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Comparative Study of Amine Solutions used in CO_2 Absorption/Desorption Cycles

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Dedicated to my parents

“The core of man’s spirit comes from new experiences”
Jon Krakauer

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Abstract

The increasing concerns about climate change and global warming has increase the interest in reducing the emissions of greenhouse gases (GHG), mainly CO_2. Thus, the chemical absorption of carbon dioxide by aqueous amine solutions has been investigated over the last decades.

The studies were performed in two distinct stages. The first one was the preliminary trials. In these trials, the absorption of carbon dioxide and the solvent regeneration/release of carbon dioxide were performed. The second one consisted on the performance of carbon dioxide absorption in a pilot unit, with the aqueous amine solutions that showed the best results in the preliminary trials and the amine solutions that were to be tested in the previous work.

In the carbon dioxide absorption tests performed in the preliminary trials, the goal was to study the energy efficiency of each tested amine solution, i.e., at which temperature the solutions would start releasing the absorbed CO_2. The following aqueous amine solutions with a concentration of 20 % by weight were tested: isopropylamine, diisopropylamine, diethylamine, bis(2-ethylhexyl)amine, dimethylethanolamine (DMEA) and triethylamine. The isopropylamine aqueous solutions was not prepared, due to the fact that its boiling point temperature was around 31-33 ºC, which meant that during the solvent regeneration/release of carbon dioxide trials, It would be impossible to assure that if it was the release of carbon dioxide or the amine that was starting to boil. The remaining aqueous amine solutions were prepared. After they had been saturated with carbon dioxide, their physical state was verified. In the case of diisopropylamine aqueous solution, this amine was not soluble in water, but only miscible, which meant that when its carbamate was formed, it immediately precipitated. For bis(2-ethylhexyl)amine, this solution showed a blue coloration and two liquid phases: organic and aqueous. This was due to the fact the molecule of this amine was amphiphilic, meaning that it has hydrophilic and hydrophobic properties. Triethylamine was not completely soluble in water. DMEA, theoretically was soluble in water, been an alkanolamine, but it was not soluble in water. This could be due to the fact that it was from 2004 and it could have already been degraded. Diethylamine was the only amine that was completely soluble in water.

Then, the tests of solvent regeneration/release of carbon dioxide were performed for all the aqueous amine solutions, except, isopropylamine and diisopropylamine. For the solutions of diethylamine and DMEA, the release of carbon dioxide was not observed. In the case of bis(2-ethylhexyl)amine, the release of carbon dioxide was observed for the temperature of 30 ºC for a period of 35 minutes. In the case of triethylamine, the release of carbon dioxide was observed for the temperature of 36 ºC for a period of 44 minutes.

In the carbon dioxide absorption tests performed in the pilot unit, the following aqueous amine solutions with a concentration of 10 % by weight were tested: diethylamine, monoethanolamine (MEA), piperazine (PZ) and ethanolamine (EDA). The tests were performed with an absorption time of 240 minutes (4 hours). The obtained results for the tested aqueous amine solutions were: 0.492 mol CO_2/mol amine for the diethylamine aqueous solution, 0.409 mol CO_2/mol amine for the MEA aqueous solution, 0.395 mol CO_2/mol amine for the PZ aqueous solution and 0.321 mol CO_2/mol amine for the EDA aqueous solution.

Then, the obtained results in this work were compared with the ones obtained in Santos (2012) [25], which were for N-methyldiethanolamine (MDEA) and diethanolamine (DEA) 10 % by weight aqueous solutions. The solutions used in Santos (2012) [25] showed a higher carbon dioxide loading capacity than the solutions used in this work. For the MDEA, the loading capacity was 1.020 mol CO_2/mol amine and for DEA, the loading capacity was 0.982 mol CO_2/mol amine.

Lastly, a cost analysis was performed in other to see which one of the amines was the most economical solvent. After analyzing the carbon dioxide loading capacity and the price per liter for each one of the amine, it was concluded that DEA was the most economical solvent, with a loading capacity of 0.982 mol CO_2/mol amine and price of 25.70 €/L.

Keywords: Carbon dioxide; Chemical absorption; Aqueous Amine Solutions; Solvent Regeneration; Isopropylamine; Diisopropylamine; Diethylamine; Bis(2-ethylhexyl)amine; Triethylamine; DMEA; MEA; PZ; EDA; MDEA; DEA.

Resumo

O aumento das preocupações relacionadas com as alterações climáticas e com o aquecimento global tem aumentado o interesse na redução das emissões de gases de efeito de estufa (GEE), principalmente o CO_2. Deste modo, a absorção química do dióxido de carbono através de soluções aquosas de aminas tem sido alvo de estudos nas últimas décadas.

Os estudos foram realizados em duas etapas distintas. Numa primeira etapa realizaram-se os ensaios preliminares. Nestes ensaios, procedeu-se à absorção do dióxido de carbono e regeneração do solvente/libertação de dióxido de carbono. A segunda etapa consistiu na realização de ensaios de absorção de dióxido de carbono numa instalação-piloto, com as soluções aquosas de aminas que apresentaram os melhores resultados nos ensaios preliminares e com as soluções aminadas que eram para ter sido testadas no trabalho realizado anteriormente.

Nos testes de absorção de dióxido de carbono realizados nos ensaios preliminares, o objetivo era estudar a eficiência energética de cada uma das soluções aminadas, isto é, averiguar a que temperatura as soluções começavam a libertar o dióxido de carbono absorvido. As seguintes soluções aquosas de aminas com uma concentração de 20 % em massa foram testadas: isopropilamina, di-isopropilamina, dietilamina, bis(2-etilhexil)amina, dimetiletanolamina (DMEA) e trietilamina. No caso da isopropilamina, a sua solução aquosa não foi preparada pois a sua temperatura de ebulição rondava os 31-33 ºC, o que posteriormente nos ensaios de regeneração de solvente/libertação de dióxido de carbono tornaria impossível observar com certeza se seria o dióxido de carbono a ser libertado ou se seria a amina a entrar em ebulição. As restantes soluções aquosas de aminas foram colocadas dentro de um balão de três tubuladuras. Fez-se borbulhar o dióxido de carbono no interior das soluções, por via de um tubo de teflon, até que estas se encontrassem saturadas. Após a saturação das soluções aquosas de aminas, verificou-se o seu estado físico. No caso da solução aquosa de di-isopropilamina, concluiu-se que esta amina não era solúvel em água, mas sim miscível, pois observou-se à formação de um precipitado branco dentro da solução à medida que a amina ia reagindo com o dióxido de carbono. Este

precipitado branco era o carbamato produzido pela reação entre a amina e o dióxido de carbono que, pelo facto de a amina ser somente miscível em água, não se conseguiu dissociar no bicarbonato correspondente, levando à sua precipitação. No caso da solução aquosa de bis(2-etilhexil)amina, esta apresentava uma coloração azulada e tinha uma separação entre a fase aquosa e a fase orgânica. Verificou-se que esta amina possuía uma molécula anfifílica, isto é, a molécula desta amina é constituída por uma secção hidrófila, que neste caso é o grupo amina, e por uma secção hidrofóbica, a cadeia alifática. Para a solução aquosa de trietilamina, verificou-se que esta amina não era completamente solúvel em água, pois observou-se a formação de uma fase aquosa e a formação de uma fase orgânica. Já com a solução aquosa de DMEA ocorreu algo de insólito. Teoricamente, a DMEA seria solúvel em água, tal como as outras alcanolaminas, mas neste caso, talvez pelo facto de ela ser de 2004 e de poder estar degradada, tal não se verificou. Ao se preparar esta solução aquosa, verificou-se que esta amina não era solúvel em água, pois mais uma vez, formou-se uma separação entre a fase aquosa e a fase orgânica. A única das aminas que era completamente solúvel em água era a dietilamina.

De seguida, foram efetuados os testes de regeneração de solvente/libertação de dióxido de carbono para todas as soluções aquosas, à exceção da solução de isopropilamina e a solução de di-isopropilamina, pelos motivos referidos anteriormente. Estes testes consistiam em aquecer as soluções aquosas de aminas que tinham sido saturadas com dióxido de carbono. Para tal utilizou-se uma placa de aquecimento (*Agimatic-N, J. P. Selecta*) para aquecer o banho de óleo para o aquecimento das soluções aquosas que se encontravam dentro do balão de três tubuladuras. Foi colocado no balão de três tubuladuras um adaptador para libertar o dióxido de carbono para dentro de uma tina com água, através de um tubo de borracha, e um termopar (*Honeywell*) para a saber qual era a temperatura da solução aquando do começo da libertação do dióxido de carbono. Para a solução aquosa de bis(2-etilhexil)amina, obteve-se uma temperatura de regeneração/ libertação de dióxido de carbono de 30 ºC e essa libertação durou cerca de 35 minutos. Pode-se concluir que, apesar de apresentar uma molécula anfifílica, a bis(2-etilhexil)amina conseguiu absorver e libertar o dióxido de carbono. O mesmo se verificou para a solução aquosa de tretilamina, apesar de apresentar duas fases líquidas. A libertação de dióxido de carbono iniciou-se à temperatura de 36 ºC e durou cerca de 44 minutos. Para a solução aquosa de DMEA, não se observou qualquer libertação de dióxido de carbono, o que leva a concluir que não chegou sequer a ocorrer absorção do mesmo, pois sendo DMEA uma amina terciária é fulcral que esta seja solúvel em água, pois caso contrário a absorção de dióxido de carbono não ocorre. Por último, para solução aquosa de dietilamina, apesar de ser a única que foi completamente solúvel em água, não se observou qualquer libertação de dióxido de carbono. Isto pode ter ocorrido devido ao facto de se ter formado sais estáveis ao aquecimento (HSS) o que torna impossível a libertação do dióxido de carbono absorvido.

Nos testes de absorção de dióxido de carbono efetuados na instalação-piloto, as seguintes soluções aquosas de aminas com uma concentração de 10 % em massa foram testadas: dietilamina, monoetanolamina (MEA), piperazina (PZ) e etanolamina (EDA). A solução aquosa de dietilamina foi também utilizada nestes testes pois, apesar de não ter sido capaz de libertar o dióxido de carbono absorveu, foi a única das aminas testadas nos ensaios preliminares que apresenta uma completa solubilidade em água. Realizaram-se na instalação-piloto, ensaios de absorção com um tempo de absorção de 240 minutos (4 horas). A cada 30 minutos, uma amostra de 20 mL proveniente da coluna de absorção, era retirada através de uma válvula instalada para esse efeito. As amostras foram posteriormente analisadas pelo método de precipitação. Este método permitiu a quantificação do dióxido de carbono absorvido através da adição em excesso de soluções de NaOH e $BaCl_2.2H_2O$ com a concentração de 1.0 molar. Essa quantificação foi apresentada através do número de moles de dióxido de carbono presentes em cada mol de amina. Os resultados obtidos para as soluções aquosas testadas foram: 0,492 mol CO_2/mol amina para a solução de dietilamina, 0,409 mol CO_2/mol amina para a solução de MEA, 0,395 mol CO_2/mol amina para a solução de PZ e 0,321 mol CO_2/mol amina para a solução de EDA.

De seguida, comparou-se os resultados obtidos neste trabalho com os resultados obtidos anteriormente para a mesma concentração de aminas em Santos (2012) [25], onde foram utilizadas soluções aquosas de N-metildietanolamina (MDEA) e dietanolamina (DEA). Concluiu-se que essas

soluções aquosas de aminas apresentavam valores de capacidade de carga em dióxido de carbono superiores aos registados para as soluções aquosas deste trabalho, sendo que a solução aquosa de MDEA obteve uma capacidade de carga de 1,020 mol CO_2/mol amina e a solução aquosa de DEA obteve uma capacidade de carga de 0,982 mol CO_2/mol amina.

Por fim, foi feita uma análise económica aos custos associados à compra de cada litro de amina em relação à capacidade de carga em dióxido de carbono. Após a comparação entre as capacidades de carga em dióxido de carbono e o seu preço por litro, concluiu-se que a amina que aparenta ser a mais económica de entre as seis consideradas foi a DEA, com uma elevada capacidade de carga em dióxido de carbono e o preço por litro mais baixo de todas elas (25,70 €/L).

Palavras-chave: Dióxido de carbono; Absorção química; Soluções aquosas de aminas; Regeneração de solvente; Isopropilamina; Di-isopropilamina; Dietilamina; Bis(2-etilhexil)amina; Trietilamina; DMEA; MEA; PZ; EDA; MDEA; DEA.

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List of Acronyms

CAPEX	Capital Expenditure
CCS	Carbon Capture and Storage
CFC	Chlorofluorocarbon
DEA	Diethanolamine
DMEA	Dimethylethanolamine
ECBM	Enhanced Coal Bed Methane
EDA	Ethanoldiamine
EOR	Enhanced Oil Recovery
GHG	Greenhouse Gases
HEED	N-(2-hydroxyethyl-)ethylenediamine
HSS	Heat Stable-salts
IEA	International Energy Agency
IPCC	Intergovernmental Panel on Climate Change
MDEA	N-methyldiethanolamine
MEA	Monoethanolamine
OPEX	Operational Expenditure
PSA	Pressure Swing Absorption
PZ	Piperazine
TSA	Temperature Swing Absorption
UN	United Nations
US	United States

1. Introduction

In the history of civilizations, the 20th century can be characterized as a century of explosive growth in energy consumption and a rapid increase in population worldwide along with unprecedented pace of inventions and new technologies and ever-increasing expansion of manmade materials. One of the greatest revolutions in the 20th century is related with transport systems. Inventions of cars, trucks and airplanes along with engine-powered trains and ships have created a completely new world that has become increasingly dependent on the combustions of hydrocarbonated fuels, such as gasoline, diesel fuel and kerosene (jet fuel). Inventions of electrical power plants, electric home appliances, personal computers and mobile cell phones have electrified the world, which is increasingly dependent on the electricity, which is largely generated from carbon-based resources such as coal and natural gas. Development of processes such as the high-pressure ammonia synthesis, as well as the development of the chemical fertilizers containing nitrogen, phosphorus and potassium, and also the engine-based machinery for crop production fueled the rapid growth of the global population, thus increasing the energy demand. [1]

Table 1 – World energy use, population and per capita in 1900 and 2001. [2]

Energy sources	1900 Use		2001 Use	
	MTOE[a]	% or Unit	MTOE[a]	% or Unit
Coal	501	55	2395	24
Petroleum	18	2	3913	39
Natural gas	9	1	2328	23
Nuclear	0	0	662	6
Renewables[b]	383	42	750	8
Total	911	100%	1004.8	100%
Population	1762	Million	6153	Million
Per Capita Energy use	0.517	TOE[a]	1.633	TOE
Global CO_2 emissions	534	MTCE[a]	6607	MTCE
Per capita CO_2 emission	0.30	TCE[a]	1.07	TCE
Atmospheric CO_2	295	ppmv[a]	371	ppmv
Life expectancy	47.3	Years	77.2	Years

[a] TOE: Ton oil equivalent; MTOE: million ton of oil equivalent; MTCE: million ton of carbon equivalent; TCE: ton of carbon equivalent; ppmv: part per million by volume. [b] including hydroelectric power, biomass, geothermal, solar and wind energy.

The above table shows a comparison between energy use, population and per capita consumption in 1900 and 2001. Currently over 85 percent of the world energy demand is supplied by fossil fuels. Fossil-fueled power plants are responsible for roughly 40 percent of total CO_2 emissions, with coal-fired power plants being the main contributor. Environmental issues due to emissions of pollutants from combustion of solid, liquid and gaseous fuels in various stationary and mobile energy systems as well as the emissions from manufacturing plants have also become major global problems involving not only pollutants such as SO_x, NO_x and particulate matter, but also greenhouse gases (GHG) such as carbon dioxide (CO_2) and methane (CH_4). There are increasing concerns related with global climate change and, thus, promoted interest, worldwide, in the reduction of GHG emissions, particularly of CO_2. [1][2]

Carbon dioxide is a colorless and odorless gas. The molecule is linear with a double bond between the carbon and oxygen atoms.

