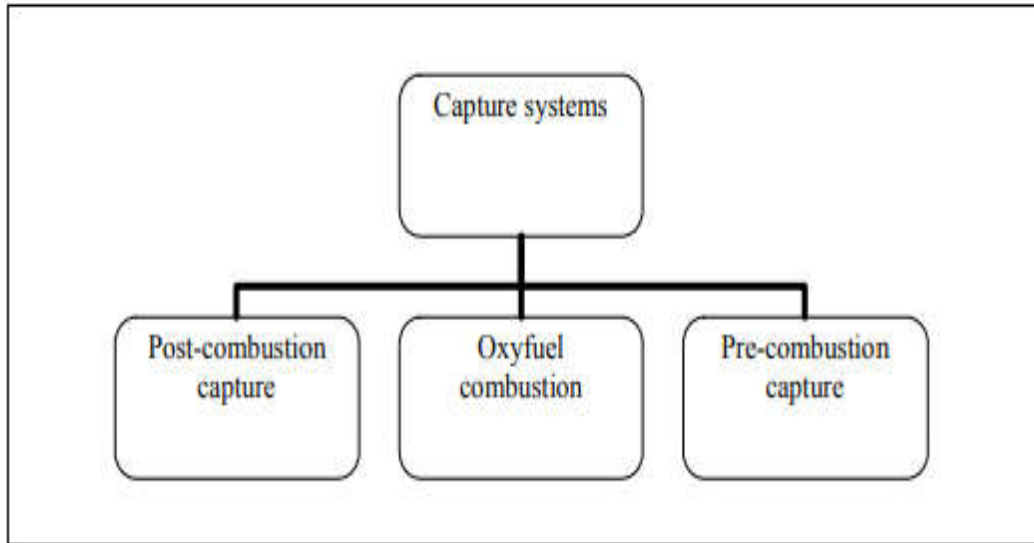
Figure (I.6): Classification of CO_2 captures systems [23].

I .4.1. Post-combustion CO_2 capture

Post-combustion capture (PCC) means that the carbon dioxide is separated from other exhaust gases produced by combustion of fossil fuel just before its release in the atmosphere. Exiting gas of power plant has a low CO_2 concentration (between 4 and 14%) and is at atmospheric pressure resulting in low thermodynamic driving force for CO_2 capture and large volume of gas to be handled. The low concentration of CO_2 implies that powerful chemical solvents need to be used to separate carbon dioxide from flue gas meaning that their regeneration will require a large amount of energy. Despite these technical difficulties, post-combustion capture is the most advanced technique because it can be retrofitted to existing units [21, 16, 22].
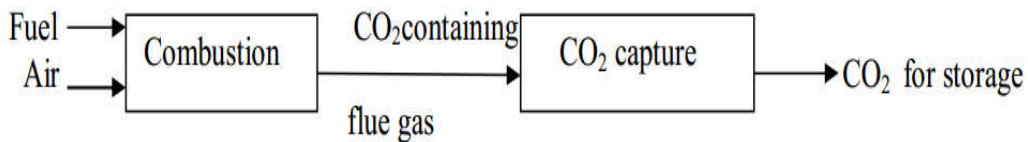
Figure (I.7): Post-combustion CO_2 capture [24].
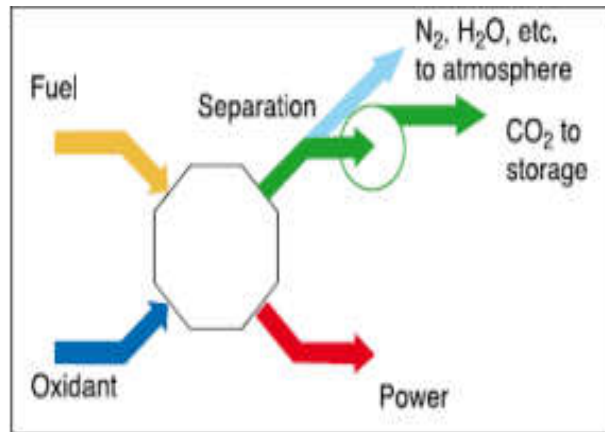
Figure (I.8): Schematic of post-combustion capture [25].

There are several post combustion gas separation and capture technologies being investigated, namely; (a) absorption, (b) cryogenic separation, (c) membrane separation and(d) micro algal bio-fixation (e) adsorption. Figure (I. 8) summarizes various technology options for post-combustion CO_2 capture.
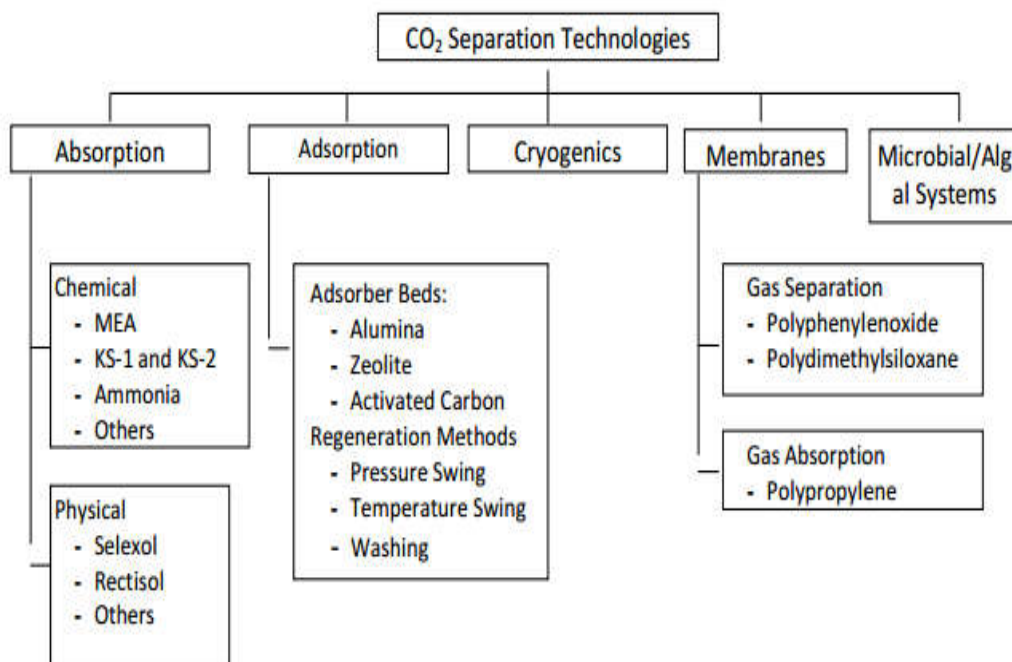
Figure (I.9): Process technologies for post combustion CO2 capture [26].

