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Modelisation and optimisation of a CO_2
capture process with a new benchmark
solvent for the Sart-Tilman cogeneration
plant

Travail de fin d'études réalisé en vue de l'obtention du
grade de master Ingénieur Civil électromécanicien

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Executive summary

Reducing CO_2 emissions which are responsible for global warming is one of the biggest challenge facing humanity. One very promising way to reduce CO_2 emissions is a process called Carbon Capture, Utilisation and Storage (CCUS).

The method used in this work to capture the CO_2 is post-combustion with amines as solvent. This technology suffers from a big drawback which is the high energy requirement for the regeneration of the solvent. Many studies to find the ideal solvent composition for our application were investigated. The choice of the solvent for this work is a ± 40 wt% formulation of PZ/AMP in a 1:2 molar ratio (3.0 molar AMP (26.74 wt%) and 1.5 molar PZ (12.9 2wt%)) because this solvent is becoming the new benchmark (IEAGHG report, 2019 [32]). Indeed, it has shown big improvements in comparison with the conventional benchmark called MEA.

The objective of this work is to validate and optimize a post-combustion CO_2 capture model using Aspen Plus V11.0 as software and then, to apply it for the Sart Tilman cogeneration plant. The goal was to treat a realistic fumes composition and mass flow exhausting from the CHP plant with the new benchmark solvent and to consume as little energy as possible.

First, the model was built and validated by trying to reproduce some experimental results from the literature. The capture rate, reboiler duty and lean and rich loading were studied to perform the validation. An Absolute Average Relative Deviation of respectively 2.2; 2; 8.7 and 9.1 % was found between our model and the experimental results which was satisfying.

Then, different sensitivity analysis were performed by varying parameters that directly affect the energy requirement of the process using equilibrium mode for the calculations in the columns. Optimized parameters are the following: 14 and 8 stages were found for the absorber and the stripper respectively; a solvent mass flow rate of 70000 kg/h was determined; the heat-exchanger temperature approach was fixed to 5°C and the stripper pressure could be increased to 2.3 bar.

The rate-based mode, taking into account heat and mass transfer limitations in the columns was used in a second step to determine the sizing of the 2 columns: 7 and 4 m for the total heights of the absorber and the stripper were found and the diameters are respectively 2.1 and 1.2 m.

Finally a comparison between the 2 types of calculation mode in the columns (equilibrium and rate-based) was done. A small decrease was got for the reboiler duty from 3.58 GJ/ t_{CO_2} for the equilibrium mode to 3.49 GJ/ t_{CO_2} for the rate-based mode due to a higher lean loading and a higher stripper pressure allowed without solvent degradation.

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Chapter 1

Introduction

Since the industrial revolution, human activities has led to a dramatical increase in CO_2 emissions. This is accentuated by the increase of world population resulting in a higher demand in energy as can be seen in Figure 1.1. Indeed people have to deal with 2 objectives in contradictions : Meet the increasing demand in energy and limit GHG emissions and in particular CO_2 which is the main responsible for climate change. This global warming can result in natural disasters such as floods that occurred last summer in Belgium [4].