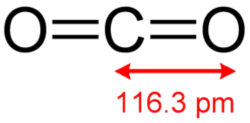

Figure 1 – Carbon dioxide molecule. [3]

CO_2 occurs freely in nature and acts as a source of carbon for photosynthesis of plants, algae and some bacteria. Combustion of most carbon-containing substances produces CO_2. Today energy utilization in modern societies is based largely on the combustion of fuels composed by hydrocarbons, which are mainly: coal, petroleum and natural gas. The complete oxidation, that is the combustion, of any carbon-based organic matter produces CO_2, but, until recently, carbon dioxide was, generally, thought to be harmless. In fact, carbon dioxide plays an important role in the Earth's carbon cycle and is a necessary component in the life cycle of animals and plants. [1]

Table 2 – Main sources of carbon dioxide emissions. [1]

Stationary sources	**Mobile sources**	**Natural sources**
Fossil fuel-based electric power plants	Cars and sport utility vehicles	Humans
Independent power producers	Trucks and buses	Animals
Manufacturing plants in industry [a]	Aircrafts	Plants and animals decay
Commercial and residential buildings	Trains and ships	Land emission/leakage
Flares of gas at natural gas and petroleum extraction fields	Construction vehicles	Volcano
Military and government facilities	Military vehicles & devices	Earthquake

[a] Major concentrated CO_2 sources include plants for manufacturing hydrogen, ammonia, cement, limestone and soda ash as well as fermentation processes and chemical oxidation processes

Analyzing the studies performed over the past five decades, particularly during the past 15 years, it is believed that increased GHG levels in atmosphere can cause global warming. [2]

Among GHG, CO_2 is the largest contributor, accounting to about 60 percent of the global warming effects, which is due to its high amount in the atmosphere[2], although methane and chlorofluorocarbons (CFC's) have much higher greenhouse effect per mass of gases. Nowadays there are increasing concerns regarding global warming caused by GHG, particularly CO_2: the International Panel on Climate Change (IPCC) predicts that, by the year 2100, the atmosphere may contain up to 570 ppmv of CO_2, causing an increase of the average global temperature of around 1.9 ºC and an increase in the average sea level of 38 m. [2]

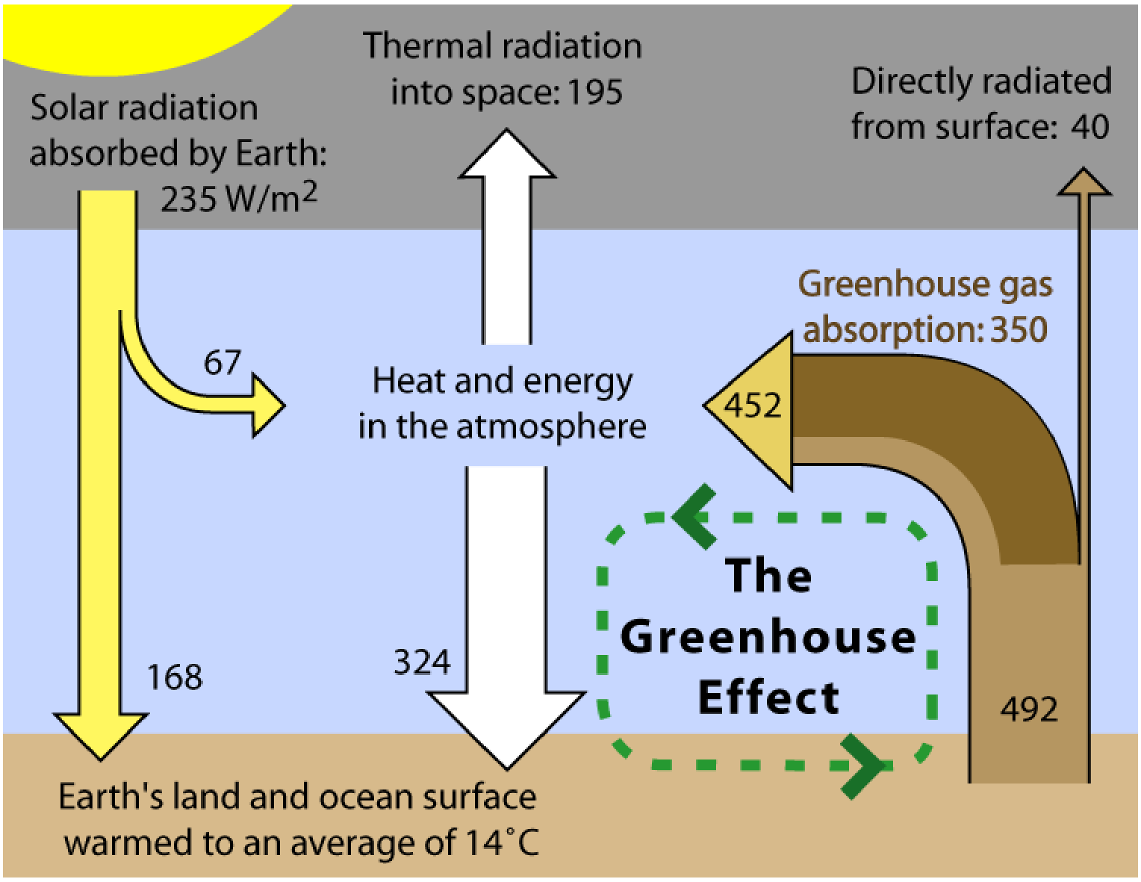

Figure 2 – Schematic representation of the flows of energy between outer space, the atmosphere and Earth's surface. [3]

These effects can also be accompanied by the extinction of some living species. The total amount of carbon on Earth is constant and its distribution among lithosphere, atmosphere and biosphere was relatively balanced until the beginning of the era of industrialized civilization. Since then, the carbon dioxide concentration has been continuously increasing. [2]

The following figure shows the change on the atmospheric carbon dioxide level over the years between 1000 and 1997 and also the actual CO_2 level during the period 1958-2004. CO_2 level increased from 280 ppmv in 1000 to 295 ppmv in 1900. These values were based on data collected from ice cores in Antarctica. It increased to 315 ppmv in 1958 and further to 377 ppmv in 2004, and these values are based on data measured in Mauna Loa, Hawaii. [2]

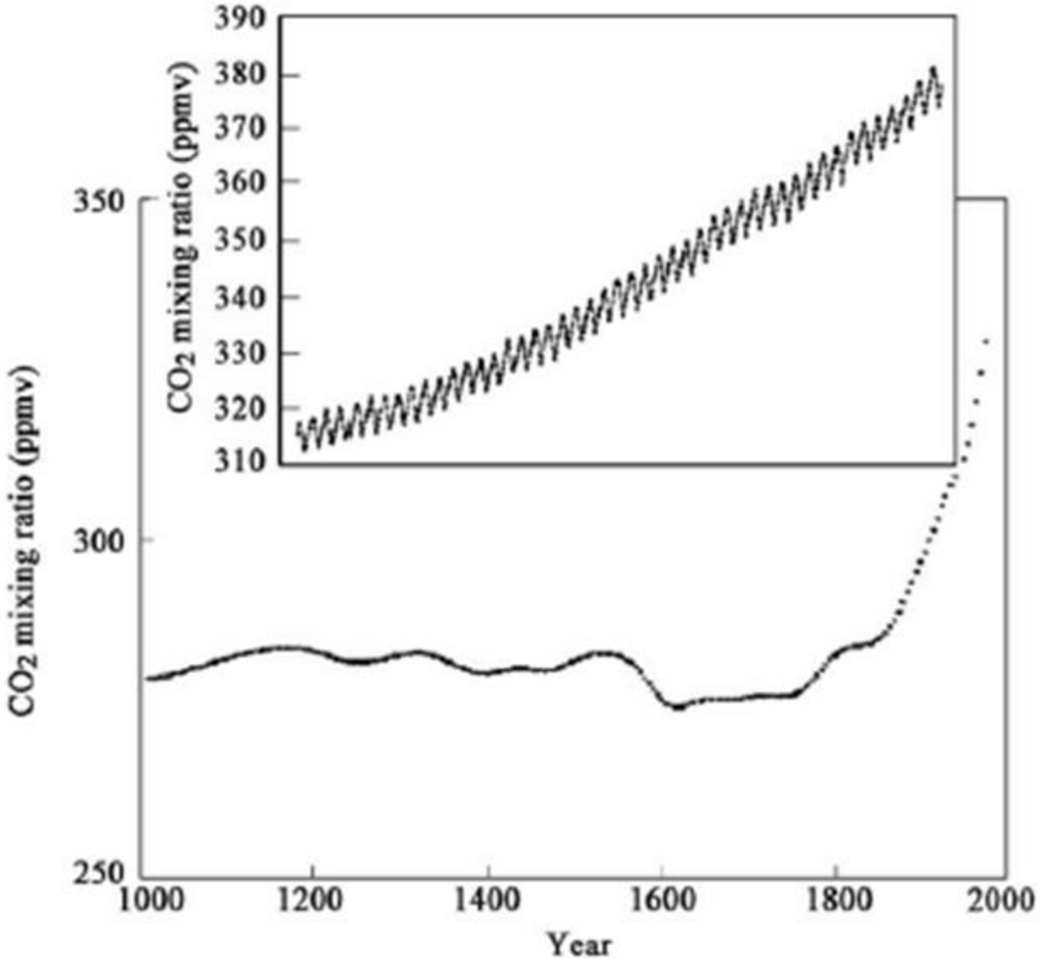

Figure 3 – Atmospheric CO_2 concentrations during 1000-1997 based on the analysis of ice cores and measured atmospheric CO_2 concentrations during 1958-2004. [2]

In order to diminish global warming, the recognition of the carbon dioxide as the main responsible for the global warming problem has prompted the United Nations (UN) to call for several international forums on climatic changes, with the aim to regulate carbon dioxide emissions in all developed and under development countries. The Kyoto Protocol, which resulted from one of the most important international forums held in Kyoto, Japan in 1997, involved 37 industrialized nations and the European Union, which agreed to reduce their greenhouse gas emissions to a level of 5.2 percent, on average, lower than those of 1990 for the period of 2008-2012. The Copenhagen Agreement also requests the global temperature increase to be limited to ± 2 ºC above the pre-industrial level by 2100. [4] [5]

1.1. Carbon Capture and Storage (CCS) technology

The International Energy Agency (IEA) pointed out that in order to achieve the goal of ± 2 ºC above the pre-industrial level, it is required to of CO_2 Capture and Storage technology and its contribution, to reduce global emissions, would be around 19 percent in 2050.[5] In a global context, among all the industries emitting CO_2, fossil-fueled power plants generate the largest amount of CO_2 emissions and that accounts for about 33-40 percent of the total. Besides power plants, the Steam Reforming facilities from petroleum refineries are also responsible for a considerable share of the total carbon dioxide emissions, although in a smaller scale. CCS would permit the continuing use of coal and other fossil fuels for power generation while significantly reducing GHG emissions. [5] [6]

The current leading carbon capture technologies, developed for power plants, can be divided in three methods which are characterized according to how or where the carbon dioxide is removed. These methods are called post-combustion capture, Oxyfuel combustion capture and pre-combustion capture. [7]

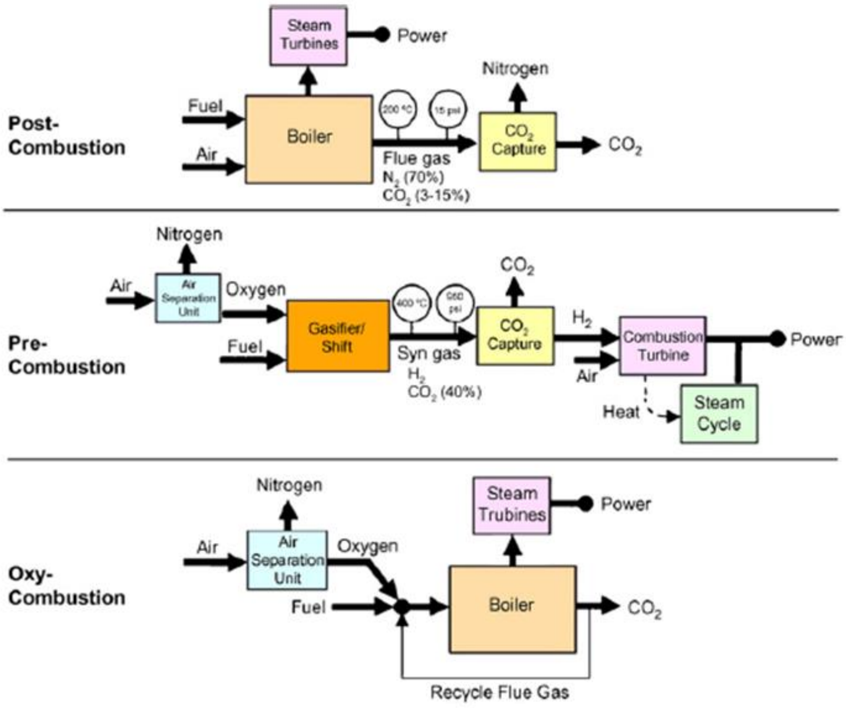

Figure 4 – Block diagram showing post-combustion, pre-combustion and oxy-combustion. [8]

Post-combustion capture means that the carbon dioxide is captured from the flue gas of a conventional power plant. This method has an additional advantage of being used to capture carbon dioxide in industrial application for decades, although on a smaller scale than required for actual power plants. This makes post-combustion capture methods a prime candidate for many CCS applications. The other important advantage is it can be installed as a retrofit to existing power plants which significantly reduces the investment costs. [7]

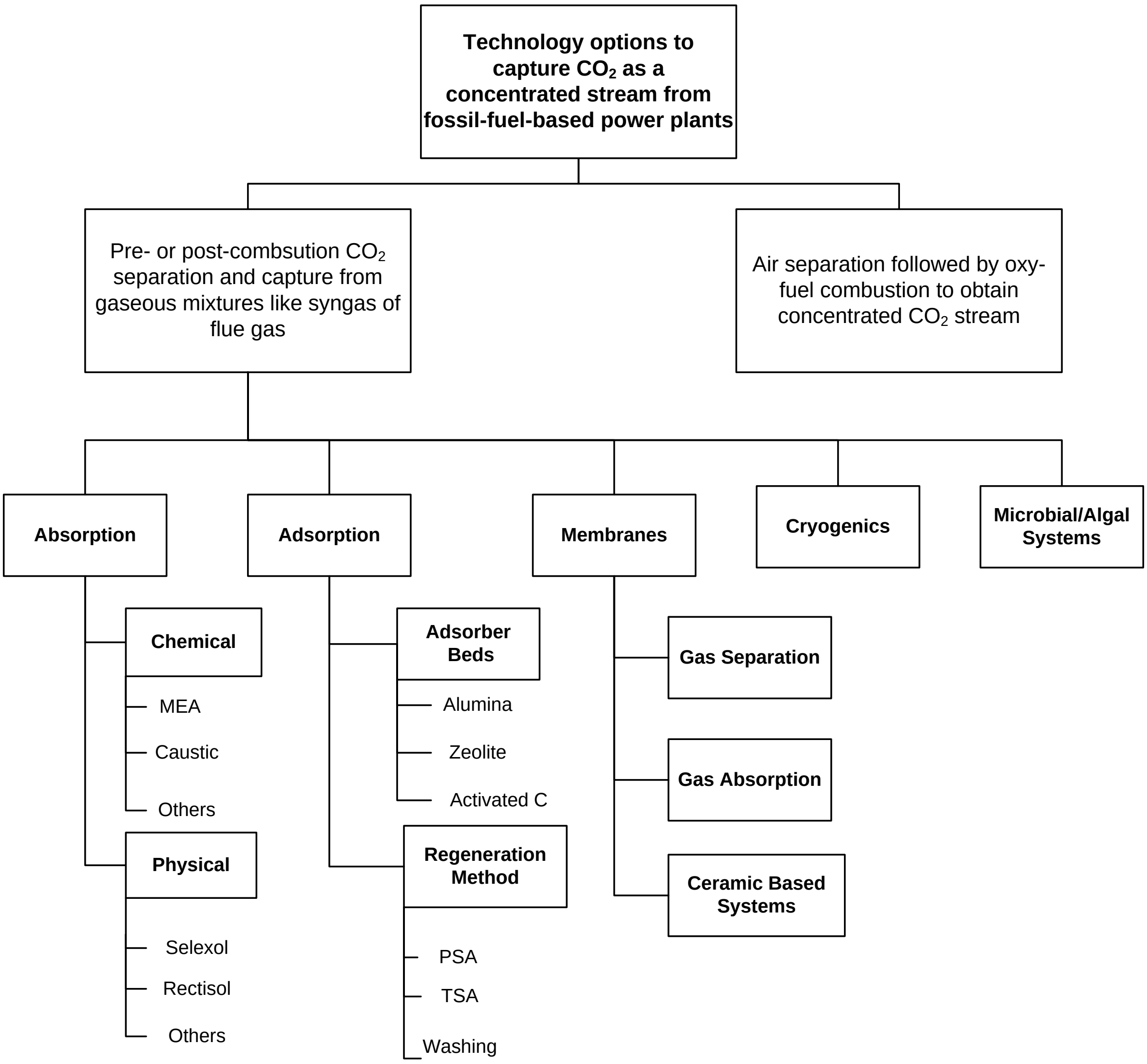

Figure 5 – Carbon Capture and Storage technological options. [9] [10]

The separation of CO_2 into a pure stream (>95 percent) can be achieved by a variety of techniques. Basically, there are six methods suitable for gaseous component capturing, which are, absorption, adsoprtion, permeation through a membrane, chemical conversion to another compound, condensation and cryogenics. From these unit operations, absorption is nowadays the most important one. During the absorption process, the gas to be treated is put in contact with a liquid stream and the gaseous components are transferred into the liquid phase (solvent) in which they are soluble. [9] [11] [12]

Table 3 – Comparison of available technology options for carbon dioxide capture and separation. [9]

Technology Option	System Requirements	Advantages	Problems/ Drawbacks
Absorption (Chemical)	Absorber and stripper sections. Chemical sorbent (e.g. MEA, DEA, MDEA)	Suitable even for dilute CO_2 streams (typical flue gas from power plants). Operates at ordinary temperature and pressure. Commercially available, proven technology	The heat of sorbent regeneration is very high. Significant sorbent losses; pre-processing (e.g. S removal) may be required.
Absorption (Physical)	Absorber and stripper sections Physical sorbent (e.g. Selexol, Purisol and Fluor Processes)	Suitable only for gas streams with high CO_2 partial pressure (typical syngas from gasification systems). Less energy required, assuming that the gas stream to be processed is already at high pressure. Sorbent are less susceptible to the impurities in the gas stream	Requires high operating pressure. Works preferently with gas streams having high CO_2 content; so it is not suitable for flue gas processing
Adsorption	Adsorber bed(s)	Commercially available gas separation process.	Low capacity and CO_2 selectivity of available adsorbents
Membranes	Membrane filter(s)	Upcoming, promising technology with diverse applications. Space efficient.	Requires high operating pressures. Low product purity; need for multiple stages/recycle
Cryogenics	Refrigeration and distillation units	Direct production of liquid CO_2.	Requires very large amount of energy for refrigeration (not suitable for dilute streams).