I. 4.1.1. Cryogenics

This process uses a principle of separation based on cooling and condensation. This method is applied to CO_2 capture where the gas stream contains high CO_2concentrations. It is presently not applied to more dilute CO_2 streams such as those encountered with typical power generation plants. This technique also requires significant amounts of energy for separation [24].

C. Font-Palma et al [27] discribed the Cryogenic distillation is a well-established technology that achieves separation based on the different boiling points of CO_2 and the gas components in the mixture.
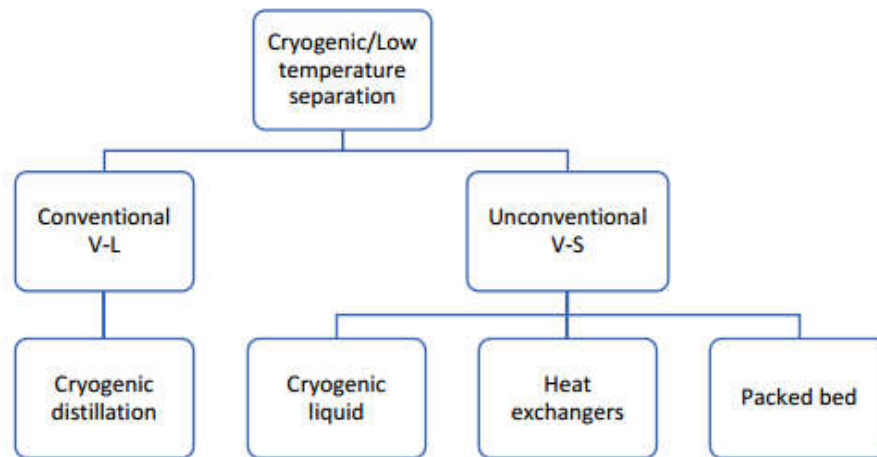
Figure (I.10): Cryogenic carbon capture technologies[24].

I. 4.1.1.1. *Convertional V-L separation*

Cryogenic distillation is a well-established technology that achieves separation based on the different boiling points of CO_2 and the gas components in the mixture. This method has been used for natural gas purification, where the CO_2 is removed in the liquid phase. However, it is an energy-intensive method due to the high pressure employed and the requirement that solid formation be avoided to protect equipment and prevent clogging. To avoid CO_2 solidification, extractive distillation, or "Ryan Holmes" technology, makes use of heavier hydrocarbons (e.g., ethane), which increases the solubility of CO_2 in the liquid phase, operating temperature, and relative volatility, facilitating separation [28]. Gas-to-liquid carbon dioxide separation is well recognized as the advanced technology for the purification and compression of CO_2 captured in oxy-combustion. A CO_2-rich flue gas derived from oxy-combustion is

ideal for integration with a carbon dioxide purification unit (CPU) for low temperature CO_2 separation.

I. 4.1.1.2.*Unconventional V-S Separation*

The relatively large energy requirements of conventional cryogenic distillation make vapour–solid (V–S) separation an attractive solution. A study that compared the two options found that for a gas mixture with a concentration of 70% vol. CO_2, the energy requirement for a conventional extractive cryogenic distillation network was 1472 kJ/kg CO_2, and the energy requirement for a cryogenic packed bed was 810 kJ/kg CO_2[29]. Low-temperature carbon capture based on solid–vapour equilibria takes advantage of solid formation, which is undesirable in cryogenic distillation and requires reaching temperatures at which CO_2 will frost. Achieving desublimation conditions entails contact with a cold medium; therefore, different options to attain the cold conditions that are needed are presented here.

a. Heat Exchangers for Cryogenic Separation

Heat exchangers are key unit operations for cryogenic industrial applications, such as process cooling, the separation and distillation of gas mixtures, and liquefaction for transportation and storage.

For the cryogenic separation of CO_2 using heat exchangers, a system that employs three heat exchangers was developed [30]. The first heat exchanger precools the rich CO_2 stream down to −100 ◦C, with a colder lean CO_2 stream of −125 ◦C in a gas/gas brazed heat exchanger. The other two act as an intermittent frosting process to capture CO_2 solids on the fins of the heat exchange at a temperature between −100 and −120 ◦C and as a CO_2 defrosting process using a heating stream at −50 ◦C to recover liquid and gas CO_2.

Song, Kitamura, Li and Ogasawara [31] proposed the use of Stirling coolers in a cryogenic CO_2 capture system. The system makes use of three Stirling coolers (SC). The first one is used to precool the feed gas to condense moisture. The second SC is the freezing tower, where the CO_2 freezes, and the third SC is used for cryogenic CO_2 storage.

b. Cryogenic Liquids

As an alternative to heat exchangers, the flue gas containing CO_2 can be directly contacted with a cryogenic liquid, causing the flue gas to form solid CO_2 particles in staged desublimating column. The CO_2 that is dissolved in the contacting liquid will form a slurry, which then goes through filtration and will subsequently provide a CO_2 pure product [32].