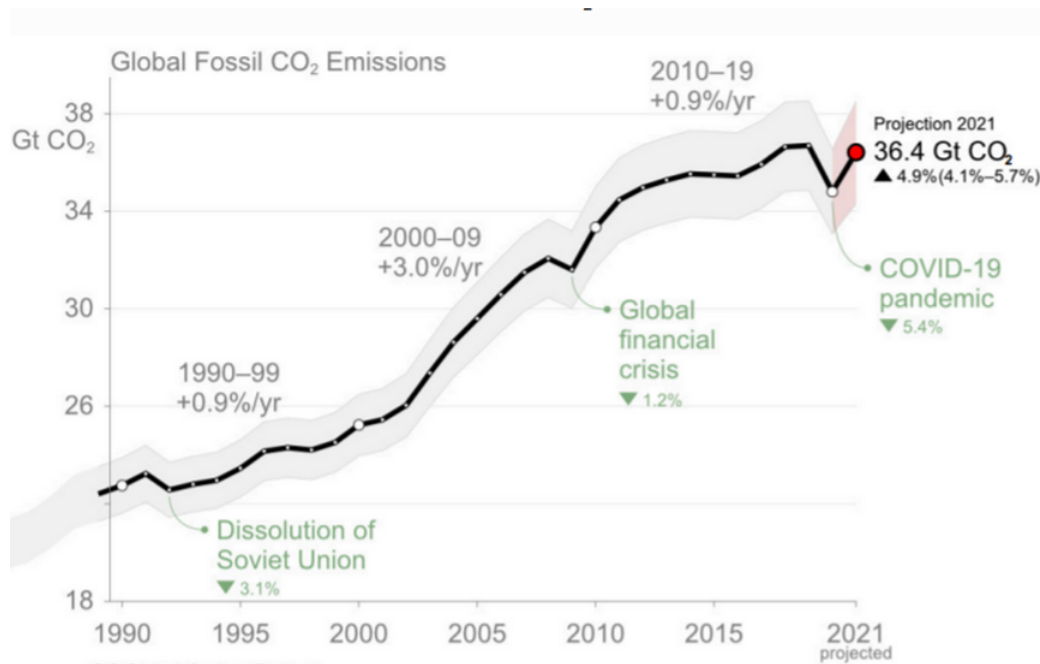


Figure 1.1: Global fossil CO_2 emissions [1]

Almost all countries are concerned for the suppression of global warming and the reduction of CO_2 emissions. There are different ways studied today to decrease CO_2 emissions and

the most common idea is to use more renewable energies. The past decade a lot of progresses were made in this domain resulting in a reduction of the levelised cost of electricity for solar and wind energy technologies by respectively 85% and 66% (Osman et al., 2021[30]). Despite these improvements, today we still need to use fossil-based sources to generate the global energy demand as can be seen in Figure 1.2. Furthermore, developing countries like India have vast reserves of coal and seemingly it has no plans and intentions to cut down coal consumption.

As it is quite challenging to get rid of fossil fuels completely and to shift to renewable energy technologies, a second important idea to fight against global warming had to be investigated. Carbon Capture Utilisation and Storage (CCUS) has gained a lot of attention recently as one of the promising ways to mitigate CO_2 emissions. CCUS can reduce carbon emissions on a large scale in the short to medium term, including the capture, transportation and storage of CO_2 . This method expected to contribute to a reduction of the total CO_2 emissions of 17% by 2035 (Li et al., 2021[21]) and to reduce by 50% the emissions from industrial-scale power generation plants by 2050 (Osman et al., 2021 [30]).