There are two types of absorption methods: physical and chemical absorption. Depending on the mechanism binding the gas compounds in solvent, one can distinguish between physical and chemical absorption. [11]

Once the CO_2 is captured, it needs to be securely stored (sequestered). Again, there are a wide range of options potentially available for CO_2 capture, as shown in Figure 6. [8] [9]

Geologic formations including deep saline reservoirs, depleted oil and gas wells, and non-mineable coal seams are some of the potentially attractive disposal sites. Among these options, there is the Enhanced Oil Recovery (EOR) and the Enhanced Coal Bed Methane (ECBM). EOR consists in the injection of carbon dioxide into the oil well, reducing oil surface tension and at the same time increasing its density, thus increasing the efficiency of oil extraction in the well. ECBM consists in the injection of carbon dioxide into the coal deposits. The coal will adsorb preferentially carbon dioxide, thereby releasing the existing methane from coal deposits. [8] [13] [14]

These options can bring revenue as well, as they lead to the production of valuable products like oil and methane, respectively. Ocean storage is another option currently being studied. [8]

The distance to a secure storage site, the availability and cost of the transportation infrastructure, and the regulatory framework will affect the choice of disposal option. In general, studies indicate that geologic formations are the most plentiful and attractive for U.S. power plants. While economic cost of CO_2 storage appears to be reasonable, its social and political acceptability are not yet clear, especially when compared to ocean sequestration. In fact, there are still a number of issues related to geologic sequestration of CO_2, including potential sites, storage capacities, environmental impacts, monitoring requirements and leakage. [9]

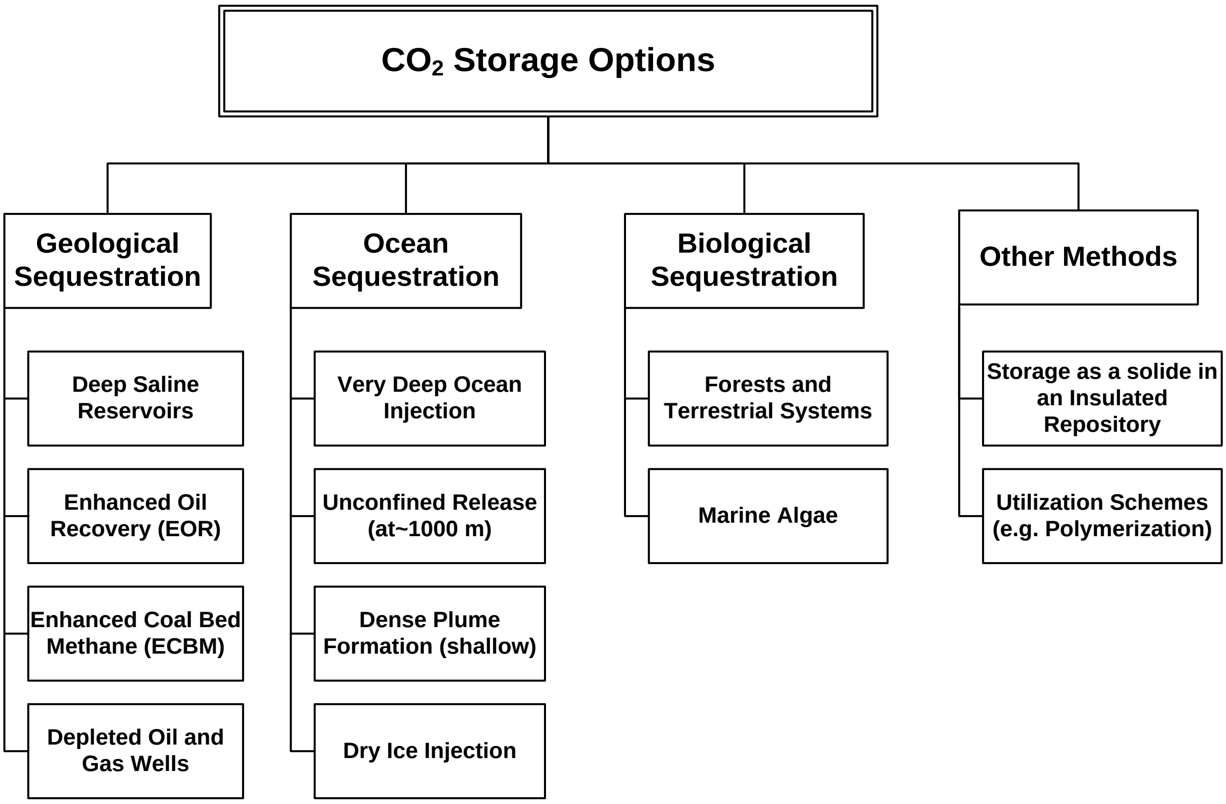

Figure 6 – Options for carbon dioxide sequestration. [9]

Another alternative is the recycling of the captured CO_2, since carbon dioxide has long been identified as renewable carbon feedstock (being nontoxic, highly abundant and economical) to access fine and commodity chemicals. However, there are only a handful of large scale industrial processes which actually use CO_2 as a raw material. A number of these rely on the physicochemical properties of carbon dioxide, such as the use of supercritical CO_2 as solvent (in particular extraction processes such as decaffeination or recovery of essential oils). [15]

The potential advantages of using CO_2 as a chemical feedstock are as follows:

1. It is relatively cheap, highly abundant and could be used to replace toxic chemicals, such as phosgene, or depleting resources, such as petrochemicals.
2. Can be transformed into totally new materials, such as new polymers, which are still difficult to produce from conventional petrochemicals.

3. Can be transformed using efficient and economical routes (i.e. catalytic processes).
4. Although the impact on global CO_2 concentrations resulting from its transformation into products (e.g. chemicals, polymers, fuels) may be modest, the products are expected to significantly improve the economics of carbon capture and storage. [15]

Table 4 lists the existing and emerging applications of CO_2 in liquid, solid and gaseous forms. Currently, CO_2 is used as a refrigerant for food preservation, a beverage carbonation agent, a supercritical agent, an inert medium (such as fire extinguisher), a pressurizing agent, a chemical reactant (urea, etc.), a neutralizing agent and as gas suitable for use in greenhouses. [15]

Table 4 – Current status of CO_2 uses in various industrial applications. [1]

Sectors	Industrial applications
Chemicals	CO_2 is used in chemical synthesis and for controlling reactor temperatures. CO_2 is employed to neutralize alkaline effluents. CO_2 is used as a blowing agent for polyurethane and polystyrene foam production and for blow molding manufacturing of plastic bottles and containers. CO_2 is used under supercritical conditions for purifying or dying polymer, animals or vegetable fibers.
Pharmaceuticals	CO_2 is used for producing chemicals such as salicylic acid and Aspirin; for use as an inert gas and for supercritical fluid extraction. CO_2 is used for product transportation at low temperature (-78 ºC) and also acidification (pH) of wastewater.
Foodstuffs	Liquid CO_2 can be used as cryogenic fluid in chilling or freezing operations or as dry ice for temperature control during the storage and distribution of foodstuffs. Packaging of foodstuffs to increase the shelf life of many food products due to its inertizing properties and growth inhibiting effect on micro-organisms. Stunning of pigs and poultry in slaughterhouses instead of using electrical stunning.
Beverage	Carbonation of beverages such as soft drinks, mineral water or beer; Supercritical CO_2 is used to remove caffeine from coffee beans by extraction. CO_2 is used as shielding gas for preserving drinking quality and propellant gas for emptying tanks of beverages CO_2 is also used in drinking water treatment in modern waterworks together with lime or chalk.

Continuation of Table 4 – Current status of CO_2 uses in various industrial applications [1]

Healthcare	CO_2 produces close-to-physiologic atmospheres for the operation of artificial organs. CO_2 is used as a component in a mixture of oxygen or air as respiratory stimulant to promote deep breathing. It is also used for the surgical dilation by intra-abdominal insufflations.
Environment	Small amount of liquid CO_2 can be used in recycling mechanical of waters from Acid Mine Drainage. Waste water treatment and waste liquid treatment by injection of CO_2 for the pH of liquid effluents. CO_2 is an excellent alternative to sulfuric acid for pH balance control.
Pulp and paper	CO_2 enables sharp tuning of the pH of recycled mechanical or chemical after an alkaline bleaching. CO_2 can be used in the Tall Oil neutralization and for increasing the performance of paper machines. Precipitated calcium carbonate obtained from CO_2 e CaO is used as a whitener for the paper industry.
Electronics	CO_2 is usually used as a cooling medium in environmental testing of electronic devices. CO_2 can be used to add conductivity to ultrapure water. CO_2 can also be used as an environmentally friendly supercritical fluid for removing photo-resist from wafers.
Metals industry	CO_2 is typically used as an inert gas or for environment protection. CO_2 is used for red fume suppression during scrap and carbon charging, for nitrogen pick-up reduction during tapping and for bottom stirring. CO_2 is used for fume suppression during ladle transfer of matte (Cu/Ni production) or bullion (Zn/Pb production) in the non-ferrous metallurgy. Special grades of CO_2 are used in CO_2 lasers.
Laboratory &analysis	Supercritical CO_2 is the mobile phase in both supercritical chromatography and extraction applications.
Safety and others	CO_2 is used as carbon dioxide snow for fire extinguishers; pH control and regulation of waste waters, swimming pools, etc.

A particular example of an industrial application of the captured CO_2 is the Messer plant in a bottling facility of Coca-Cola in the city of Jundiaí, Brazil. CO_2 is extracted from the waste gases from the factory power plant, in a chemical absorption facility using amine solutions. The CO_2 is further purified and liquefied to food grade quality and used to carbonize the soft drinks. [16]

Figure 7 –Purified and liquefied CO_2 storage tanks in the Coca-Cola factory in Jundiaí, Brazil. [16]

1.2. Chemical absorption

The concept of separating CO_2 from flue gas streams started in the 70s, not due to the concern about the greenhouse effect, but as a potentially economic source of CO_2, mainly for enhanced oil recovery (EOR) operations. Several commercial CO_2 capture were constructed in the U.S. in the late 70s and early 80s. CO_2 was also produced for other industrial applications such as carbonation of brine and production of products such as dry ice, urea and beverages. Some of these CO_2 capture plants are still in operation today, but all these plants are much smaller than a typical power plant. Chemical absorption is a well-known technology and it has been widely deployed on a large scale across several industries. [10] [15]

1.2.1. Amine chemistry

It is the solvent chemistry that determines the type and seriousness of any environmental and public health impacts associated with fugitive emissions of organic solvents, or of the products resulting from solvent degradation or solvent-induced equipment corrosion. Therefore, the selection of appropriate solvents for use in these processes is far from being a simple task. [15]

In terms of solvent selection, amines have traditionally been the solvents of choice, with a primary alkanolamine, monoethanolamine (MEA) typically considered as the benchmark solvent to which alternative solvents must be compared. Other compounds that are often considered are sterically hindered compounds such as piperazine (PZ); secondary amines such as diethanolamine (DEA) and tertiary amines such as methyldiethanolamine (MDEA). [15]

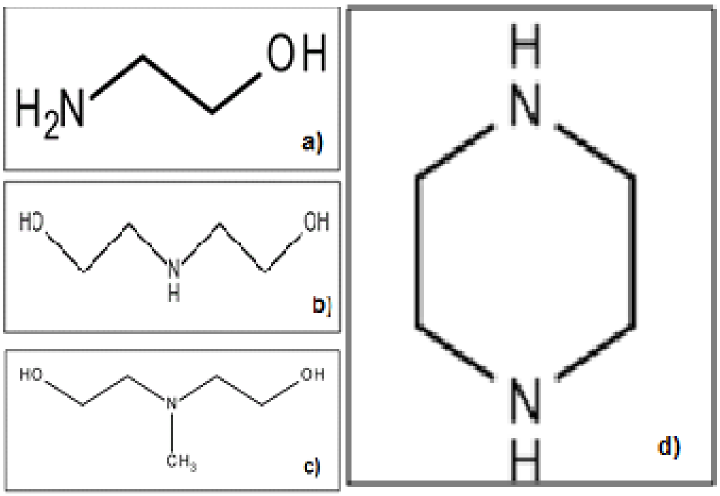

Figure 8 – Amines molecular structures: a) primary (MEA) b) secondary (DEA) c) tertiary (MDEA) d) sterically hindered (PZ). [17]

One of the major disadvantages of using MEA is related with its high energy requirements for CO_2 capture when compared to DEA and MDEA. The major setback is that MEA has a limitation that its maximum CO_2 loading capacity, based on stoichiometry, is about 0.5 mol CO_2/mol amine, unlike tertiary amine such as MDEA, which has an equilibrium CO_2 loading capacity nearly of 1.0 mol CO_2/mol amine. [18]

The reactive nature of the aqueous amine solutions with CO_2 is well known, and there is considerable experimental and theoretical work done detailing the mechanism and rates of these reactions. In addition to the ionic formation equilibrium owing to the dissociation of CO_2 and the amines in aqueous solution, the principal reaction of interest between CO_2 and a primary or secondary amine (in water) is the formation of a carbamate, which is typically considered to occur *via* the formation of a “zwitterion”. Combining these two reactions can be represented as: [15]

$$RR'NH + CO_2 \leftrightharpoons RR'NH^+COO^-(Zwitterion) \tag{1}$$

The “zwitterions” mechanism originally proposed by Caplow in 1958 and reintroduced by Danckwerts in 1979, is generally accepted as the reaction mechanism for the carbamate formation between CO_2 with primary and secondary amines. [19]

The subsequent removal of the proton by base B, which can be an amine, is as follows:

$$RR'NH^+COO^- + \ RR'NH \leftrightharpoons RR'NCOO^-(Carbamate) + \ RR'NH_2^+ \tag{2}$$

Then, the overall reaction is: [5]

$$2RR'NH + CO_2 \leftrightharpoons \ RR'NCOO^- + \ RR'NH_2^+ \tag{3}$$

$$RR'NCOO^- + \ H_2O \ \leftrightharpoons RR'NH + HCO_3^- \tag{4}$$

Other important reactions, which contribute to the overall reaction, are the reversion of carbamate to bicarbonate *via* a hydrolysis reaction and the formation of bicarbonate. [15]

$$R_1R_2NCO_2^- + H_2O \rightleftharpoons R_1R_2NH + HCO_3^- \tag{5}$$

$$CO_2 + OH^- \rightleftharpoons \ HCO_3^- \tag{6}$$

In the case of non-sterically hindered compound, the reversion of carbamate to bicarbonate by chemical reaction is considered to occur only at high CO_2 concentrations in the liquid phase. In the case of a sterically hindered compound such PZ, the reaction is particularly important, as the presence of the methyl group significantly reduces the stability of the carbamate bond, resulting in the preferred formation of the bicarbonate, leading to the particularly high loading capacity of this solvent. [15]

The mechanism involved in the absorption of CO_2 by aqueous solutions of tertiary amines, such as MDEA, are somewhat different to those of primary and secondary amines as they do not react directly with CO_2. In fact, they act as a base, catalyzing the hydration of CO_2. Thus the reaction of interest in aqueous solutions of tertiary amines is: [15]

$$CO_2 + H_2O + R_1R_2R_3N \rightleftharpoons R_1R_2R_3NH^+ + HCO_3^- \qquad (7)$$

1.2.2. Process description

Technologically, a typical chemical absorption process consists of an absorber and a stripper, in which the absorbent is thermally regenerated. In a chemical absorption process, the flue gas containing CO_2 enters a packed bed absorber from the bottom and contacts counter-currently with a CO_2-lean absorbent. After absorption, the CO_2-rich absorbent flow into a stripper for thermal regeneration. After regeneration, the CO_2-lean absorbent is pumped back to the absorber cyclic use. The pure CO_2 released from the stripper is compressed for the subsequent transportation and storage. The operation pressure is around 1 bar and the temperatures in the absorber and stripper are usually in the ranges of 40-60ºC and 120-140ºC, respectively. [5]

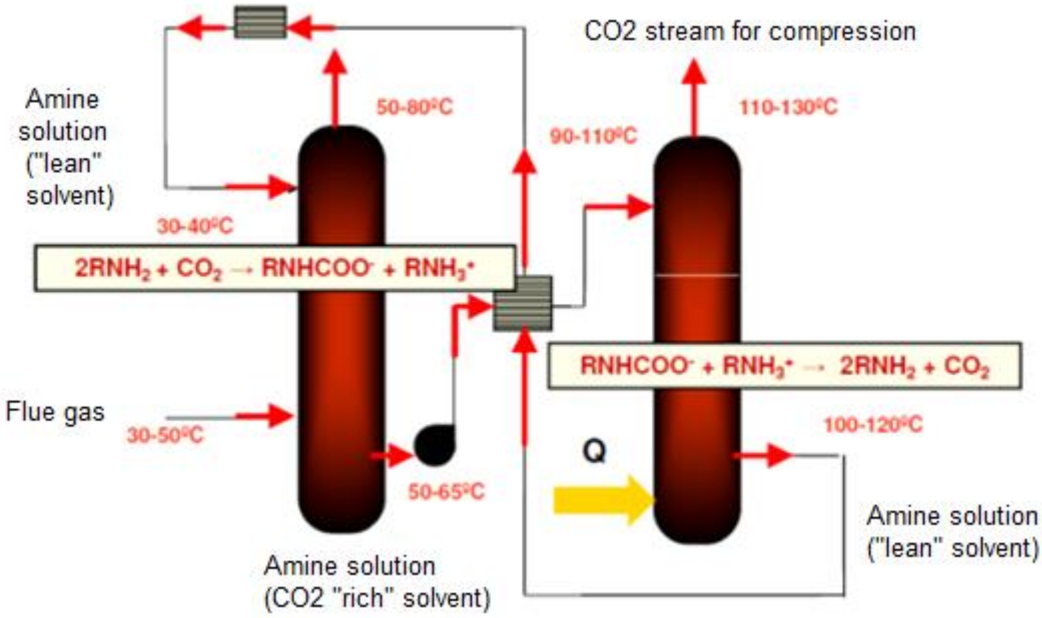

Figure 9 – Process diagram for CO_2 absorption, using amines, with the respective temperatures and reactions. [20]