Cryogenic carbon capture with an external cooling loop (CCC-ECL) uses heat exchange to desublime CO_2 frost. The flue gas first passes through a dryer that removes the water content from the flue gas, the dry flue gas then passes through a heat exchanger and is mixed with a contact liquid, where 99% of the CO_2 is desublimed out of the gas phase. The heat exchanger cooling is supplied via an external cooling loop refrigerant.

After the CO_2 solid is separated from the gas stream and the contact liquid, the CO_2 solid stream is pressurised to 70–80 bar. After this compression stage, the CO_2 solid stream and the CO_2 lean gas stream pass through a second heat exchanger, which provides energy recovery to the ECL refrigerant and melts the CO_2 solid stream into a high pressure liquid stream [27].

C. Packed Beds

Packed beds filled with cold bed material have been used as a heat transfer surface for CO_2 capture [29]. Cryogenically cooled nitrogen gas is fed into the packed bed to precool bed material as a cooling step. Once the precooling step is complete, the nitrogen cooling gas flow is stopped, and a simulated flue gas containing CO_2 is fed into the packed column. When the flue gas containing CO_2 is sufficiently cooled by the bed material, the CO_2 desublimates onto the surface of the bed material to form a frost. The CO_2 frost will continue to grow on the surface of the bed material until the bed material reaches saturation. When the bed material becomes saturated, the CO_2 frost will begin to form on the fresh bed material that is further into the capture column. This leads to a frost front that advances through the packed column. The rate at which the frost front advances through the column is called the frost front velocity. The capture column is saturated with CO_2 frost when the frost front advances through the capture column and requires a regeneration step to remove the CO_2 frost from the packed bed. Tuinier et al. [33] performed a numerical study of three packed beds

operating in parallel cycling between the capture, regeneration, and cooling steps to create a pseudo-continuous process. The cooling duty is dependent on the initial bed temperature and the concentration of CO_2 in the flue gas but typically ranges between 1.2–2.6 MJ /kg CO_2 [33].

I. 4.1.2. Membranes

The operation of membranes is based on the differences in physical or chemical interactions between gases and the membrane material is modified to allow one component to pass through membrane faster than the other. The membrane modules can either be used as conventional membrane separation units or as a gas absorption column. In the former case, CO2 removal is achieved due to the intrinsic selectivity of the membrane between CO2 and other gases involved, while in the latter case, CO2 removal is accomplished by gas absorption where the membranes, usually microporous, hydrophobic and nonselective, are employed as a fixed interface for CO2 transfer. This method of gas separation using a membrane is relatively new and the selectivity is generally low while energy consumption is high[24].
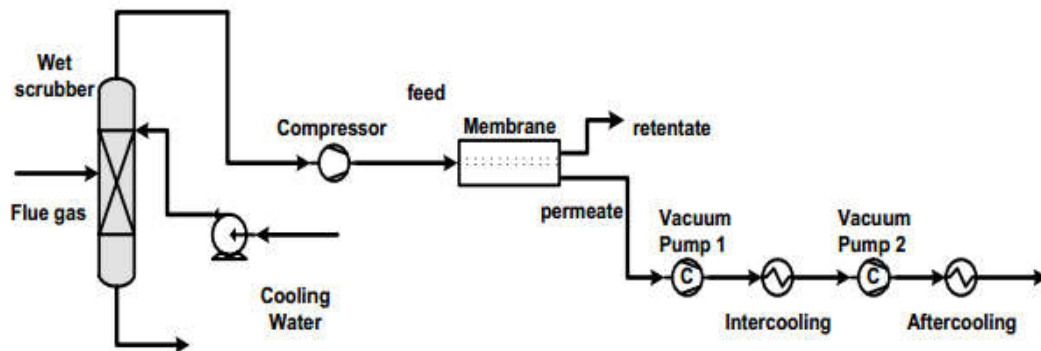
Figure (I.11): Scheme of the post-combustion CO2 capture method using a membrane separation process [34].

Recently, CO_2 capture using membranes technology is widely studied all over the world due to their excellent performance. Debangsu Bhattacharyya[35] report that, the use of Hybrid membrane–solvent processes for post-combustion CO_2 capture, support the flexibility of capture systems by synergistically exploiting the advantages of the membrane and absorption systems.

I. 4.1.3. Use of microbial/algae

Apart from physicochemical methods of CO2 removal, biological methods using algae, bacteria and plants have also been adopted. Micro algal bio-fixation of

carbon dioxide in photo-bioreactors has recently gained renewed interest for CO_2 mitigation. Insufficient illumination would limit the microorganism growth and hence would reduce the CO_2 removal. The use of chemoautotrophic microorganisms which use inorganic chemicals instead of light energy for CO_2 removal has also been successfully attempted [23].

I. 4.1.4. Adsorption

Solid adsorbents such as activated carbons, zeolites and mesoporous silicates, alumina, metal oxides have been extensively used for gas separation. Recently, gas adsorption by activated carbon fibres and carbon fibre composites has been identified as a promising alternative. Lately, structured porous monolith materials made from carbon fibres, which have the ability to selectively adsorb gases due to their molecular sieving characteristics, have been investigated. Carbon fibre composite in monolith form reduce inter-particle voids and maximize bulk density, thereby increasing the adsorption capacity of the material. While conventional wet solvent processes (used for example in CO_2 removal on a large scale in applications such as natural gas processing) is commercially available, and has been trialled for capturing CO_2 from flue gas at pilot-scale, this method is costly, requires pre-treatment, and produces large volumes of wastewater and sludge from the solvent processes, and its efficiency is not high. Therefore, to make CO_2 capture economically viable it is very important to create new ideas and develop novel cost-effective technologies for such applications. At present, developing carbon fibre composite adsorbents for CO_2 capture is very promising. It is a dry process, and different to the conventional solvent processes. Carbon fibre monolithic composite adsorbents have been made in the form of either one single block or cylinder. Recently, CSIRO devised a new type of carbon fibre composite adsorbent, which is made with multiple channels. This exhibits unique features including low pressure drop, good mechanical properties, ability to handle dust-containing gas streams, good thermal and electrical conductivity and selective adsorption of gases [24].