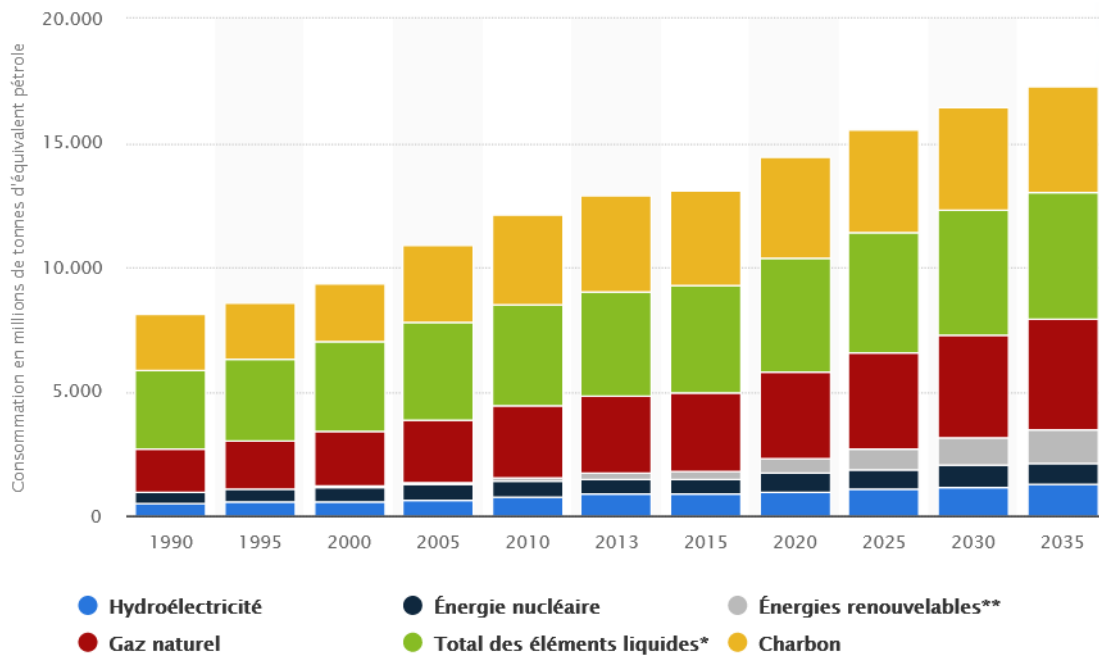


Figure 1.2: Projected world energy consumption between 1990 and 2035 [8]

To achieve the carbon neutrality imposed by the European Union in 2050, one solution is to use carbon capture technologies at the exit of power plants producing electricity.

The objective of this thesis is to develop a carbon capture model that treat gases from the CHP plant of the Sart Tilman in order to decrease the CO_2 emissions in the atmosphere.

Chapter 2

Objectives

The objective of the present work is to develop a process simulation model of a CO_2 capture unit for an existing combined heat and power (CHP) plant at Sart-Tilman, Liège. This biomass cogeneration plant has a maximum rated electrical power of 3.25 MW and a thermal power of 7 MW.

Different configurations of CO_2 capture are studied in order to determine which option is the most suitable for this CHP plant. One of the options is to use a new benchmark solvent for this kind of application which is a 40% aqueous solution of AMP and PZ (1:2 molar ratio). Indeed, it has shown big improvements in comparison with the conventional benchmark called MEA. This will be detailed later in this thesis. The process simulation, validation and optimization will be performed using a process simulation software, Aspen Plus V11.0. Different parameters will be varied in order to decrease as much as possible the energy consumption related to the capture plant which is one of their main drawback.

The present thesis begins in Chapter 3 with a brief presentation of the most common CCUS and different carbon capture techniques (chemical, physical and membrane) and technologies (pre-combustion, oxyfuel combustion and post-combustion). The post combustion capture (PCC) with chemical solvent will be explained in detail as it is the most mature technology for CO_2 capture.

Then, in Chapter 4 a description of the characteristics of a good solvent will be given and the interest in a new benchmark solvent will be justified through comparisons with the traditional MEA solvent. Different pilot plant studies and techno-economic researches using AMP+PZ as solvent and promising results will be described.

In other words, Chapter 3 and 4 will review a very large amount of carbon capture techniques and the goal is to justify the process and the solvent used for the following of this work.

In Chapter 5, a brief description of the CHP plant in Sart Tilman will be presented

through different characteristics and mode of operation. The exact composition of the fumes will also be given.

Then, in Chapter 6 focus will be kept on the construction and validation of the model. First the process will be described with the role of the different blocks and then the thermodynamic model and reactions evolving in the simulations will be presented. Finally, the validation will be performed by trying to reproduce experimental results from a pilot plant study.

In Chapter 7, parametric optimisation will be performed with the objective to reduce energy consumption of the capture process by varying different parameters in the model. The new benchmark solvent will be used and a typical flue gas composition coming from the CHP plant in Sart Tilman will be treated. The optimisation will first be performed using equilibrium mode calculation in the columns and then in rate-based mode in a second step to take into account heat and mass transfer limitations and also performing the sizing of both columns.

To conclude, it is possible to implement different improvements in the process developed in this work to obtain bigger savings in energy. Different suggestions to still decrease the energy consumption of the process will be presented.

Chapter 3

Carbon Capture Use and Storage (CCUS)

As mentioned earlier, CCUS is one of the most promising ways to reduce CO_2 emissions. Figure 3.1 depicts various processes involved in CCUS. First CO_2 is captured at the exit of a power plant. Then, this CO_2 is transported via pipelines or ships to an injection site where it will be sequestered for long-term storage in some suitable geologic formations. The CO_2 can also be transported to be re-used for chemical or biological applications.