The term "lean" refers to the fact that the solvent stream entering at the top of the column contains little or none of the components that are meant to be absorbed. In the context of CO_2 capture, this means that the mole fraction of CO_2 in the liquid phase is small. Once the solvent stream reaches the bottom of the absorption column, it is now considered "rich", and it is send to a solvent regeneration process, consisting of a further gas-liquid contacting column with a reboiler at the bottom and a condenser at the top. [15]

For the de-absorption process, a "rich" stream of amine and CO_2 from the absorption column is pumped to the top of the stripping column, where it flows down over the packing within the stripping column. Stripping steam from the reboiler enters the column at the bottom and flows up the column in a counter-current flow arrangement. As the "rich" liquid flows down the column, the chemical reactions act as the reverse reaction and release CO_2 into the aqueous solution, which then diffuses into the gas phase. The "lean" amine solution exits at the bottom of the stripping column and is returned to the absorption process. [12]

A percentage of the "lean" amine solution is directed to the reboiler to provide the stripping steam for the process. The condenser cools the outgoing gas and thus reduces the water content and up-concentrates the amount of CO_2. Typically, the captured CO_2 requires more post processing treatment such as dehydration and compression. [15]

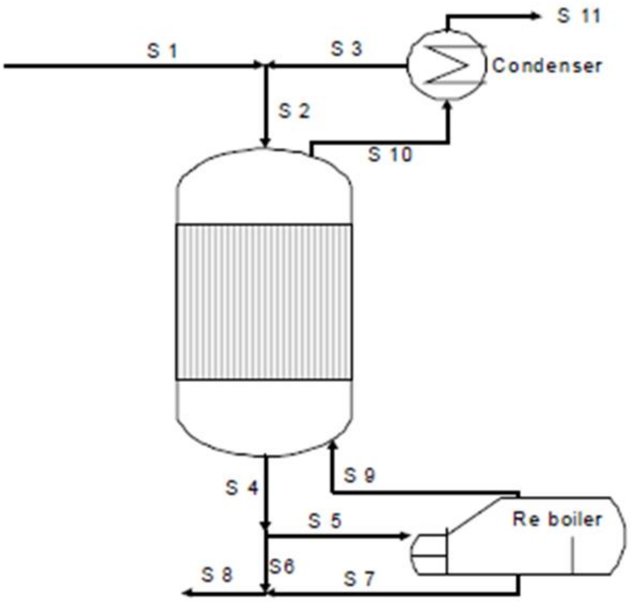

Figure 10 – Process flow diagram of stripping column. [12]

In these systems, the major part of the operational costs is caused by the solvent regeneration (up to 40 percent). The regeneration process is usually done at an excess temperature its boiling temperature, as the chemical kinetics of regeneration increases with temperature. The energy consumption, in the stripping column, is estimated to be 15-30 percent of the net power production of a coal-fired power plant, considering about 90 percent of CO_2 being removed. [21]

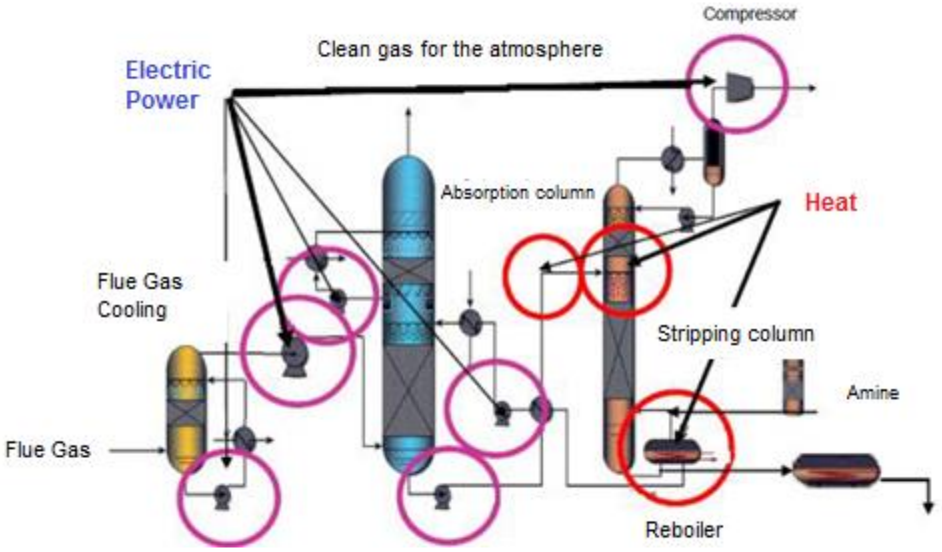

Figure 11 – Energy dissipaters in a conventional process for CO_2 capture. [22]

The development of improved solvents with lower regeneration energy requirements can, therefore be identified as the highest priority in R&D objective for amine-based CO_2 capture systems. Such improvements are needed to reduce the too high-energy consumption of current systems, which makes them less competitive. [21]

Mixed amines have been reported to maximize the desirable properties of the individual amines. The use of mixed amines consist in having a solution formed of tertiary and primary or tertiary plus secondary amines, that uses much of the reactivity of primary amines or secondary amines at similar or reduced circulation rates, but offers low regeneration costs similar to those of tertiary amines. There are reports of substantial reduction in energy requirements and modest reduction in circulation rates for amine blends relative to the corresponding single amine systems of similar total amine concentration. [2]

This technology option has the inherent advantage that it is an “end-of-pipe” technology. Moreover, its addition to power plants, either as a retrofit or as a new build, will not unduly affect the flexibility of operation demanded for these facilities. [15]

However, as with all of the proposed capture technologies show in Table 3, chemisorption processes have the distinct disadvantage of their cost, both investment costs (CAPEX) and also operation costs (OPEX) associated with its implementation and operation. In the case of chemical absorption process, it is anticipated that the deployment of this technology will result in a reduction of the thermal efficiency of a modern power plant from approximately 45 percent to approximately 35 percent. This efficiency penalty accounts for the cost of solvent regeneration, CO_2 compression and transport as well as the additional costs associated with transporting flue gases and solvents. Moreover, owing to the low CO_2 partial pressure in the flue gas, relatively high solvent flow rates are required to achieve a high rate of CO_2 capture. [15]

One drawback of this process is the susceptibility of amines to thermal and oxidative degradation. This amine breakdown deteriorates the performance of the amine in the absorption process. Not only does it reduce the CO_2 removal capacity, but also, corrosion and foaming are induced due to the presence of degradation products. This obviously leads to significant costs associated with the solvent make-up. [15] [18]

Oxidative degradation has been extensively investigated in literature, particularly for alkanolamines. Here, the main degradation products are volatile compounds, amines, aldehydes and carboxylic acids, such as formic acid, acetic acid and oxalic acid. [15] [18]

Most, if not all, amines are irreversibly degraded by CO_2, O_2 e SO_X. The problem is that the gases mentioned before are also likely to be present in the flue gases to be treated. The concentration of these compounds and the temperature of operation are considered to be important variables conditioning the degree of degradation. It is known that secondary amines are more stable than primary amines, but the reaction paths are not yet well understood and there may be some subtle effects of the amines structures on the stability of the degradation products. [15]

For example, in a MEA system, as shown in Figure 12, the reaction with CO_2 generally results in the reversible formation of a carbamate, but a small fraction may react further to form degradation products, such as 2-oxazolidone, which reacts again with MEA to form N-(2-hydroxyethyl-)ethylenediamine (HEED) *via* intermediates of N,N'-di(hydroxyethyl) urea e 1-(2-hydroxyethyl)-2-imidazolidone. [15]

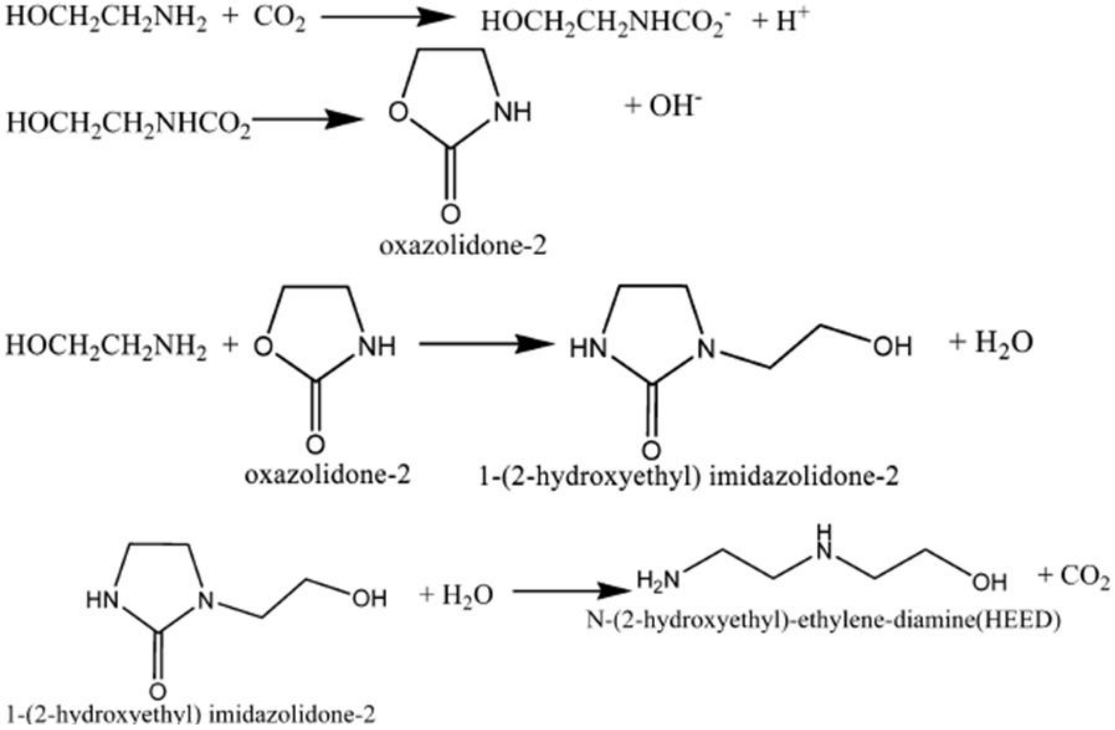

Figure 12 – Mechanism of oxidative degradation of MEA. [23]

Thermal degradation has also been studied in some detail, for, at least some amines. It was found that the main thermal degradation products in the presence of O_2 were amines, amino-acid derivatives and carboxylic acids. [15]

With industrial flue gases, the process becomes much more complicated owing to the presence of a mixture of CO_2, O_2, CO, SO_x, NO_x and fly ash. Fly ash refers to the fine particulates in the flue gas consisting of inorganic oxides such as SiO_2, Fe_2O_3, CaO, MgO, Na_2O, K_2O and P_2O_5. [15] [18]

Finally, given the relatively low degradation temperatures of most amines, the solvent regeneration processes takes places at approximately 120 ºC and 0.2 MPa, meaning that the CO_2 stream is produced at a low pressure, relative to the one required for transport and storage, leading to considerable costs associated with the compression of the CO_2. [15]

Apart from questions about the degradation chemistry, there are other important questions that have not been answered yet, involving the atmospheric fate of emissions of amines and its degradation products: how close from the emission source are these products being deposited, the effects of the atmospheric chemistry on these compounds or how can an emission legislation be defined for these compounds. [15]

What is actually known is that most of the molecules considered to be used in CO_2 capture applications are strongly polar, and therefore highly soluble in water. Thus, it is possible to foresee a scenario where fugitive amine emissions mix with rain water and quickly become part of the water cycle and biosphere. Thus, of the thermophysical properties often considered in solvent selection for CO_2 capture, the volatility of the amines is very important, and should be given significant importance in any solvent design work in this area. [15]

2. Experimental

The experimental studies done during this work had the main goals of assessing performance of amine absorption in preliminary laboratory trials for subsequent studies of CO_2 absorption which took place in a pilot unit.

2.1. Preliminary trials

At this stage, studies regarding the regeneration efficiency of the amine solution were performed. In order to observe the amine regeneration, it was required that the amine was saturated with CO_2. Therefore, CO_2 absorption was tried and assessed.

2.1.1. Experimental procedure

As mentioned before, in order to study the amine regeneration, it is necessary to saturate the amine solution with CO_2. Therefore, the first step was to search for the structural and thermophysical properties of the amines being studied.

2.1.1.1. Studied amines

The main properties and respective structure of the studied amines is indicated in the Tables 5 to 10, and Figures 12 to 17.

Table 5 – Structural properties of isopropylamine. [17]

Isopropylamine	
CAS Number	75-31-0
Molecular Formula	C_3H_9N
Molar Weight (g/mol)	59.11
Density (g/cm^3)	0.69 (20 ºC)
Boiling Point (ºC)	31-33 ºC (1013 hPa)
Melting Point (ºC)	-101 ºC
Flash Point (ºC)	-37 ºC
Supplier	Merck
Emission Limit Value (ppm) [24]	5

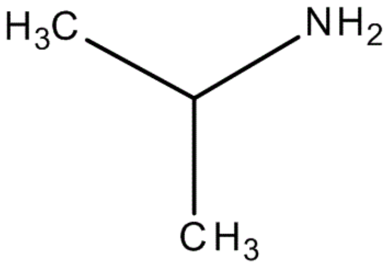

Figure 13 – Molecular structure of isopropylamine. [17]

Table 6 – Structural properties of diisopropylamine. [17]

Diisopropylamine	
CAS Number	108-18-9
Molecular Formula	$C_6H_{15}N$
Molar Weight (g/mol)	101.19
Density (g/cm^3)	0.72 (20 ºC)
Boiling Point (ºC)	83-84 ºC (1013 hPa)
Melting Point (ºC)	-96 ºC
Flash Point (ºC)	N/A
Supplier	Merck
Emission Limit Value (ppm) [24]	5

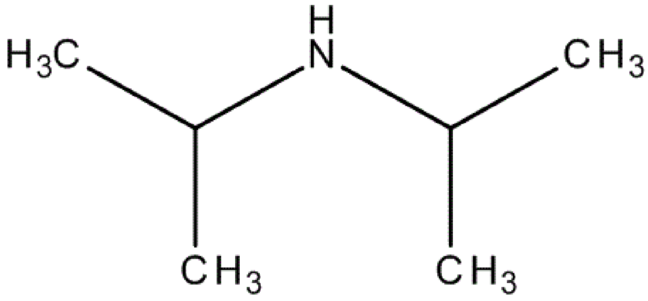

Figure 14 – Molecular structure of diisopropylamine. [17]

Table 7 – Structural properties of diethylamine. [17]

Diethylamine	
CAS number	109-89-7
Molecular formula	$C_4H_{11}N$
Molar weight (g/mol)	73.14
Density (g/cm^3)	0.71 (20 ºC)
Boiling point (ºC)	56 ºC (1013 hPa)
Melting point (ºC)	-50 ºC
Flash point (ºC)	-23 ºC
Supplier	Merck
Emission Limit Value (ppm) [24]	5

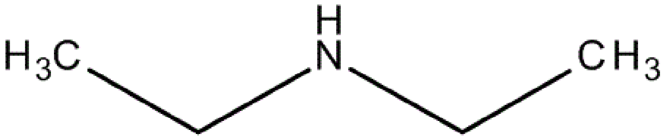

Figure 15 – Molecular structure of diethylamine. [17]

Table 8 – Structural properties of bis(2-ethylhexyl)amine. [17]

Bis(2-ethylhexhyl)amine	
CAS number	106-20-7
Molecular formula	$C_{16}H_{35}N$
Molar weight (g/mol)	241.45
Density (g/cm^3)	0.80 (20 ºC)
Boiling point (ºC)	122-124 ºC (7 hPa)
Melting point (ºC)	N/A
Flash point (ºC)	121 ºC
Supplier	Merck
Emission Limit Value (ppm) [24]	N/A

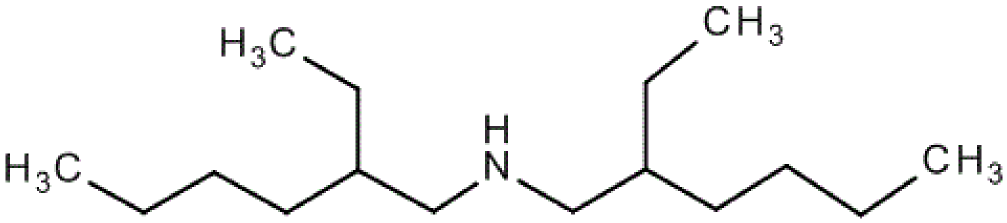

Figure 16 – Molecular structure of bis(2-ethylhexyl)amine. [17]

Table 9 – Structural properties of dimethylethanolamine. [17]

Dimethylethanolamine (DMEA)	
CAS number	108-01-0
Molecular formula	$C_6H_{15}N$
Molar Weight (g/mol)	89.14
Density (g/cm^3)	0.89 (20 ºC)
Boiling point (ºC)	132-135 ºC (1013 hPa)
Melting point (ºC)	-59
Flash point (ºC)	39
Supplier	CPB
Emission Limit Value (ppm) [24]	N/A

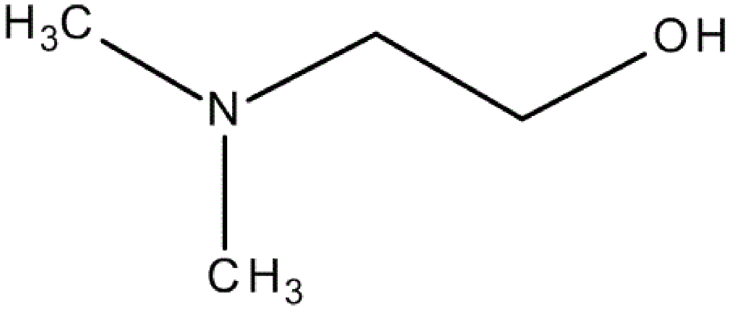

Figure 17 – Molecular structure of dimethylethanolamine. [17]

Table 10 – Structural properties of triethylamine. [17]

Triethylamine	
CAS number	121-44-8
Molecular formula	$C_6H_{15}N$
Molar weight (g/mol)	101.19
Density (g/cm^3)	0.73 (20 ºC)
Boiling point (ºC)	90 ºC (1013 hPa)
Melting point (ºC)	-115
Flash point (ºC)	-11
Supplier	Sigma-Aldrich
Emission Limit Value (ppm) [24]	3

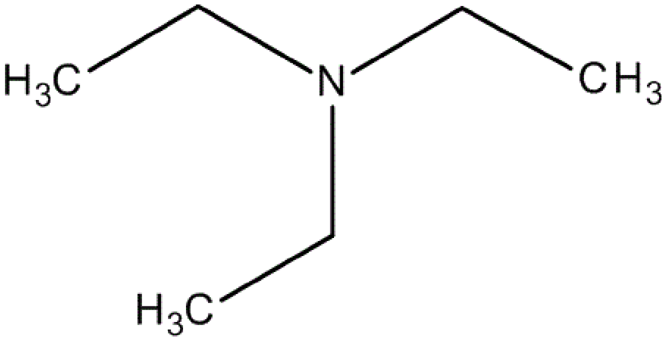

Figure 18 – Molecular structure of triethylamine. [17]

2.1.2. CO_2 absorption using amine solutions

Regarding the CO_2 absorption stage, the procedures indicated in Santos (2012) [25] were followed and adapted for this study. In order to perform the tests, a 500 mL three–necked flask was used, as shown in Figure 19.