I. 4.1.5. Absorption

This is a well established CO_2 capture system primarily used in the chemical and oil industries. Solvent scrubbing involves the use of a chemical solvent which reacts with the CO_2 in the flue gas and is regenerated at higher temperature, producing a purified CO_2 stream suitable for compression and storage. The exhaust gas is first

cooled, then treated to remove particulates and other impurities before being fed to the absorption column, where the amine solvent absorbs CO_2 by chemical reaction. The CO_2-rich solution is fed into a stripper column where the temperature is increased (to about 120 °C) in order to release the CO_2. The released CO_2 is compressed and the regenerated absorbent solution is recycled to the stripper column.
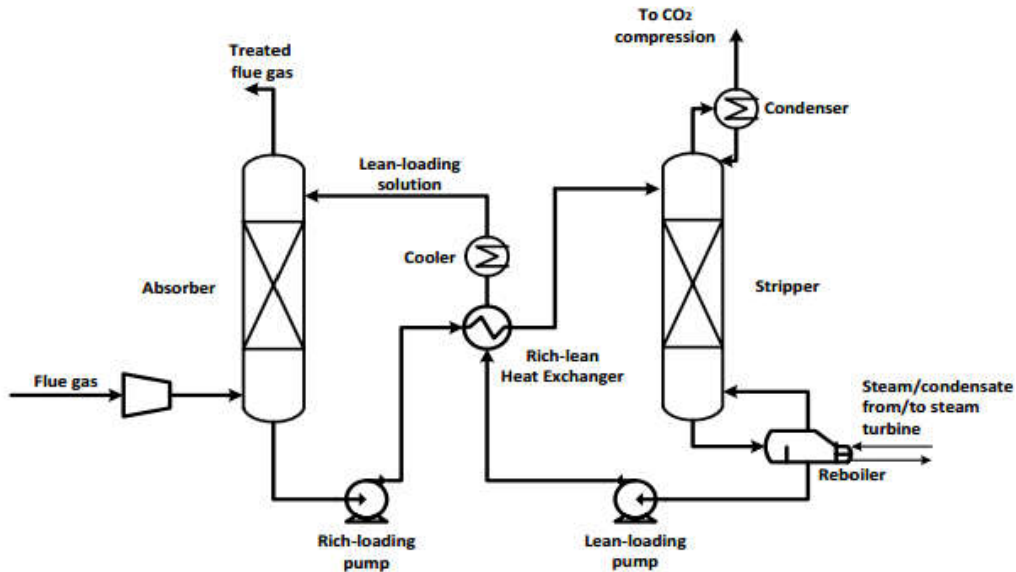
Figure (I.12): Scheme of the post-combustion CO2 capture method using a chemical absorption process [35].

- **Chilled ammonia:** The chilled ammonia system was evaluated since it has potential for direct application in post-combustion capture of CO_2 from power plants as well as in retrofitting of power plants and hence, would serve as a good comparison with the MEA system. In addition, since the chilled ammonia system has a desorber that operates at a high pressure, it allowed us to study the interplay between the energy required for regeneration of solvent and for CO_2 compression.

- **Monoethanolamine (MEA):** MEA is the most widely-studied solvent for CO2 capture and is the system for which abundant experimental data is available[23].

I. 4.2. Pre-combustion CO$_2$ capture
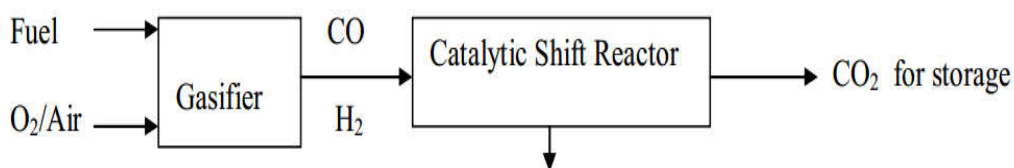
Figure (I.13): Pre-combustion CO$_2$ capture [24].

CO2 is of course not available for capture before combustion. Nonetheless, by modifying the conventional power unit, one can achieve the separation of CO_2 from other gases before the production of power [36]. This can be achieved if fuel is reacted with oxygen, air or steam to give mainly carbon monoxide and hydrogen by a process called gasification, partial oxidation or reforming (eq.(I.2))[21]. This mixture rich in H and CO is passed through multiple catalyst beds to achieve the "water-gas shift" reaction (eq.(I.3)) producing more CO2. The latter will be separated while H_2 is used as a fuel in a gas turbine combined-cycle plant.