CO_2 capture is a fluid separation process to be integrated into industries and power plants. It is mature and used for many years especially in very big industries but the main problem involved in CCUS is the high operating cost involved in the capture process. It decreases a lot the efficiency of the power plant so it is not always interesting on a financial point of view for industries to install it.

In next years, in parallel with developing renewable energy sources and reducing energy waste, this technology should be part of an energy mix to reduce CO_2 emissions as the price to pay to use carbon capture will be lower.

This work will be focused on the first step of the CCUS process and in the following sections 3.1 and 3.2, the most famous techniques used to capture CO_2 will be presented. Next, the different processes which use these techniques will be briefly explained. For each of them tables describing advantages, disadvantages and maturity level of each technology will be shown. In section 3.3, some information about transport, storage and re-use of CO_2 will be given.

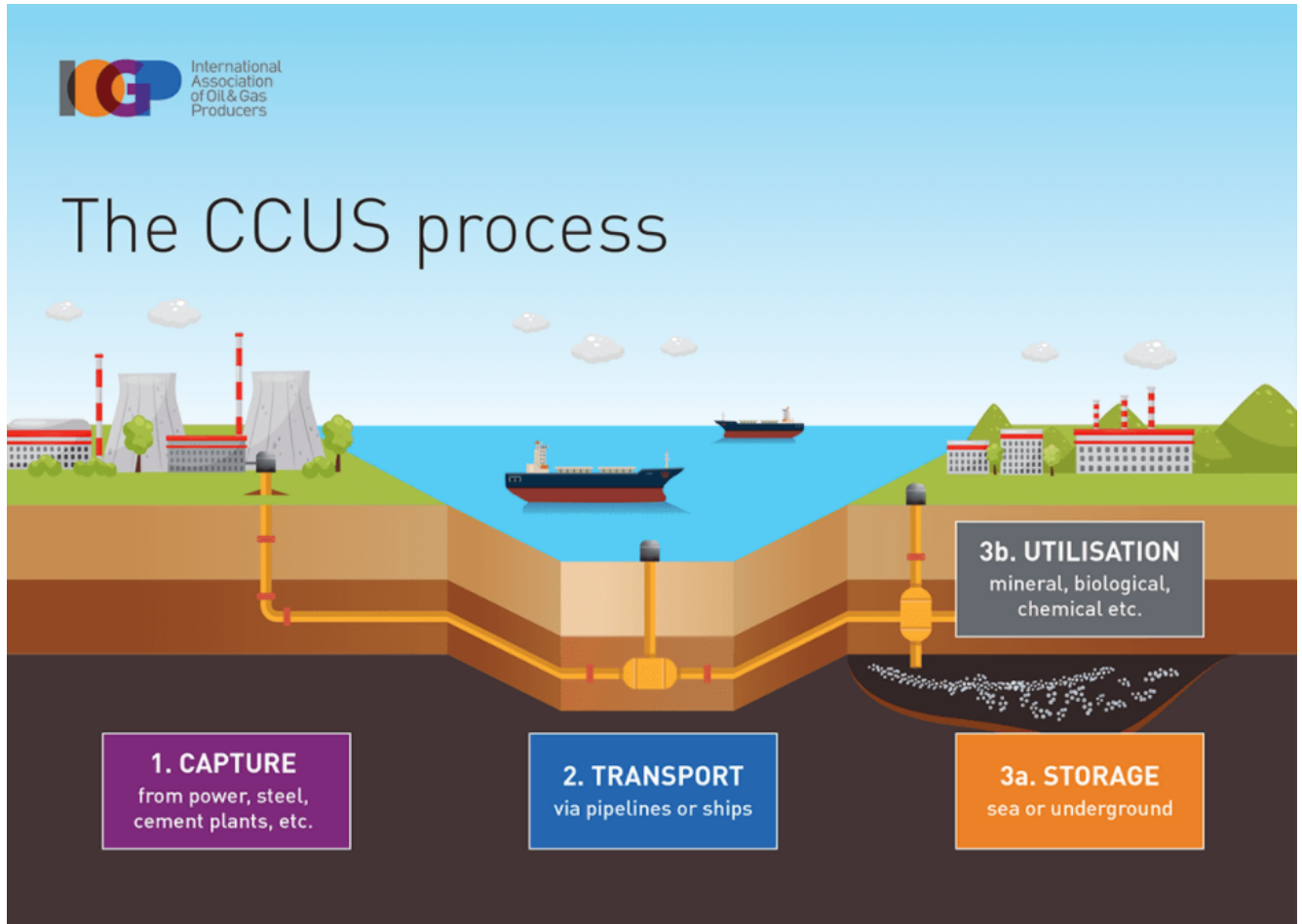


Figure 3.1: CCUS process [29]

3.1 Different techniques to capture CO_2

Up to now, the three most mature technologies used for capturing CO_2 in energy applications are chemical absorption, physical separation and membrane separation. These 3 techniques will be discussed in detailed in this section.

3.1.1 Chemical solvents

Chemical absorption is the most commonly used technique and the most mature capture method. CO_2 is separated from the flue gas by a reversible reaction with a chemical solvent. The solvent is typically amine-based but can also be salt solutions or ammonia.

Chemical absorption with an amine solvent is a cyclic process and uses two distillation columns (called absorber and stripper) which are the 2 most important components. In the

first column the CO_2 is absorbed by the solvent at quite low temperature around $50^\circ C$ and then in the second column the temperature is higher (around $120^\circ C$) so the chemical equilibrium of the reaction between the solvent and the CO_2 is reversed and the CO_2 is released. This thesis will be based on this technique and will be described later in chapter 6.

The main advantages of chemical solvents are ability to work with low acid gases partial pressures, high absorption and desorption mass transfer coefficients and capture level of acid gases up to ppm (Tohid et al., 2019 [28]).

The main disadvantages of these solvents are high energy requirement for solvent regeneration, the high price of materials, high heat of absorption, existence of side reactions, high corrosion, environmental damages and occasionally the treated gas will be saturated with water when using aqueous solution.