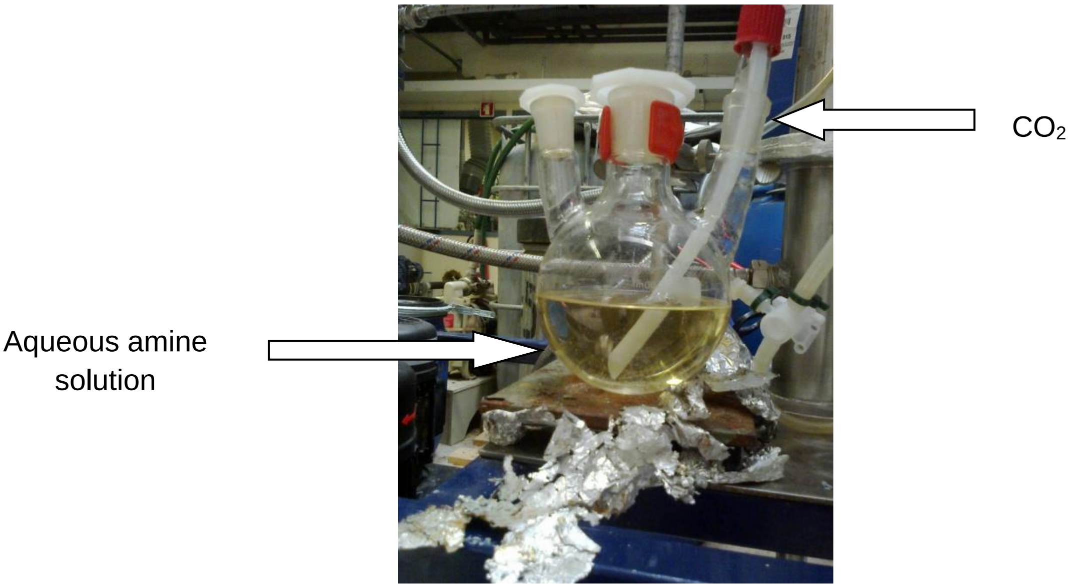

Figure 19 - Illustration of experimental tests carried out to study the absorption of CO_2 from aqueous amines solutions (diethylamine aqueous solution).

A volume of the 250 mL of the aqueous amine solution, in a concentration of 20% w/w, was placed inside the three-necked flask. Then, CO_2 was carefully inserted into the flask, using a Teflon tube which was immersed into the amine solution, to ensure the saturation of the solution. The solution saturation was observed visually through the occurrence of CO_2 bubbles in the amine solution. When the bubbles remained, from the bottom of the flask to the solution surface, it meant that the solution was already fully saturated. For the rest of the studied amines, the same method was used.

The system was studied at room temperature. The gas used for the amine saturation was supplied from a CO_2 bottle (L'Air Liquide).

At the end of each test, the saturation of the solution was again observed. The next step was to determine at what temperature the studied amines solutions would start releasing the CO_2 that was absorbed or, in other words, the starting temperature of the amine regeneration.

2.1.3. Regeneration of the CO_2 saturated aqueous amine solutions

In order to proceed to the regeneration of the CO_2 saturated aqueous amine solutions, the procedures indicated in Santos (2012) [25] were followed and adapted for this study.

The tests were conducted by heating the three-necked flask containing the amine solution, CO_2 saturated, in an oil bath, as shown in Figure 20.

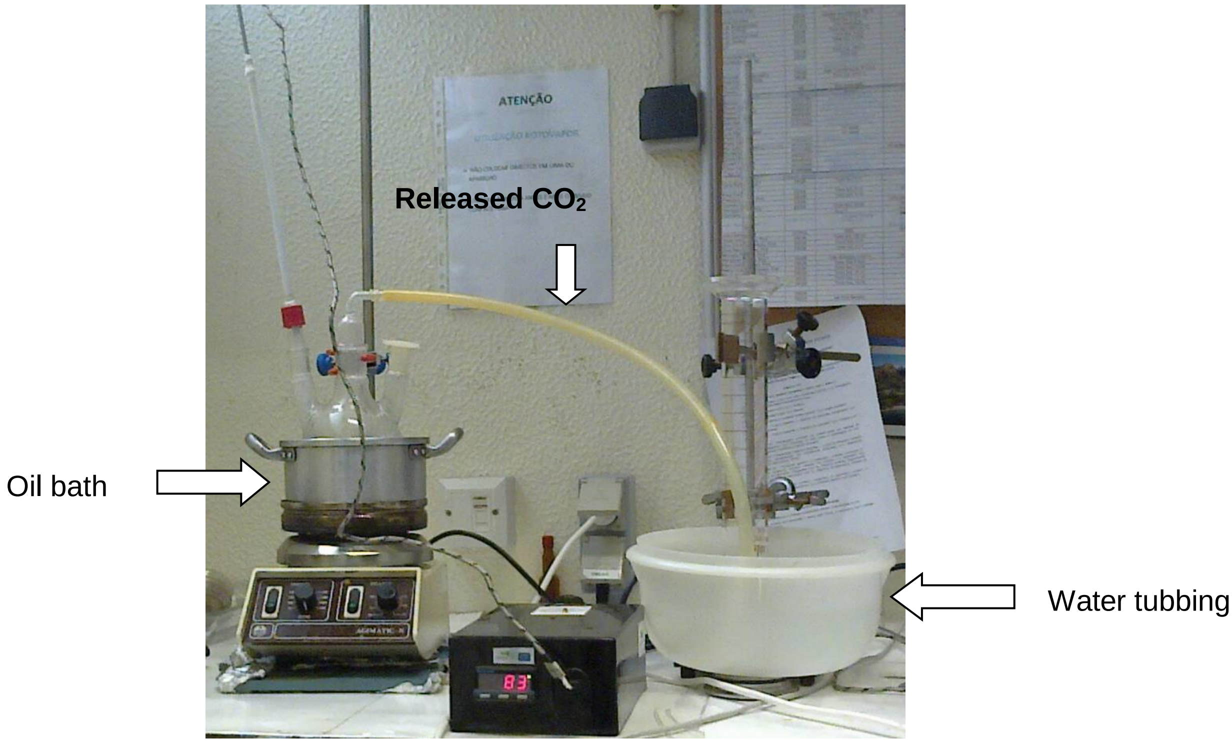

Figure 20 - Illustration of experimental tests performed to regenerate amines from aqueous solutions saturated with CO_2.

Since the oil has a higher boiling point than water, the amine solution could be heated to higher temperatures, until the temperature of which CO_2 started being released from the amine. In order to perform this study, the oil bath was placed on top of a heating plate (Agimatic-N, J.P. Selecta) and a Honeywell thermometer was placed on the left neck of the flask. Also, the adapter allowing the released CO_2 to be directed inside the water tubbing through a rubber tube was placed on the middle neck. Thus, when the CO_2 release started, the bubbles were visible in the water and it was possible to register the temperature at that precise moment.

2.2. Pilot unit

2.2.1. Assembly of the sampling valve downstream the absorption column

To perform the sample collecting from the absorption column, it was necessary to install a valve. This valve was placed downstream the column so that samples containing the CO_2"rich" amine solution could be taken out, as shown in Figures 21 and 22.

Figure 21 – Sampling valve downstream of the absorption column.

After adding this valve, the sample collecting was much easier to perform than in the original configuration of the pilot unit, allowing collecting the sample in a faster way, but also measuring the amine solution temperature immediately after it had been in contact with the CO_2.

Apart from that, the original configuration of the pilot unit, described in Santos (2012) [25], was used.

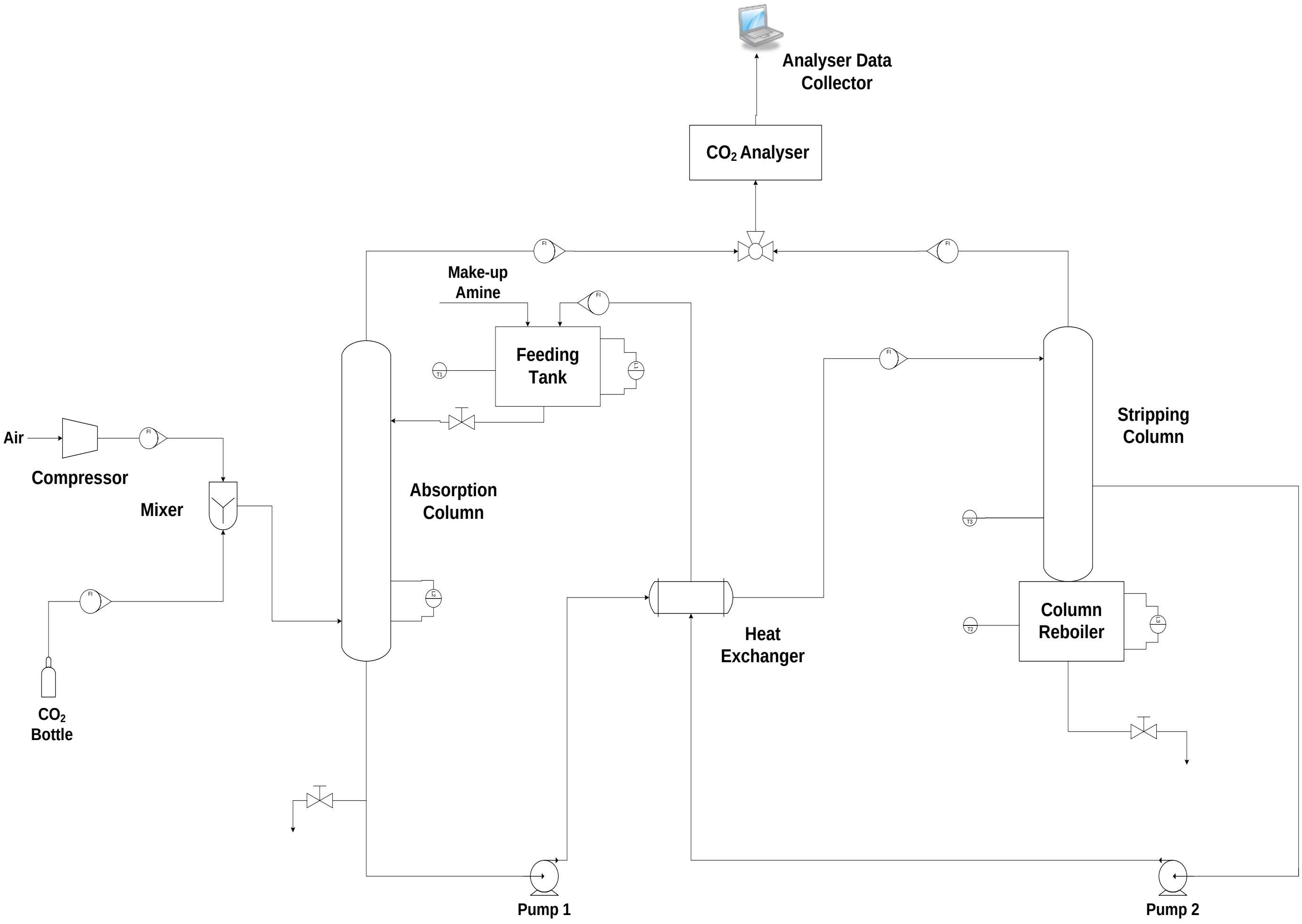

Figure 22 – Pilot unit flowsheet.

2.2.2. Studies of CO_2 absorption in amine solutions

CO_2 absorption studies were conducted in the pilot unit, using amine solutions with a concentration of 10 % w/w. In these studies, the amines used in the preliminary tests that showed the best results were selected, as well as the amines that were expected to be used in the pilot unit during the tests previously performed as described in Santos (2012) [25]. Summary tables are given below containing the typical values of their structural properties for the studied amines and also their respective molecular structures.

2.2.2.1. Studied amines

Table 11 – Structural properties of MEA. [25]

Monoethanolamine (MEA)	
CAS number	141-43-5
Molecular formula	C_2H_7NO
Molar weight (g/mol)	61.08
Density (g/cm^3)	1.0164 (20 °C)
Boiling point (ºC)	171 (1013 hPa)
Melting point (ºC)	10.5
Flash point (ºC)	93
Supplier	VWR
Emission Limit Value (ppm) [24]	0.5

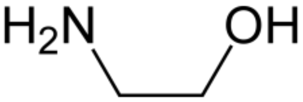

Figure 23 – Molecular structure of MEA. [17]

Table 12 – Structural properties of EDA. [25]

Ethylenediamine (EDA)	
CAS number	107-15-3
Molecular formula	$C_2H_8N_2$
Molar weight (g/mol)	60.10
Density (g/cm^3)	0.898 (20 °C)
Boiling point (ºC) b)	117 (1013 hPa)
Melting point (ºC) b)	8,5
Flash point (ºC) b)	34
Supplier	VWR
Emission Limit Value (ppm) [24]	0.5

Figure 24 – Molecular structure of EDA. [17]

Table 13 – Structural properties of PZ. [23]

Piperazine Anhydrous (PZ)	
CAS number	110-85-0
Molecular formula	$C_4H_{10}N_2$
Molar weight (g/mol)	86.14
Ignition temperature (ºC)	320 DIN 51794
Solubility (g/l)	150 (20 °C)
Melting point (ºC)	108 - 111
Density (g/cm³)	1.1 (20 °C)
Bulk density (kg/m³)	400
pH value	12 (150 g/l, H_2O, 20 °C)
Boiling point (ºC)	145 - 146 (1013 hPa)
Vapor pressure (hPa)	< - 10 (20 °C)
Explosion limit (%)	4 - 14 (V)
Flash point (ºC)	65
Supplier	Merck
Emission Limit Value (ppm) [24]	N/A

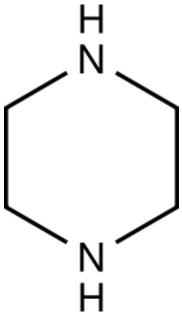

Figure 25 – Molecular structure of PZ. [17]

The information about the structural and thermophysical properties of the amines chosen from the preliminary tests is described in before in chapter 2.1.1.

2.2.2.2. Experimental procedure

The main goal, for this pilot unit study, was to replace the flue gas stream of power plants by mixtures containing air and CO_2 or even pure CO_2, with the purpose of approaching the concentration values registered in power plants. In order to simulate the expect concentration in the gaseous stream, the CO_2 from a bottle (3) was mixed with compressed air from a compressor (4). Then, the gaseous solution enters the absorption column (2) and contacts with the aqueous amine solution coming from the feeding tank (1), thus occurring the chemical absorption of CO_2. The gaseous stream leaving the top of the absorption column was connected to a CO_2 meter (8), so that the amount of CO_2 existing in that stream could be measured. The cold liquid stream leaving the bottom of the absorption column flowed through a dosing pump (5) and then went through a heat exchanger (7) where it was heated. Then, the liquid stream reaches the top of the stripping column (6) where the releasing of CO_2 occurred. The gaseous stream leaving the top of the stripping column was connected, likewise to the stream leaving the top of the absorption column, to a CO_2 meter (8), so that the amount of CO_2 existing in that stream could be also measured. The liquid stream leaving the stripping column at high temperature flowed through a dosing pump (5) and went through the heat exchanger (7), where it heated the stream leaving the bottom of the absorption column. This stream, on the other hand, was cooled down in the heat exchanger and went back to the feeding tank (1), where the amine make-up was done. Then, it enters the top of the absorption column (2), thus closing the cycle. [25]

The pilot unit and all the equipment described before are shown in Figures 26 and 27.

Figure 26 – Pilot unit.

The next figure shows, in more detail, the heat exchanger and the absorption column.