$$2C + O_2 + H_2O \rightarrow H_2 + CO + CO_2 \qquad (I.2)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (I.3)$$
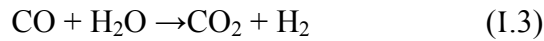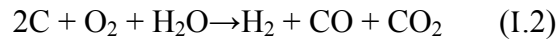
The separation is typically achieved using a physical solvent. Because CO_2 is more concentrated and has a higher partial pressure than in post-combustion, it is more easily separated from flue gas and the regeneration operation requires less energy. Furthermore, the installations are smaller than in the post-combustion case [21; 36]. Pre-combustion technique does induce an energy penalty with the gasification but the overall energy balance is much more favourable than in the post-combustion case [36]. The main advantage of pre-combustion capture relies on the use of carbonless fuel. Indeed, the reforming transforms the chemical energy of carbon to chemical energy of hydrogen [14]. The combustion of hydrogen offers advantages such as the absence of SO_2 emissions [21] but the efficiency of hydrogen-burning gas turbines is smaller than conventional units. It seems that pre-combustion technology is applicable for integrated gasification combined cycle (IGCC) that relies on coal gasification but is less attractive to treat liquid or solid fuels for which more energy losses would be involved in the gasification step [36].
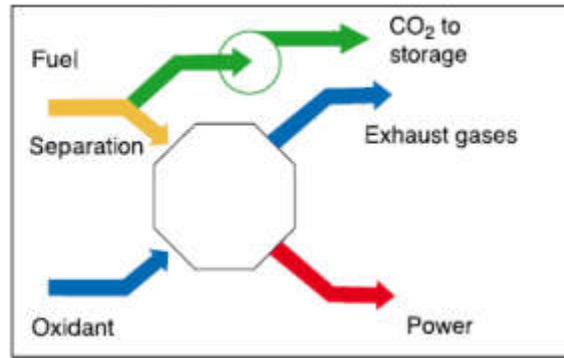
Figure (I.14): Schematic of pre-combustion decarbonization [25].

A synthesis gas is produced in the first step of pre-combustion decarbonization. If natural gas is used as a fuel, this is obtained by either steam reforming or self-thermal reforming. If coal is used as the fuel, synthesis gas is obtained by gasification. In the next step, the synthesis gas is subjected to the water gas shift reaction to produce carbon dioxide and hydrogen. The hydrogen and carbon dioxide can be separated by pressure swing adsorption or physical absorption and the pure CO_2 stream is compressed and sent for storage. When pressure swing adsorption is used to produce a pure stream of CO_2 and another pure stream of H_2, an additional step is needed for CO_2 purification before the H_2purification. The hydrogen stream is either used as a feedstock for a chemical process or is burnt to produce electricity [23].

I. 4.2.1. Steam reforming

Natural gas can be steam reformed and then subjected to water gas shift reaction to produce a mixture consisting mainly of carbon dioxide and hydrogen. The reactions in steam reforming are outlined below:

$$CH_4 + H_2O + heat \rightarrow CO + 3H_2 \qquad (I\text{-}4)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (I\text{-}5)$$
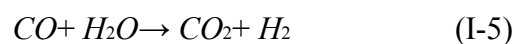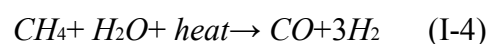
Steam reforming is endothermic and hence, some of the natural gas has to be used for firing in the reformer furnace to provide the heat required for the reforming reaction. This can lead to significant exergy losses in the process. Since there is a more concentrated stream of CO_2 available, the energy penalty for absorption is not as high. The CO_2 can also be separated by pressure swing adsorption. However, the water gas shift reaction also requires steam to be withdrawn from the power cycle. Hence, this

process is advantageous only if the energy savings made from capturing a purer stream of CO_2 are greater than the exergy losses due to loss of natural gas used for firing and loss of steam from the steam cycle for the shift reaction [23].

I. 4.2.2 .Autothermal reforming

Autothermal reforming is a combination of steam reforming and partial oxidation. Since the partial oxidation reaction is exothermic, it provides the energy required for the endothermic steam reforming and only minimal firing of additional natural gas as fuel is required. The reactions in autothermal reforming are given below. The autothermal reforming is the third reaction - (1-8)- and it is the sum of the first two reactions (1-6) and(1-7)

$$C_mH_n + \frac{m}{2}O_2 \rightarrow mCO + \frac{n}{2}H_2 \qquad (I\text{-}6)$$

$$\frac{n}{2}H_2 + \frac{n}{4}O_2 \rightarrow \frac{n}{2}H_2O \qquad (I\text{-}7)$$

$$C_mH_n + \frac{2m+n}{4}O_2 \rightarrow mCO + \frac{n}{2}H_2O \qquad (I\text{-}8)$$

Figure (I. 15): Flowsheet of autothermal reforming process [23].

After reforming and water gas shift reaction, the carbon dioxide is separated from the hydrogen and the nitrogen by absorption or by PSA. The hydrogen and nitrogen are then sent to a gas turbine for firing. It is expected that 20-25% of the energy of the fuel is dissipated irreversibly in the conversion of natural gas to hydrogen [38].

The capture of CO_2 takes place at the same pressure as in the turbine. Hence, the stripping does not consume too much energy because of the pressure differential between the absorber and the stripper. When a lower pressure in the stripper is used, there is enough heat available from the cooling of the products from the water gas shift reactor for the stripping process [39]. An optimization can be performed by not fully releasing the pressure in the stripper, thus saving on compression costs of CO_2 in the end.

A fuel containing more than 50% hydrogen may not be very well suited for a gas turbine with modern low NO_x combustors. Hence, combustion issues need to be addressed [40].