A very critical issue in using the absorption-desorption system is the energy requirement for solvent regeneration which required around 20–30% of the power produced by a power plant. The majority of energy consumption of the capture process is related to the regeneration unit so the design and operation of the regeneration unit have very high importance in the chemical absorption process (Tohid et al., 2019 [28]).

Tables 3.1 and 3.2 show the 3 different families mentioned before and their respective advantages and disadvantages:

The amine's family is the most developed and the most used in the literature and it is possible to combine both of them to compensate their disadvantages.

The use of ammonia is more complex and it is not really efficient.

Finally, one of the biggest problem to use salt solutions as solvent is the formation of precipitates in the reboiler .

In section 4.1 the characteristics of an ideal solvent will be deeper explained and the interest of developing new solvents like AMP+PZ used in this work will be shown.

Family	Name/Type	Advantage	Disadvantage
Amine	MEA/primary	<ul style="list-style-type: none"> • Cheap and easy to produce • Very reactive with CO_2 • High solution capacity 	<ul style="list-style-type: none"> • High corrosiveness • Poor thermal stability • Low capacity to absorb CO_2 • High heat of reaction with CO_2 and high energy consumption for regeneration
	DEA/Secondary	<ul style="list-style-type: none"> • Low vapor pressure • Less corrosive compared to primary amines 	<ul style="list-style-type: none"> • Difficult reclaiming of contaminants • Not proper for treatment of gas streams with a high amount of CO_2 • risk of formation of nitrosamines when secondary amines degrade • Forming corrosive degradation products with CO_2
	TEA/Tertiary	<ul style="list-style-type: none"> • Less solvent regeneration cost compared to MEA • Very resistant to degradation 	<ul style="list-style-type: none"> • Slower absorption rate in comparison with MEA
	MDEA/Tertiary	<ul style="list-style-type: none"> • Low corrosive • The CO_2 loading is higher than MEA 	<ul style="list-style-type: none"> • It has lower heat of reaction • Slow reaction with CO_2
	AMP/Hindered	<ul style="list-style-type: none"> • Ease of regeneration compared to MEA • High CO_2 loading • Very good CO_2 absorption • Higher degradation resistance than MEA 	<ul style="list-style-type: none"> • Lower CO_2-amine mass transfer rates than MEA • Comprises of bigger substituents that cause its carbamate unstable and easy to form a bicarbonate
	PZ/Cyclic	<ul style="list-style-type: none"> • Low corrosion rate • Higher resistance to oxidative and thermal degradation • Rapid formation of carbamates when it reacts with CO_2 	<ul style="list-style-type: none"> • Not highly soluble • Higher volatility compared to MEA