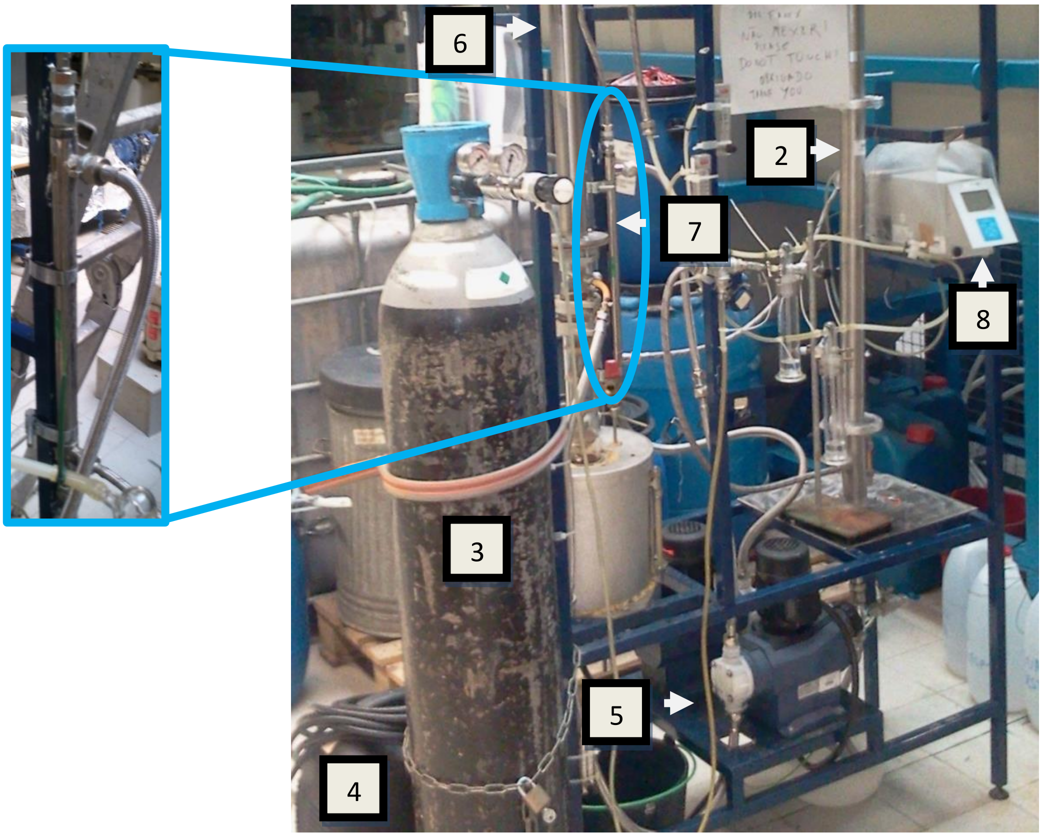

Figure 27 – Detail of the pilot unit.

In order to study the loading capacity of the studied amines, the aqueous solutions were prepared, in a concentration of 10% by weight, and were placed in the feeding tank. Then, CO_2 was circulated jointly with the aqueous amine solution, and samples were collected, every 30 minutes, until the amine saturation was achieved.

NOTE: Initial absorption studies were conducted during 3 hours for each aqueous amine solution, collecting the samples to be analyzed every 30 minutes. After the analysis of the collected samples has been done, it was concluded that by the end of 3 hours the amines were not fully saturated. In order to make sure that the amine was fully saturated, the tests were then conducted during 4 hours.

In order to determine the CO_2 loading capacity of each aqueous amine solutions until saturation, the method of barium chloride precipitation was used. To use this method, the procedures referred in Santos (2012) [25] and Li et al. (1994) [26] were followed and adapted so that studies could be conducted as described below.

After the amine solution had been saturated with CO_2, a sample of 20 mL was collected from the pilot unit into a cup. Then, a solution of sodium hydroxide (NaOH) 1.0 M, previously prepared from commercial sodium hydroxide (Solvay), was added in excess to the sample so that the dissolved CO_2 was converted to non-volatile ionic species. Then, a solution of barium chloride dihydrate ($BaCl_2.2H_2O$) 1.0 M, prepared previously from barium chloride dehydrate (Panreac) was added in excess. The solution was well stirred to ensure that all the CO_2 was absorbed, so that it could precipitate as a carbonate, in this case, barium carbonate ($BaCO_3$). Afterwards, the solution containing the precipitate was filtrated, dried and weighted. The amount of precipitate was used to calculate the CO_2 loading capacity, as CO_2 moles per mol of amine. The equations used for those calculations are described below:

$$w_{amine} = w_{sample} \times \%_w \tag{8}$$

Where:

w_{amine} – corresponds to the amine weight (g);

w_{sample} – corresponds to the weight of the sample collected from the pilot unit (g);

$\%_w$ – corresponds to the concentration of aqueous amine solution.

$$n_{amine} = \frac{w_{amine}}{MW_{amine}} \tag{9}$$

Where:

n_{amine} – corresponds to the number of moles of amine (mol amine);

w_{amine} – corresponds to the amine weight calculated before in expression (8);

MW_{amine} – corresponds to the molecular weight of the amine (g/mol).

$$n_{CO_2} = \frac{m_{precipitate}}{MW_{BaCO_3}} \tag{10}$$

Where:

n_{CO2} – corresponds to the number of moles of the obtained CO_2 (mol CO_2);

$m_{precipitate}$ – corresponds to the weight of the obtained precipitate (g);

MW_{BaCO3} – corresponds to the molecular weight of $BaCO_3$ (g/mol).

$$\alpha = \frac{n_{CO_2}}{n_{amine}} \tag{11}$$

Where:

α – corresponds to the CO_2 loading capacity of the aqueous amine solution (mol CO_2/mol amine);

n_{CO2} – corresponds to the number of moles of the obtained CO_2 calculated before as in equation (10) (mol CO_2);

n_{amine} – corresponds to the number of moles of the amine calculated before as in equation (9) (mol amine);

3. Results and Discussion

3.1. Preliminary trials

3.1.1. CO_2 absorption using amine solutions

At the end of each absorption trials, and after the saturation with CO_2, the aspect of the amine solution (20 % (w/w)) was observed. It was found that, for every solution, the amines used to prepare the aqueous solutions were not completely soluble in water, except for the diethylamine and the diisopropylamine, thus showing two liquid phases: an organic and an aqueous phase, as can be seen in Figure 28.

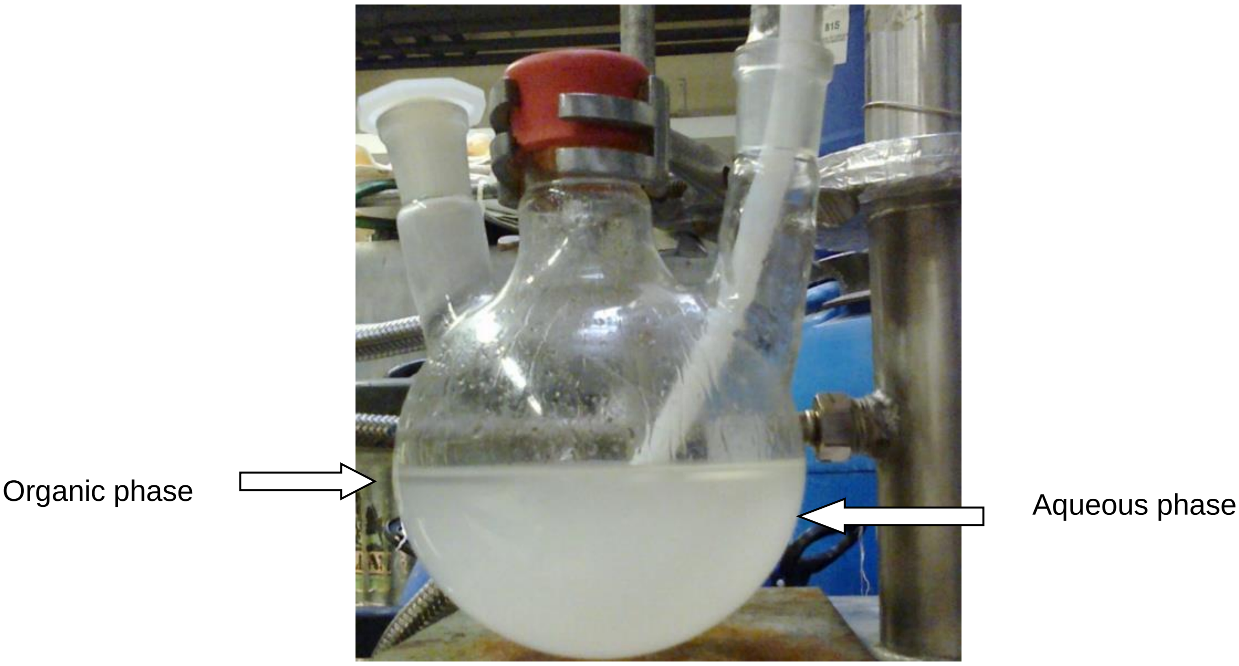

Figure 28 – Amine aqueous solution with two liquid phases during the saturation with CO_2.

The isopropylamine was not used in this trials, due to its low boiling point temperature (around 31-33 ºC). This was not the most suitable amine to use in this trial and, thus, in the regeneration trials. Although, it could possibly absorb the CO_2 and it is soluble in water, it has such a low boiling point temperature, that when the time came for the regeneration trial, the isopropylamine would boil before the absorbed CO_2 would start to be released.

The diisopropylamine, at room temperature (20 ºC), was only miscible in water. Nevertheless, the saturation with CO_2 was performed, but, after 45 minutes, the aqueous solution started to form a white precipitate and sometime after that, the solution had already turned into a solid amine salt. What usually occurs in these chemical absorption systems is that when the used amine is soluble in water, the carbamate salt is able to dissociate into free ions, as shown in Figure 29, and form bicarbonate salt that is soluble in water. However, in anhydrous amines the salt remains as associated ion pair because of the low dielectric constants of these solvents. The diisopropylamine-carbamate salt formed as, the diisopropylamine is only miscible in water, was not able to dissociate in order to form the bicarbonate salts, which lead to its precipitation. [27] [28]

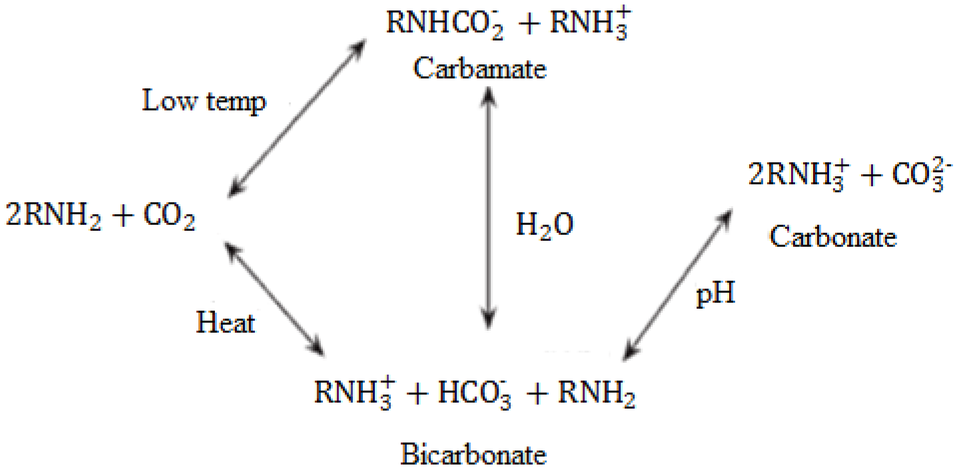

Figure 29 – Reaction sequence for the capture of carbon dioxide by using aqueous solutions of primary and secondary amines. [2]

The rest of the tested amines, with the exception of diethylamine, had a low solubility. That was observed, when the amine aqueous solutions were prepared, by the formation of two liquid phases. In the case of the bis(2-ethylhexyl)amine and the triethylamine, they were not completely soluble in water, but in the case of the dimethylethanolamine (DMEA), although it was soluble in water, and the package dated from 2004, it is believed that it has been degraded, which may have altered its physical and chemical properties.

Nevertheless, the saturation with CO_2 was performed. The final aspect of the aqueous solutions is as shown in Figure 28.

In the case of bis(2-ethylhexyl)amine, the aqueous phase showed a bluish coloration. This could be due to the fact this alkylamine is an amphiphilc molecule. An amphiphilic molecule, of which soap is a typical example, possesses antagonistic hydrophilic and hydrophobic moieties in the same molecule. Analyzing the bis(2-ethylhexyl)amine molecule, as shown in Figure 16, the hydrophilic and hydrophobic moieties can be identified. The hydrophilic moiety corresponds to the nitrogen atom in the amine group and the hydrogen bonded to it. The hydrophobic moiety corresponds to the long aliphatic and branched hydrocarbon chain in the alkylamine molecule. This justifies the low solubility in water that this molecule presented and also the separation of the aqueous solution into two liquid phases. [29] [30] [31]

In the case of triethylamine, as it was not completely soluble in water, the aqueous solution had the two liquid phase mentioned before. As triethylamine is a tertiary amine, it was unable to form carbamates and therefore it does not react directly with the CO_2. Instead, the reaction between CO_2 and tertiary amines can be described with the base catalysis of the hydration of CO_2. The reaction between CO_2 and tertiary amines is shown in expression (7), presented already in chapter 1.2.1. The bicarbonate formed from the base catalyzed CO_2 hydration was soluble in water. As triethylamine was not completely soluble in water, only the amount of the amine that was soluble could form the bicarbonate, due to the fact that, in non-aqueous conditions, no reaction occurs for tertiary amines. [32]

That is exactly what happened for the DMEA. As mentioned before, the DMEA was soluble in water, just like the others alkanolamines tested before by Santos (2012) [25] (MEA, DEA and MDEA), but because the package dates from 2004, it is believed that has been degraded, which may have altered its physical and chemical properties. After the preparation of the aqueous solution of DMEA, the formation of two liquid phases was visible, which suggested that this amine has not soluble in water. This could mean that the reaction did not occur. [32]

Diethylamine, was the only tested amine that was completely soluble in water. The diethylamine aqueous solution, during the saturation with CO_2, did not show any trace of precipitate or two liquid phase formation, which indicates that the reaction went through without any problems. The aspect of the aqueous solution, at the end of the absorption trial, is shown in Figure 19.

3.1.2. Regeneration of the CO_2 saturated aqueous amine solutions

The tests were conducted by heating the three-necked flask containing the amine solution, saturated with CO_2, in an oil bath. When the CO_2 release started, the bubbles were visible in the water and it was possible to register the temperature at that precise moment.

The temperatures on the beginning of CO_2 release were registered, for each one of the aqueous solutions of the studied amines. These results are shown in Table 14.

Table 14 – Obtained results in the experimental tests carried out for studying the regeneration of the CO_2 saturated aqueous amine solutions.

Aqueous Amine Solution	CO_2 Release Temperature (ºC)	Duration of CO_2 Release (min)
Isopropylamine	-	-
Diisopropylamine	-	-
Diethylamine	RNO [a)]	RNO
Bis(2-ethylhexyl)amine	30	35
DMEA	RNO	RNO
Triethylamine	36	44

[a)] RNO – Release Not Observed.

The aqueous solutions of isopropylamine and diisopropylamine did not show any results, due to the fact that they were not used in this study. The reasons why they were not studied are mentioned in the previous chapter.

For diethylamine aqueous solution, the CO_2 release was not observed. This could mean that the salts formed from the reaction between CO_2 and diethylamine are, in fact, a problem of solvent degradation that generates a number of non-regenerable heat-stable salts (HSS) and not the desired carbamates. These heat-stable salts are reaction products from amines with CO_2. By nature, the heat-stable salts are non-regenerable under solvent regenerations conditions. As such, they remain and accumulate in the absorption solvent. The accumulation of heat-stable salts not only causes a reduction in CO_2 absorption capacity, but also it is also claimed to cause a significant increase in the system corrosiveness. [33]

In the case of the bis(2-ethylhexyl)amine aqueous solution, as mentioned in the previous chapter, it is not completely soluble due to the fact that the amine was an amphiphilic molecule. However, the release CO_2 was observed. This means that, despite the low solubility of the amine, it reacted with the CO_2 to form carbamate salts, which in turn dissociated, in the presence of water, to form bicarbonate salts and when the aqueous solutions was heated for the solvent regeneration, the release of CO_2 occurred. [29]

Regarding the DMEA, the suspicions referred in chapter 3.1.1 for the fact that it is not soluble were confirmed. A proof of that was the fact that the release of CO_2 was not observed meaning that the reaction between DMEA and CO_2 did not occur. Being a tertiary alkanolamine, the DMEA cannot react directly with CO_2. The only reaction path is the base catalyzed CO_2 hydration, which unless the DMEA is soluble in water, cannot occur. [32]

As for triethylamine, despite not being completely soluble in water, the amount of amine that was soluble was able to form the bicarbonate salt through the catalysis of the CO_2 hydration. The occurrence of this reaction was confirmed by the observation of the CO_2 release, when the aqueous solution was heated, in order to perform the solvent regeneration. [32]

Analyzing the obtained results from these preliminary tests, it can be concluded that, besides not being completely soluble, bis(2-ethylhexyl)amine and triethylamine were the only amines that were capable of both absorbing and releasing the CO_2, although in small amounts, as can be seen by the short release duration showed in Table 14.

Comparing the results for the two amines, it can be concluded that bis(2-ethylhexyl)amine requires a lower temperature (30 ºC) than triethylamine (36 ºC), in order to perform the release of CO_2, and took less time to do it. This could also mean that bis(2-ethylhexyl)amine absorbed and released a smaller amount of CO_2 than triethylamine.

It should be noted that the purpose of these preliminary tests was not to find new solvents and see how much CO_2 they could absorb and release, but how energy efficient they were throughout the process, i.e. what was the necessary temperature in order to obtain solvent regeneration.