I. 4.2.3. Integrated Gasification Combined Cycle (IGCC)

If coal is to be integrated into a gas turbine cycle, it is necessary that it first be gasified to produce coal gas that can be combusted in a gas turbine. If CO2 capture is desired, it is preferable to use O2 blown systems at high pressures since this leads to higher CO2 partial pressures. A flowsheet of an IGCC process with CO2 capture is shown in figure(I. 14).
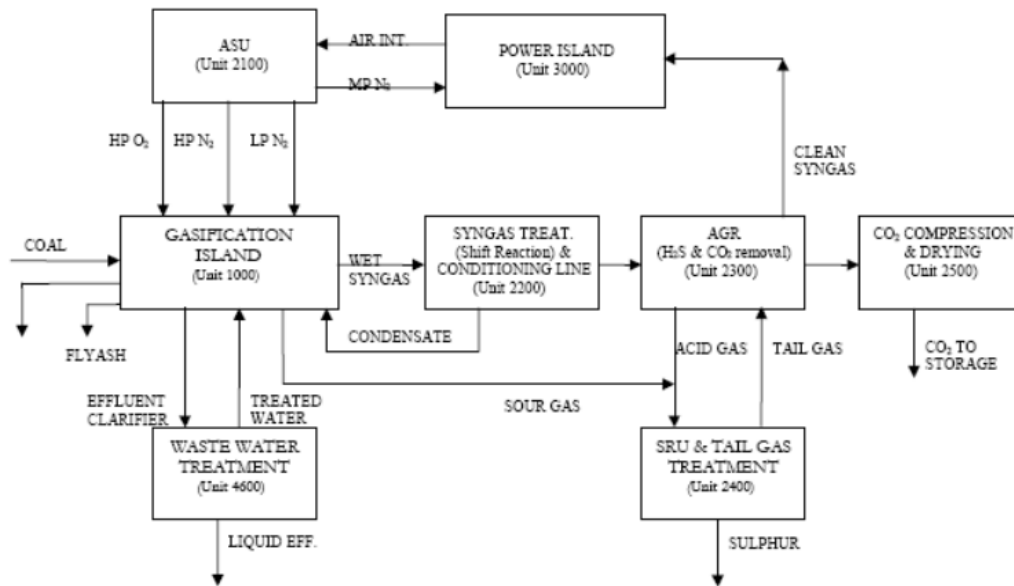
Figure (I.16): Block diagram of IGCC power plant [23].

The gasifier output contains syngas, CO_2 and impurities such as N_2, H_2S, COS, HCN, NH_3 and trace amounts of Hg which must be treated appropriately [25].

The syngas is treated for removal of ash and particulates and then subjected to water gas shift to produce carbon dioxide and hydrogen. There will also be contamination due to H_2S. This is treated and the gas is then sent for CO_2 capture. Since the CO_2 is at a relatively high pressure, it can be easily captured by a physical absorption process which is less energy intensive. Usually, H_2S is removed in one physical absorption unit followed by recovery of CO_2 in the next one [41]. The recovered H_2S is then sent to a Claus plant for reduction to elemental sulfur and tail gas clean-up. Recovered CO_2 is compressed and sent for storage. Hydrogen is then sent for combustion in the gas turbine and for power generation. In addition, power is generated from the steam cycle that utilizes the steam obtained from syngas cooling [23].

I.4.3. Oxyfuel combustion

Oxycombustion is a combustion process in which the combustion gas is no longer air but "pure" oxygen (purity generally greater than 95%). The objective is to increase the content of CO_2 from the combustion fumes by eliminating the nitrogen ballast, which then contains mainly CO_2 and water. The purer the oxygen used for combustion, the more the fumes of combustion approach a binary H_2O/CO_2 mixture,

the main stage of CO_2 capture then consists of condensing the water. Another important advantage is that the volume of fumes to be treated is significantly reduced and the residual contaminants are less diluted than in air post-combustion [42].
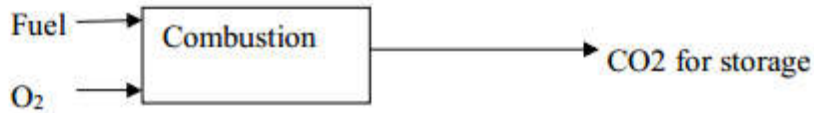
Figure (I.17): Oxyfuel combustion [24].

The main disadvantage of post-combustion capture systems is the dilution of the flue gases due to nitrogen. This problem can be mitigated if the combustion is carried out in the presence of oxygen instead of air. The burning of fossil fuel in an atmosphere of oxygen leads to excessively high temperatures – as high as 3500°C. The temperature is moderated to a level that the material of construction can withstand by recycling afraction of the exhaust flue gases. Figure(I.18) depicts a schematic of oxyfuel combustion.
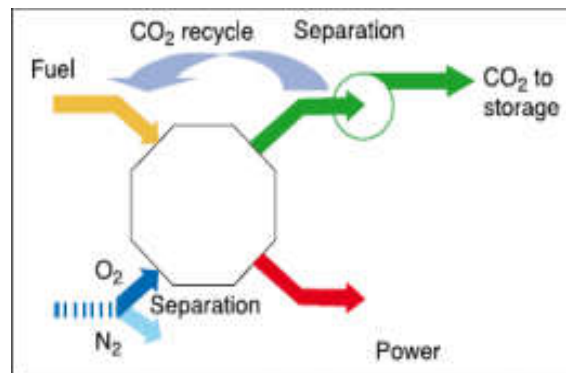
Figure (I.18): Schematic of oxyfuel combustion [25].

The flue gas contains mainly CO_2 and water. It may also contain other products of combustion, such as NO_x and SO_x, depending on the fuel employed. One of the advantages of oxyfuel combustion is that the formation of NO_x is lowered since there is negligible amount of nitrogen in the oxidant. Any formation of NO_x will only arise from the nitrogen in the fuel [43]. The CO_2 capture efficiency is very close to 100% in

these systems. It may be necessary to remove acidic gases such as SO_x and NO_x if their levels are above those prescribed for CO_2 sequestration [44].

The main energy penalty in oxyfuel combustion occurs due to the energy intensive separation of oxygen from air in the air separation unit (ASU). Cryogenic separation is employed to obtain an oxygen stream of 95% purity. At this level of purity, only separation of N_2 is needed and the energy requirement is typically around 0.2 kWh/kg O_2, although some recent improvements may be able to reduce the energy requirement to 0.16 kWh/kg O_2 [45,46]. If the noble gases are removed in the ASU, then there will be lesstreatment of the flue gases required since the flue gas has to be stripped of the noble gases before storage.