Table 3.1: Advantages and disadvantages of amine as chemical solvent (Tohid et al.,2019 [28])

Family	Name/Type	Advantage	Disadvantage
Ammonia		<ul style="list-style-type: none"> • High CO_2 absorption efficiency and capacity • Low energy necessity for stripping and low heat of reaction compared to MEA • No degradation • Lower price compared to amines • Producing value-added chemicals, such as ammonium sulfate and ammonium nitrate 	<ul style="list-style-type: none"> • More complex process compared to amine processes • Can not reduce the amount of CO_2 to very low levels in the product gas • Slow rates of reaction • Unwanted side reactions and problems of high ammonia levels entrained in the treated gas (need to work at temperature close to $0^\circ C$)
Salt solutions	Potassium salts	<ul style="list-style-type: none"> • High chemical solubility of CO_2 in solution • Easy desorption due to high temperature absorption • Low cost of solvent • Low toxicity and volatility • Low corrosion rate • Low tendency to degradation 	<ul style="list-style-type: none"> • Slow reaction rate and low mass transfer • Carbon steel corrosion problem (less than amines) • Precipitation in reboiler and pipeline of the process • Unsuitable for CO_2 capture from low CO_2 partial pressure sources (limited solubility of both carbonate and bicarbonate)
	Hydroxide	<ul style="list-style-type: none"> • Low solvent cost • High accessibility • Low toxicity and non-volatility 	<ul style="list-style-type: none"> • Precipitation in reboiler and pipeline of the process
	Amino acids	<ul style="list-style-type: none"> • High stability towards oxidative degradation • High chemical reactivity with CO_2 • Low vapour pressure and volatility • Environmentally friendly and non-toxic 	<ul style="list-style-type: none"> • Precipitation of carbonates at high CO_2 loadings • High desorption energy requirement • More expensive

Table 3.2: Advantages and disadvantages of Ammonia and salt solutions as chemical solvents (Tohid et al., 2019 [28])

3.1.2 Physical separation

Physical separation represents a family of technologies like absorption, adsorption or also cryogenic separation. Focusing on physical absorption and adsorption, the solvent or adsorbent is physically attached to the CO_2 in both cases. The solvent is liquid in the first case whereas we have a solid surface for the adsorption. Solid sorbents are potentially a lower-energy alternative to liquid absorbents.

In these processes, once the saturation in CO_2 is reached, the regeneration is often done by a reduction of pressure called Pressure Swing Adsorption and an addition of heat is not necessary in contrast to the chemical absorption. However, other techniques to regenerate the sorbent also exist such as temperature (TSA), vacuum (VSA) or electric (ESA) swing adsorption (Chao et al., 2021 [6]).

Physical solvents have also greater absorption capacity resulting in lower solvent recirculation rates than chemical absorption. Finally, another advantage of the physical solvent is their selectivity between acid gases. The disadvantages are their sensitivity to acid gas partial pressures (it must be high), difficulty in meeting H_2S specification and necessity to have a low concentration of inert gases because it becomes too expensive to compress if too much inerts are present (Tohid et al., 2019 [28]).

A summary of different physical solvent used in the literature (Dimethyl Ether of Polyethylene Glycols, Methanol, Propylene Carbonate and N-methyl 2Pyrrolidone) with their respective advantages and drawbacks is developed in Table 3.3.

Physical solvent will not be used in this work due to their lower interest for our application but more information about physical solvents can be found in the paper of Tohid et al. (2019 [28]).