NOTE: Due to the fact that DMEA was believed to be not in the best conditions, because it was not soluble in water like it was supposed to be, an order of three liters of this amine was made, so that it could be tested. If this new amine showed good results in the preliminary tests, it could be used in the tests performed in the pilot unit. Two other amines were also ordered. Triethanolamine was ordered in order to see what effect the three ethanol groups had in absorbing and releasing the CO_2. Diethylenetriamine was ordered in order to see what effect the presence of three amino groups had in absorbing and releasing CO_2. By the time this thesis was written, none of the ordered amines had arrived, which made impossible to realize these tests

Pilot unit

3.1.3. Studies of CO_2 absorption in amine solutions

In the tests performed in the pilot plant, besides the studied amines that were mentioned before, it was also studied the amine that showed the best results in the preliminary trials. In this case, the chosen amine was diethylamine, because it was the only one that was completely soluble in water.

In order to determine the CO_2 loading capacity by the aqueous amine solutions, the precipitation method was used. The amount of formed precipitate from the addition of $BaCl_2.2H_2O$ was used to calculate the CO_2 loading capacity, in terms of moles of CO_2 per moles of amine using expressions (8), (9), (10) and (11). The obtained results are shown in Table 15.

Table 15 – Obtained results for CO_2 absorption by aqueous amine solutions (10 % (w/w)) using the precipitation method.

Absorption Time (min)	**Amine Aqueous Solutions 10 % (w/w)**	**Diethylamine**	**MEA**	**PZ**	**EDA**
	n_{amine} (mol)	0.027	0.033	0.021	0.033
30	$m_{filtrate}$ (g)	0.310	1.110	0.640	0.570
	n_{CO2} (mol)	0.002	0.006	0.003	0.003
	α (mol CO_2/mol amine)	**0.058**	**0.171**	**0.138**	**0.088**
60	$m_{filtrate}$ (g)	3.130	1.350	1.620	0.560
	n_{CO2} (mol)	0.016	0.007	0.008	0.003
	α (mol CO_2/mol amine)	**0.581**	**0.209**	**0.349**	**0.086**
90	$m_{filtrate}$ (g)	3.510	1.160	2.080	1.000
	n_{CO2} (mol)	0.018	0.006	0.011	0.005
	α (mol CO_2/mol amine)	**0.652**	**0.179**	**0.449**	**0.154**
120	$m_{filtrate}$ (g)	3.190	2.520	1.420	1.710
	n_{CO2} (mol)	0.016	0.013	0.007	0.009
	α (mol CO_2/mol amine)	**0.592**	**0.389**	**0.306**	**0.263**
150	$m_{filtrate}$ (g)	3.100	2.290	2.410	2.160
	n_{CO2} (mol)	0.016	0.012	0.012	0.011
	α (mol CO_2/mol amine)	**0.575**	**0.354**	**0.520**	**0.332**
180	$m_{filtrate}$ (g)	3.080	2.510	2.230	2.380
	n_{CO2} (mol)	0.016	0.013	0.011	0.012
	α (mol CO_2/mol amine)	**0.572**	**0.388**	**0.481**	**0.365**
210	$m_{filtrate}$ (g)	3.810	3.150	2.210	2.400
	n_{CO2} (mol)	0.019	0.016	0.011	0.012
	α (mol CO_2/mol amine)	**0.707**	**0.487**	**0.477**	**0.369**
240	$m_{filtrate}$ (g)	2.650	2.650	1.830	2.090
	n_{CO2} (mol)	0.013	0.013	0.009	0.011
	α (mol CO_2/mol amine)	**0.492**	**0.409**	**0.395**	**0.321**

When analyzing the results shown in Table 15, it can be noted that the CO_2 loading capacity for each aqueous amine solution increases, with some fluctuations, over time. In other words, the aqueous amine solutions initially act like a “lean” solvent because they had not absorbed any CO_2 yet. As the contact time (in the pilot unit) between the solutions and the CO_2 increases the amount of absorbed CO_2 also increases.

It can also be noted that, for the precipitation method, the aqueous amine solution that showed a higher CO_2 loading capacity was diethylamine. Despite the results obtained for this amine in the solvent regeneration at the preliminary trials, when compared with the other amines, it can absorb 0.492 mol of CO_2 per mol of amine, against the 0.409 mol of CO_2 per mol of amine obtained by MEA, typically considered as the benchmark solvent to which alternative solvents must be compared. The loading capacity achieved by PZ at the end of the test was very close to what MEA presented. This means that PZ could be a good alternative solvent for CO_2 absorption. EDA was the amine that showed the worst loading capacity (0.321 mol of CO_2 per mol of amine). [15]

For better understanding of the results from this test, the following figure is provided:

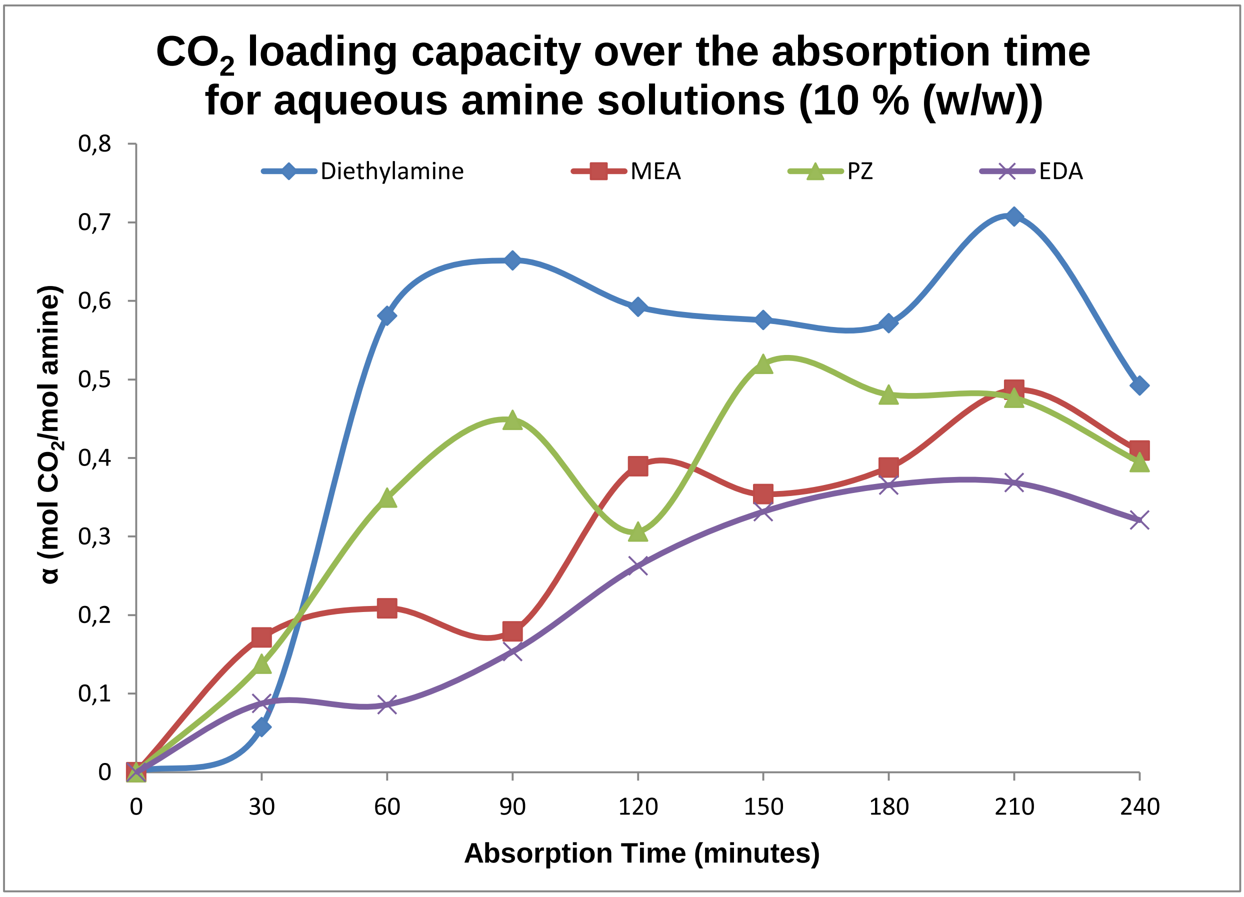

Figure 30 – Obtained results for CO_2 loading capacity over the absorption time for the tested aqueous amine solutions (10 % (w/w)).

By analyzing figure 30 it can be observed that diethylamine, a secondary alkylamine, showed the highest CO_2 loading capacity of the four amine solutions that were tested, although in the first sample taken, at the moment of 30 minutes, it was the one that had absorbed the lowest amount of CO_2. The curve that shows the loading capacity of PZ over absorption time has, at the moment of 120 minutes, a strange fluctuation. The reason why, at this particular instant the loading capacity of PZ decreased was due to the fact that the CO_2 flow inside the absorption column was higher than the flow of the PZ solution. This created a problem, as the CO_2 flow inside the column was such that it did not allow the PZ solution to flow downwards, thus not allowing the reaction to take place normally. Besides that, when comparing with MEA, which is the benchmark solvent, PZ showed, in some moments, a higher loading capacity. In the case of a sterically hindered compound such as PZ, the reaction is particularly important, as the presence of the methyl group significantly reduces the stability of the carbamate bond, resulting in the preferred formation of the bicarbonate, and thus leading to the particularly high loading capacity of this solvent. For EDA, its loading capacity over absorption time curve indicates that, despite the result at 30 minutes, it was the amine solution that showed the worst results through the whole duration of the absorption test. [15]

The fluctuation that is seen in the absorption curves of the four amine solutions was caused by experimental errors. These experimental errors are associated with the precipitation method, more specifically the precipitate filtration and drying processes.

3.1.4. Comparison with the obtained results from the earlier performed tests

The pilot unit used to perform the CO_2 absorption tests is the same that was used in Santos (2012) [25], where the tests that were performed used the aqueous solutions of MDEA and DEA, at the concentrations of 10 %, 20 % and 30 % (w/w).

In order to make a comparison between the aqueous amine solutions used in this work and the ones that were used before in Santos (2012) [25], the obtained results for the concentration of 10 % (w/w) were the only ones that were considered.

Table 16 – Results in absorption of CO_2 by each aqueous amine solution at 10% (w/w) by the method of precipitation of the samples. [25]

Absorption Time (minutes)	Aqueous Amine Solution 10 % (w/w)	MDEA	DEA
	n_{amine} (mol)	0.017	0.019
30	$m_{filtrate}$ (g)	2.960	2.368
	n_{CO2} (mol)	0.015	0.012
	α (mol CO_2/mol amine)	**0.882**	**0.613**
60	$m_{filtrate}$ (g)	3.157	3.354
	n_{CO2} (mol)	0.016	0.017
	α (mol CO_2/mol amine)	**0.961**	**0.877**
90	$m_{filtrate}$ (g)	3.354	3.294
	n_{CO2} (mol)	0.017	0.017
	α (mol CO_2/mol amine)	**1.020**	**0.877**
120	$m_{filtrate}$ (g)	3.093	3.749
	n_{CO2} (mol)	0.016	0.019
	α (mol CO_2/mol amine)	**0.961**	**0.982**
150	$m_{filtrate}$ (g)	3.421	3.664
	n_{CO2} (mol)	0.017	0.019
	α (mol CO_2/mol amine)	**1.020**	**0.982**
180	$m_{filtrate}$ (g)	3.275	3.768
	n_{CO2} (mol)	0.017	0.019
	α (mol CO_2/mol amine)	**1.020**	**0.982**

By analyzing the table 16, it can be concluded that the obtained results for MDEA and DEA show that these amine had a higher CO_2 loading capacity than the amine solutions used in this work.

For better understanding and compare the obtained results for all aqueous amine solutions, the following figure is provided:

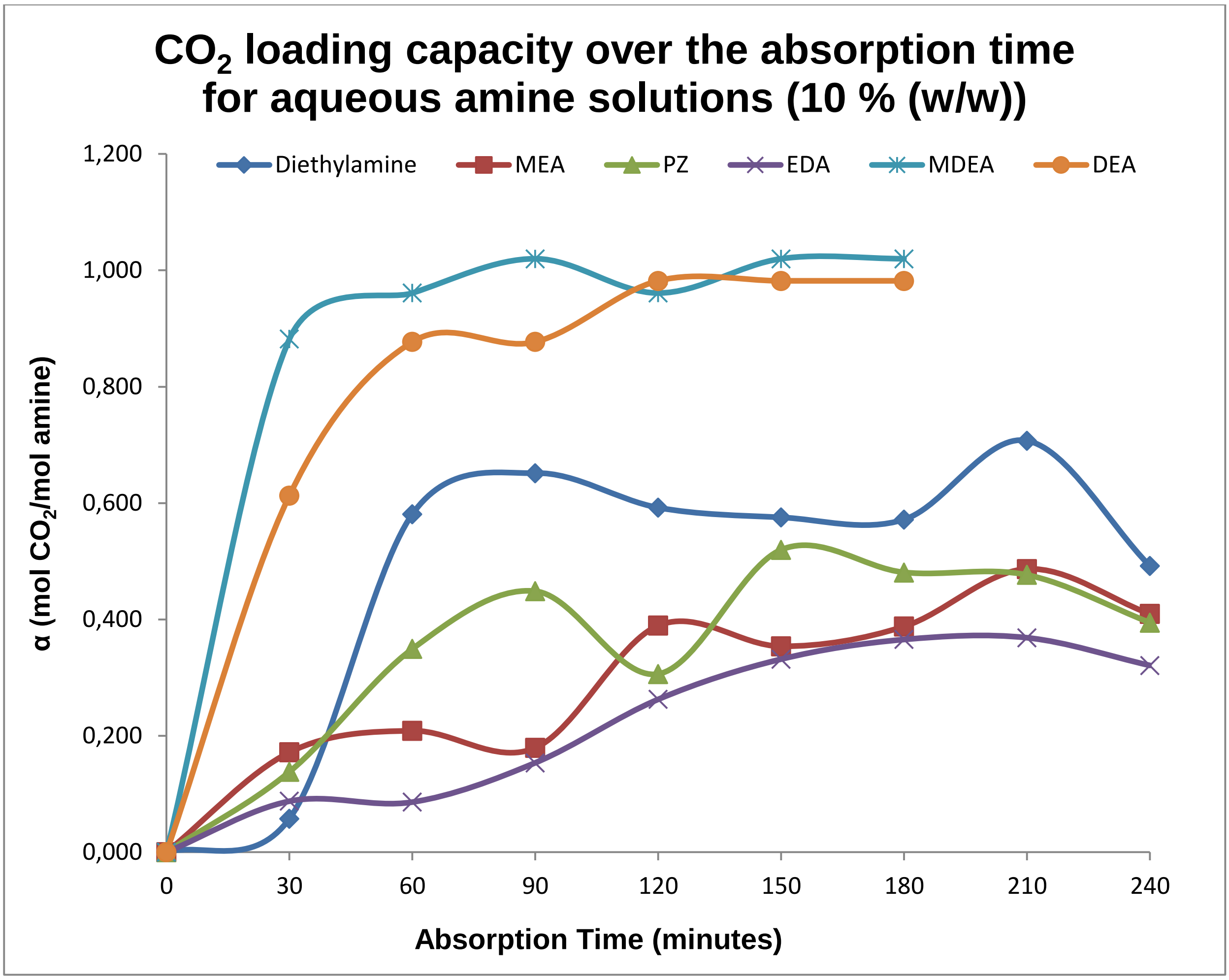

Figure 31 – Comparison of the obtained results for CO_2 loading capacity over the absorption time for all the tested aqueous amine solutions (10 % (w/w)).

As it can be seen in figure 30, MDEA and DEA showed a higher loading capacity throughout the absorption tests and needed a shorter absorption time (180 minutes) to be saturated.

In the case of MDEA, as it is a tertiary amine and it does not react directly with CO_2, but acts as a base, catalyzing the hydration of CO_2, meaning that it has an equilibrium CO_2 loading capacity nearly of 1.0 mol CO_2/mol amine, the obtained results are consistent with what was expected. [18]

For DEA, as it is a secondary amine, based on stoichiometry, the expected CO_2 loading capacity was 0.5 mol CO_2/mol amine. However, the obtained results showed that the loading capacity of DEA was close to 1.0 mol CO_2/mol amine. [18]

The observed discrepancy between the obtained results, showed in figure 30, could be due to experimental errors. As mentioned before, the precipitation method that was used to quantify the amount of CO_2 absorbed by the amine solution, as associated experimental errors, more specifically regarding the precipitate filtration and drying processes.

3.1.5. Cost analysis

In order to make a cost analysis for the studies performed in the pilot unit the market value of each amine was researched and related to the CO_2 loading capacity presented in figure 32.