✓ The advantages and disadvantages of these capture technologies are presented in Table

Table(I.2): Advantages and disadvantages of CO_2 capture technologies [21].

Capture technology	Advantages	Disadvantages
Post-combustion	Existing technology Retrofit to existing power-plant designs Extra removal of NO_x and SO_x	Energy penalty due to solvent regeneration Loss of solvent
Pre-combustion	Existing technology Very low emissions	Cooling of gas to capture CO_2 is necessary Efficiency loss in water-gas shift section
Oxyfuel combustion	Existing $\rightarrow$ technology Absence of nitrogen $\rightarrow$ no NO_x emissions Absence of N_2 low volume of gases and reduction of the entire process size	High energy input for air separation Combustion in pure oxygen is complicated

I. 5.Characteristics of carbon dioxide capture and storage

CO_2 capture can be applied to large point sources. The CO_2 is then compressed and transported for storage in geological formations, the ocean, natural carbonate sorfor use in industrial processes. Large point sources of CO_2 include large

fossil fuel or biomass power plants, main industries that emit CO_2, natural gas production, synthetic fuel production and production of hydrogen using fossil fuels.

Potential technical types of storage are: geological storage (in geological formations, such as oil and gas fields that do not have industrial value coal seams and deep saline formations), ocean storage (direct release in to a column of ocean water or into a sea basin) and the industrial fixation of CO_2 in inorganic carbonates.

In CCS, it depends on the share of CO_2 capture, the increase in CO_2 production resulting from a reduction in the overall efficiency of power plants or industrial processes due to the additional energy that is required for capture, transport and storage, anyleakageas a result of transportation and the share of CO_2 that remained when stored for a long period of time [47].

I. 6.Importance of CO_2 Capture and Gas Separation

Emissions of long-lived greenhouse gases (GHGs) are believed to be a major driver of climate change. Carbon dioxide (CO_2) is the most important greenhouse gas, accounting for 56.6% of the total annual greenhouse gas emissions in 2004 (latest available data) [48]. One of the most prominent strategies to lower CO_2 emissions currently under investigation is carbon capture and sequestration (CCS). According to estimates by the International Energy Agency (IEA) [49], more than 80% of CO_2 emissions from power generation plants can be captured using CCS technology, which can contribute to $21 - 45$ % reduction in anthropogenic emissions of CO_2 by the year 2050.

An additional approach for CO_2 reduction is its re-use in various applications. CO_2 is typically captured from fossil fuel burning power plants, steel and iron manufacturing plants, cement, ammonia, and other chemical plants or other CO_2-intensive industries and transported to a storage site. The initial CO_2 concentration in the stream in any of the processes above is relatively low, since a number of other gases (such as N_2, O_2, SOx, NOx) and even H_2O are found in substantial or lower concentrations (impurities). For example, in a post-combustion stream, CO_2 concentration is below 15% while in a pre-combustion process CO_2 concentration in the flue gas [43] is approximately 40%. Finally, in oxy-combustion, the CO_2 concentration [50] is above

60%. In all cases, CO_2 needs to be separated from other gases in order to be safely and economically transported to its final storage location.

I. 7. Aqueous solutions for removal of CO_2 from industrial gases

The removal of carbon dioxide (CO_2) from a process gas stream is an important step in many industrial processes and can be required for operational, economical and/or environmental reasons. In an aqueous environment, CO_2 can react with water to form a weak acid known as carbonic acid which lowers the pH of water and promotes corrosion of industrial equipment. Carbon dioxide is also a common impurity in natural gas streams and must often be removed to a large extent to meet the heating value requirements of the gas or to meet pipeline specifications. Other examples can be found in the production of liquefied natural gas (LNG), where CO_2 must be removed to prevent freezing in the low-temperature chillers, and in the manufacture of ammonia, where small amounts of CO_2 can act as a poison to the catalytic process. Finally, CO_2 as a major greenhouse gas is held responsible for the observed global warming over the past decades and the concerns for related climate change and its possible effect on mankind. In general, technologies to separate CO_2 from gas streams are based on absorption, adsorption, membranes or other physical, chemical and biological separation methods [51].
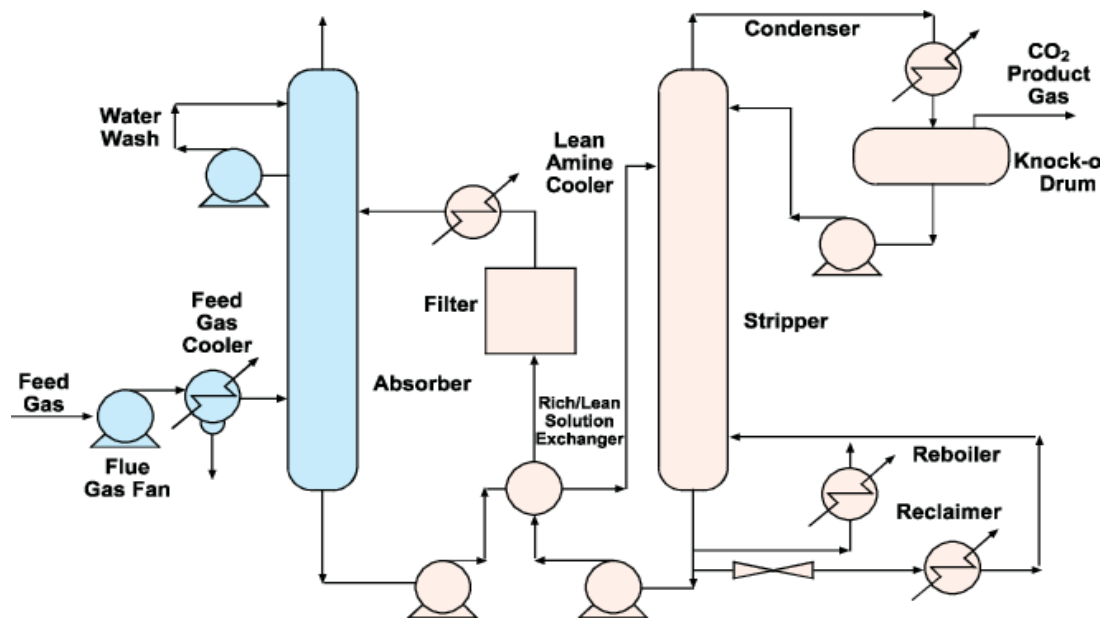

Figure (I.19): Process flow diagram for CO_2 removal with chemical solvent [52].