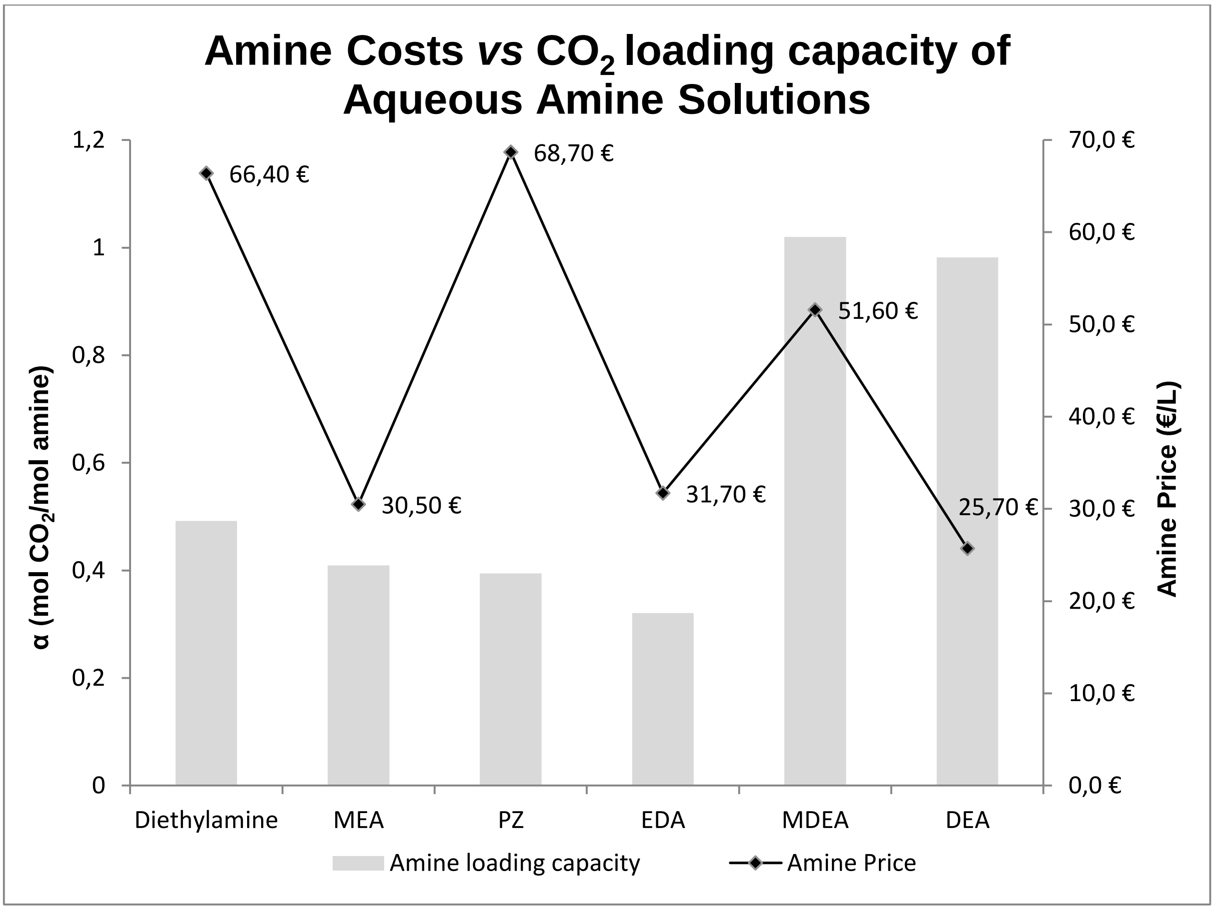

Figure 32 – Amine Price versus CO_2 loading capacity of Aqueous Amine Solutions.

NOTE: The amine prices shown in figure 32 correspond to the lowest market value that was found in the Portugal. The prices are for the pure amines. Due to the fact that in the performed tests, the amine solutions had the same concentration (10 % (w/w)) these prices do not need to take into account with the dilution factors.

As can be seen in figure 31, MEA shows the second highest loading capacity (0.409 mol of CO_2 per mol of amine) and the lowest price per liter (30.50 €/L). As it is the benchmark solvent, for the chemical absorption of CO_2, the other amine solutions were compared to it. PZ is the one that showed a loading capacity close to MEA (0.395 mol of CO_2 per mol of amine) but it has the highest price per liter of all the four amines tested in this study (68.70 €/L). Diethylamine was the one that showed the highest loading capacity (0.492 mol of CO_2 per mol of amine), but its price per liter was very close to the price for PZ (66.40 €/L). EDA had the lowest loading capacity (0.321 mol of CO_2 per mol of amine) and its price per liter is close to the price for MEA (31.70 €/L). By analyzing these results, it can be concluded that the amine studied in this work that showed the best cost/loading capacity ratio was with no doubt the MEA.

This can be justified because, although MEA had a lower loading capacity than diethylamine (0.409 mol of CO_2 per mol of amine against 0.492 mol of CO_2 per mol of amine) the price per liter was the lowest one (30.50 €/L).

When comparing with the amines studied in [25], it can be concluded that the amine with the best cost/loading capacity and, therefore, the best choice for the chemical absorption of CO_2 would be DEA, because it shows a high loading capacity (0.982 mol of CO_2 per mol of amine) and its price it is even lower than MEA (25.70 €/L).

4. Conclusions

4.1. Preliminary trials

The main goal of the preliminary trials was to find an alternative solvent to replace MEA that showed lower energy consumption, i.e. a lower solvent regeneration temperature. In order to perform these studies, six amines were tested: isopropylamine, diisopropylamine, diethylamine, bis(2-ethylhexyl)amine, DMEA and triethylamine. These amines were used to prepare aqueous amine solutions with a concentration of 20 % (w/w). These solutions were put inside a three-necked flask and CO_2 was bubbled within the amine solution. Firstly, the amine solutions were saturated with CO_2. In this stage, two of amines solutions were dismissed from the studies. One of them was isopropylamine, because of its low boiling point temperature (31-33 ºC), it could boil and evaporate even before the CO_2 release starts. The other excluded amine was diisopropylamine, because it was only miscible with water and when its carbamate was formed, it precipitated. Regarding the remaining amines, only diethylamine was completely soluble. Bis(2-ethylhexyl)amine was amphiphilic, meaning that its molecule possessed hydrophilic and hydrophobic properties; the triethylamine solution showed two liquid phases, meaning that this amine was not completely soluble and DMEA, which was supposed to be a water-soluble alkanolamine, showed a solution also with two liquid phases. Nevertheless, they were all saturated with CO_2.

During the solvent regeneration stage of the study, only two aqueous amine solutions accomplished the release of CO_2: bis(2-ethylhexyl)amine and triethylamine. Bis(2-ethylhexyl)amine solution had a solvent regeneration temperature of 30 ºC and it released CO_2 for a period of 35 minutes. The triethylamine solution had a solvent regeneration temperature of 36 ºC and the CO_2 was released for a period of 44 minutes. This means that, despite these solutions presented two liquid phases, they were able to absorb and release CO_2. The same did not happen to diethylamine and DMEA. Diethylamine, as mentioned before, was the only amine solution that was completely soluble in water, but the release of CO_2 during the solvent regeneration tests was observed. This could mean that the salts formed from the reaction between CO_2 and diethylamine are, in fact, a problem of solvent degradation that generates a number of nonregenerable heat-stable salts (HSS) and not the desired carbamates. For DMEA, a proof that this was not water-soluble was the fact that the release of CO_2 was not observed meaning that the reaction between DMEA and CO_2 did not occur. Being a tertiary alkanolamine, the DMEA cannot react directly with CO_2. The only reaction path is the base catalyzed CO_2 hydration, which unless the DMEA is soluble in water, cannot occur.

In conclusion, bis(2-ethylhexyl)amine aqueous solution was the one that had the lowest regeneration temperature, but because it had an amphiphilic molecule, it was the diethylamine the chosen one to be used in the tests performed in the pilot unit, as it was the only one that was completely soluble in water, which meant that no precipitate (that could put in danger the pilot unit) was formed.

4.2. Pilot unit

In the studies performed in the pilot unit, four amines were tested: diethylamine, MEA, PZ and EDA. These amines were used to prepare aqueous amine solutions with a concentration of 10 % (w/w). These tests were performed with the same absorption time of 240 minutes for all the amine solutions. When analyzing the obtained results, it can be concluded that the amine solution that showed the best results, with the highest CO_2 loading capacity (0.492 mol of CO_2 per mol of amine) was the diethylamine aqueous solutions. The MEA aqueous solution that in this study was considered as the benchmark amine aqueous solution for the chemical absorption of CO_2, showed the second highest loading capacity, followed very closely by the PZ aqueous solution. The EDA aqueous solution showed the lowest loading capacity, which means that this amine solution could not be the best alternative solvent to replace MEA as a solvent of choice in CO_2 chemical absorption.

The obtained results in these tests were compared with the ones that were performed by Santos (2012) [25] in the same pilot unit. When the comparison was made, it was possible to see that the MDEA and DEA solutions that were used in Santos (2012) [25] obtained better results, with both the solutions showing higher CO_2 loading capacities that the solutions used in the studies performed in this work. The discrepancy of values and the fluctuation seen in the obtained results were due to experimental errors associated with the precipitation method.

A cost analysis was also made in order to see which one of the amines was the most economical choice of solvent for the chemical absorption of CO_2. For the amines tested in this work, MEA turned out to be the most economical, because it showed the lowest price per liter (30.50 €/L) and although its loading capacity was the second highest, the difference for diethylamine was almost insignificant, meaning a saving of 38.20 €/L. When comparing with the other two amine solutions used in Santos (2012) [25], DEA was the one that turned out to be the most economical choice, because it showed a higher CO_2 loading capacity (0.982 mol of CO_2 per mol of amine), although it was not the highest (MDEA had a loading capacity of 1.020 mol of CO_2 per mol of amine), and the lowest price per liter (25.70 €/L).

5. Perspectives for Future Work

The increasing concerns related with global climate change and in the reduction of GHG emissions, particularly of CO_2, means that there is a growing motivation to the development of more efficient CCS processes from large point sources of CO_2 emissions. Therefore, there is an important set of complementary works yet to be done, that could increase the knowledge about this subject.

Thus, and taking into account the continuation of this work, some suggestions for future work are presented:

- Perform the needed adjustments so that the pilot unit could work with continuous flow (simultaneous CO_2 absorption and solvent regeneration);
- Work with simulated flue gases, i.e., to test mixtures of CO_2 with air, so that the CO_2 concentration could match the concentration in the power plants flue gases;
- Study the use of the aqueous amine solutions as solvents for the chemical absorption of other flue gases, like NO_X and SO_X;
- Study the performance of the tested amines in other concentrations (20 % and 30 % (w/w));
- Continuing the research of new alternative solvents with lower energy consumption in order to replace MEA, giving emphasis to alkanolamines and diamines;
- Study the value of CO_2 as a raw material in polymer production, especially in the production of polyurethanes.

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7. Appendices

Appendix 1 – Experimental procedure for the absorption trials performed in the pilot unit.

Preparation of the solutions used in the $BaCO_3$ precipitation method:

NaOH 1.0 M aqueous solution

To prepare this solution, a 250 mL volumetric flask was used. Firstly, the amount of NaOH needed to prepare the 1.0 M solution was calculated, considering the volume of the flask. Then, after the NaOH was weighted, it was placed inside the volumetric flask and dissolved with distilled water, until the desired volume was achieved.

$BaCl_2.2H_2O$ 1.0 M aqueous solution

To prepare this solution, a 250 mL volumetric flask was used. Firstly, the amount of $BaCl_2.2H_2O$ needed to prepare the 1.0 M solution was calculated, considering the volume of the flask. Then, after the $BaCl_2.2H_2O$ was weighted, it was and placed inside the volumetric flask dissolved with distilled water, until the desired volume was achieved.

Absorption trials in the pilot unit:

The absorption trials in the pilot unit started by first preparing the aqueous amine solutions that were used, with a concentration of 10 % (w/w). The amount of amine needed for the solution, was calculated considering that the feeding tank in the pilot unit had a volume of 7 L.

After the solution had been prepared, it was placed inside the feeding tank. Then, the valve below the feeding tank was opened in order to enable the solution to flow into the absorption. The flow rate of the aqueous amine solutions inside the absorption column was approximately 24 L/h.

The CO_2 stream entered the absorption column from the bottom with a flow rate of approximately 20 mL/min.

The first dosing pump was turned on, in order to allow the CO_2 “rich” aqueous amine solution, which left the absorption column, to be directed inside the stripping column. Then the second dosing pump was turned on, in order to allow the aqueous amine solution that left the stripping column to be directed inside the feeding tank, thus closing the absorption cycle.

Every 30 minutes, a sample of 20 mL was collected from the absorption column, in order to ascertain whether the solution was or was not saturated, through a sampling valve. The sample was then analyzed by the $BaCO_3$ precipitation method.

The $BaCO_3$ precipitation method:

The sample taken from the absorption column, was place inside a 250 mL Erlenmeyer. Then, an excess amount of 1.0 M NaOH solution was added to the sample, thus converting free dissolved CO_2 into the non-volatile ionic species.

In order to quantify the amount of absorbed CO_2 by the $BaCO_3$ method, an excess amount of 1.0 M $BaCl_2.2H_2O$ solution was then added to the solution. The solution was very well stirred in order to allow all the absorbed (physically and chemically) CO_2 to precipitate in the form of $BaCO_3$.

Then, the $BaCO_3$ was filtered by vacuum filtration. For this procedure, a 500 mL Kitasato, a Büchner funnel, filter paper and a small vacuum pump (KUF) were used.

After filtration, the precipitate was allowed to dry and then it was weighted. With the weight of the precipitate, the number of moles of $BaCO_3$ was determined.

The number of moles of $BaCO_3$ was consider to be the same as the number of moles of the CO_2 that was absorbed by aqueous amine solutions. Knowing the number of moles of the amine present in the aqueous amine solution, the CO_2 loading capacity of each one of the tested amines was calculated.

Appendix 2 – Obtained results for the CO_2 absorption with the diethylamine solution using the precipitation method.

Samples			
Time (min)	**Filter weight (g)**	**Filter + $BaCO_3$ weight (g)**	**T (ºC)**
30	1.62	1.93	29
60	1.67	4.80	31
90	1.67	5.18	29
120	1,67	4.86	30
150	1.66	4.76	29
180	1.66	4.74	29
210	1.65	5.46	29
240	1.65	4.30	28

Absorption				
Time (min)	**$BaCO_3$ weight (g)**	**n $BaCO_3$ (mol)**	**n CO_2 (mol)**	**α (mol CO_2 / mol amine)**
30	0.31	0.0016	0.0016	0.058
60	3.13	0.0159	0.0159	0.581
90	3.51	0.0178	0.0178	0.652
120	3.19	0.0162	0.0162	0.592
150	3.1	0.0157	0.0157	0.575
180	3.08	0.0156	0.0156	0.572
210	3.81	0.0193	0.0193	0.707
240	2.65	0.0134	0.0134	0.492

Appendix 3 – Obtained results for the CO_2 absorption with the MEA solution using the precipitation method.

Samples			
Time (min)	**Filter weight (g)**	**Filter + $BaCO_3$ weight (g)**	**T (ºC)**
30	1.69	2.80	64
60	1.63	2.98	49
90	1.69	2.85	42
120	1.66	4.18	40
150	1.67	3.96	34
180	1.68	4.19	32
210	1.66	4.81	32
240	1.7	4.35	27

Absorption				
Time (min)	**$BaCO_3$ weight (g)**	**n $BaCO_3$ (mol)**	**n CO_2 (mol)**	**α (mol CO_2 / mol amine)**
30	1.11	0.0056	0.0056	0.171
60	1.35	0.0068	0.0068	0.209
90	1.16	0.0059	0.0059	0.179
120	2.52	0.0128	0.0128	0.389
150	2.29	0.0116	0.0116	0.354
180	2.51	0.0127	0.0127	0.388
210	3.15	0.0160	0.0160	0.487
240	2.65	0.0134	0.0134	0.409

Appendix 4 – Obtained results for the CO_2 absorption with the PZ solution using the precipitation method.

Samples			
Time (min)	**Filter weight (g)**	**Filter + $BaCO_3$ weight (g)**	**T (ºC)**
30	1.68	2.32	53
60	1.72	3.34	48
90	1.72	3.80	36
120	1.67	3.09	30
150	1.63	4.04	27
180	1.68	3.91	34
210	1.68	3.89	25
240	1.72	3.55	23

Absorption				
Time (min)	**$BaCO_3$ weight (g)**	**n $BaCO_3$ (mol)**	**n CO_2 (mol)**	**α (mol CO_2 / mol amine)**
30	0.64	0.0032	0.0032	0.138
60	1.62	0.0082	0.0082	0.349
90	2.08	0.0105	0.0105	0.449
120	1.42	0.0072	0.0072	0.306
150	2.41	0.0122	0.0122	0.520
180	2.23	0.0113	0.0113	0.481
210	2.21	0.0112	0.0112	0.477
240	1.83	0.0093	0.0093	0.395

Appendix 5 – Obtained results for the CO_2 absorption with the EDA solution using the precipitation method.

Samples			
Time (min)	**Filter weight (g)**	**Filter + $BaCO_3$ weight (g)**	**T (ºC)**
30	1.68	2.25	89
60	1.67	2.23	70
90	1.71	2.71	53
120	1.66	3.37	54
150	1.66	3.82	38
180	1.70	4.08	31
210	1.68	4.08	27
240	1.69	3.78	28

Absorption				
Time (min)	**$BaCO_3$ weight (g)**	**n $BaCO_3$ (mol)**	**n CO_2 (mol)**	**α (mol CO_2 / mol amine)**
30	0.57	0.0029	0.0029	0.088
60	0.56	0.0028	0.0028	0.086
90	1.00	0.0051	0.0051	0.154
120	1.71	0.0087	0.0087	0.263
150	2.16	0.0109	0.0109	0.332
180	2.38	0.0121	0.0121	0.365
210	2.40	0.0122	0.0122	0.369
240	2.09	0.0106	0.0106	0.321

Appendix 6 – Obtained results for the CO_2 absorption and amine regeneration/CO_2 release in the preliminary trials performed by Santos (2012) [25].

Absorption

Aqueous amine solution	n_{amine} **(mol amine)**	$w_{absorption}$ **(g)**	n_{CO2} **(mol CO_2)**	**α (mol CO_2 /mol amine)**
MEA	0.327	6.35	0.144	0.440
EDA	0.333	12.38	0.281	0.844
HDA	0.172	7.73	0.176	1.023
PZ	0.232	10.58	0.240	1.036

Amine regeneration/CO_2 release

Aqueous amine solution	$w_{desorption}$ **(g)**	$\alpha_{desorption}$ **(mol CO_2 /mol amine)**	$T_{desorption}$ **(ºC)**
MEA	1.98	0.138	69
EDA	1.30	0.089	89
HDA	2.09	0.276	93
PZ	5.18	0.507	88