I. 7.1. Amino Acid Salts

Amino acid salts be an attractive alternative to alkanolamines as solvent for carbon dioxide absorption [53]. The advantages of the amino acid salts are their higher resistance to degradation [54], lower vapor pressure [55], and smaller amounts of oxidative degradation products [56]. The amino acid salts are commonly prepared from a solution of the salt of a strong inorganic base and a weak organic nonvolatile amino acid [54, 57].

I. 7.2.Ionic Liquids

ILs are salts that remain in liquid form around room temperature, and consist of large organic cations and anions (can be either organic or inorganic) [58], shape of organic cations depress the melting points of ILs to room temperature or below [59], and hence they remain in liquid form around room temperature.

Due to coulombic attraction between cations and anions [60], ILs are generally non-volatile, non-flammable, chemically and thermally stable over a wide temperature range. Therefore, ILs are more environmentally friendly compared to conventional solvents, as they do not release harmful compounds during processing. Another key feature of ILs is that they can dissolve a vast range of inorganic and organic components to very high concentrations, by reducing by-products from side reactions [52]. In addition, ILs are reported to have a wide range of thermophysical properties. Through proper choice of cations and anions, they can be customized to fit certain properties for specific purposes [61]. However, some of the ILs feature some disadvantages, such as high manufacturing cost, toxicity and corrosiveness [62]. Nonetheless, the other properties of ILs are useful from an industrial point of view, and hence ILs are suggested to replace amine-based solvents for carbon capture purposes.

Ionic liquids, especially those functionalized with amine groups, show significant potential for a wide variety of CO_2 separations, including post-combustion CO_2 capture. By tethering the amine to the anion, the stoichiometry of the reaction can be doubled from one CO_2 for every two amines (as is the case with aqueous Monoethanolamine) to one CO_2 for each amine. Moreover, the reaction enthalpy can

be ₐcₜᵢᵥₑₗy tuned by the design of the anion, adjusting capacity and regeneration energy. In addition, ILs can be used without added water, further reducing the parasitic energy required for CO_2 removal from flue gas .Ionic liquids are also emerging filter reagents for capturing carbon dioxide from industrial gases.

Te solubility of CO_2 in ILs compared to other gases such as methane and nitrogen enables ILs to separate CO_2 from the source, be it a power plants flue gas or natural. Even when there are low concentrations of CO_2 in mixed gas, the IL can be designed to incorporate a functional group, such as an amine, thus rendering it task specific. Capacity for CO_2 solubility in ILs originates from the asymmetrical combination of the anion and cation, which results from short-range repulsive forces between their ionic shells. Therefore the more incompatible the ionic constituents are the greater the solubility is[63].

Ionic liquids (ILs), particularly functional ILs, are known as unique absorbents for the removal of H2S from gas mixtures because they can absorb a large amount of H2S at high pressure. Ionic liquids (ILs) have been widely studied for CO_2 and H2S absorption, as they have several advantages, such as environmentally friendliness, extremely low vapor pressure, tuneable structure and high thermal and chemical stability [63]. Most of the research found that functionalized ILs can act as catalysts or substitutes for aminobased, metal-based, substituted benzoate-based and pyridinium-based solvents for H2S removal [64].

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Conclusion

Conclusion

The aim of our study is to investigate the use of imine salt solutions in CO_2 capture from flue gas of coal fired power plants. We have focused on the experimental study of biphasic solution equilibrium behavior. So we have started by the synthesis and structural study of Salicylidene-2-nitroaniline HNSA.

The obtained results show that the synthesized imine was stable solid species characterized by yellow flakes pouder, and it is soluble in the polar solvents at standard temperature. However, they do not dissolve in water and apolar solvents at the 25°C and are of low solubility at high temperature as a result, the period found to be adequate to reach equilibrium of deprotonation was 15-20 min, 25-30min, 25-30min when we use NaOH, $NaNO_3$, Na_2CO_3, respectively.

Comparison between the three bases, we have found that sodium carbonate (Na_2CO_3) in aqueous solution, a weak inorganic base, will not deprotonate HNSA to its ionic forme, because it is not strong enough. However, treatment with NaOH, a strong inorganic base, can change imines to its ionic (salt) form. However, the deprotonation becomes greater according to the following order of bases:

$$NaOH > NaNO_3 > NaCO_3$$

As a final conclusion; the use of a strong base, such as NaOH, promotes the deprotonation reaction of HNSA. HNSA can lose a hydrogen ion because the phenolate ion formed is stabilized by the delocalization of the negative charge on the oxygen atom around the ring al the molecule. The more stable the ion is, the more likely it is to form the sals.

The ionic from of the imine salts (NSA-, Na+) are more soluble in water than the neutral forms due to its improved polarity. IR characterization of the obtained salts, indicate substitution of aromatic rings of HNSA and suggesting that the free functionalities of HNSA have been occupied by Na+. All imine salts exhibited well-defined absorption band at 310 nm, which were assigned to the O-, Na+ band.