Solvent Process	Advantage	Disadvantage
DPEG	<ul style="list-style-type: none"> • Low vapour pressure of solvent, hence the water wash is not essential to recover solvent • Applicable in wide temperature range (18 to 175 °C) • Proper for selective H_2S removal 	<ul style="list-style-type: none"> • Higher viscosity in comparison with other physical solvents
Methanol	<ul style="list-style-type: none"> • Available and low price • Not the most toxic • Flexible with different possible flow schemes 	<ul style="list-style-type: none"> • High vapour pressure and high solvent lost • Complex process configuration • Higher selectivity for H_2S over CO_2
Propylene Carbonate	<ul style="list-style-type: none"> • High solubility of CO_2 and other gases. • Low heat of solution for CO_2 • Low vapour pressure at operating temperature • Low solubility of light hydrocarbons • Nonreactive toward all natural gas components • Low viscosity • Noncorrosive 	<ul style="list-style-type: none"> • Solvent is not suitable if H_2S is present in more than trace concentrations • Higher vapour pressure than DEPG • The reaction between solvent and water and CO_2 is slow and irreversible at 90°C
NMP (N-methyl-2-pyrrolidone)	<ul style="list-style-type: none"> • Able to deliver gas flows that contain less than 0.1% CO_2 • Applicable to other processes such as acetylene recovery from pyrolysis gases 	<ul style="list-style-type: none"> • Higher vapour pressure than DEPG and PC • Higher selectivity for H_2S over CO_2 • Water washing for solvent recovery

Table 3.3: Advantages and disadvantages of selected physical solvents [28]

Physical-chemical solvent and mixture of solvents

Nowadays, it is a very interesting approach to combine different properties of different solvents and to take advantages of both and to compensate their disadvantages. A lot of combinations are possible, giving flexibility to the solvent design in order to obtain a desired specific characteristic.

Typically, a mixture of two different chemical solvents or one chemical solvent with a physical solvent can be made.

In the first case, by combining cleverly different amines, the benefit of low energy requirement for regeneration and fast reaction kinetics with high absorption capacity can be reached (this is typically what will be used later in this work with AMP and PZ).

In the second case, the chemical solvent purifies the gas stream to rigorous levels and the physical solvent captures the acid gas bulk simultaneously (Tohid et al.,2019 [28]). Further information can be found in the paper of Tohid et al. (2019 [28]).

3.1.3 Membrane separation

The membrane separation is another common technique to capture CO_2 . Membranes are thin barriers over which one species in a gas mixture is more mobile than others so the partial pressure difference across the membrane provides the driving force for the separation of the gases (IEAGHG report,2019 [32]). They can be made with different materials such as polymeric, inorganic, metallic or ceramic materials. They are developed so that they can be a semipermeable membrane that allows CO_2 molecules to pass through in contrary of the rest of the flue gas content.Using membrane separation for CO_2 capture is simple and does not involve chemicals or regeneration and capital costs are moderate (Chao et al., 2021[6]).

Polymeric and hybrid membranes are the most investigated ones because they have relatively high separation selectively, low cost and good membrane processability (Chao et al., 2021[6]). Most membrane applications are still under development because the efficient membrane separation needs a much higher initial pressure with a concentration in CO_2 of 20% or higher which is a big difference with other techniques.

When comparing membrane separation and basic amine absorption, the energy consumption of a membrane separation is higher than that of a basic amine system for CO_2 streams containing 10% or less CO_2 . Furthermore, commercial membranes cannot be applied at high temperature because it necessitates compression and cooling steps. There are also issues of membrane stability at higher temperature. More information about membranes are available in the papers of Chao et al.(2021 [6]) and Osman et al. (2021[30]).

3.2 Different processes for CO_2 capture

In literature, mainly three processes are available to capture CO_2 , which are pre-combustion, oxy-combustion and post-combustion carbon capture. Figure 3.2 presents them respectively. The biggest difference between each processes is the position of the separation of CO_2 in the flowsheet of the process as it is clearly mentioned in their respective name and visible in Figure 3.2 . In this section, these 3 main different processes will be described and compared.

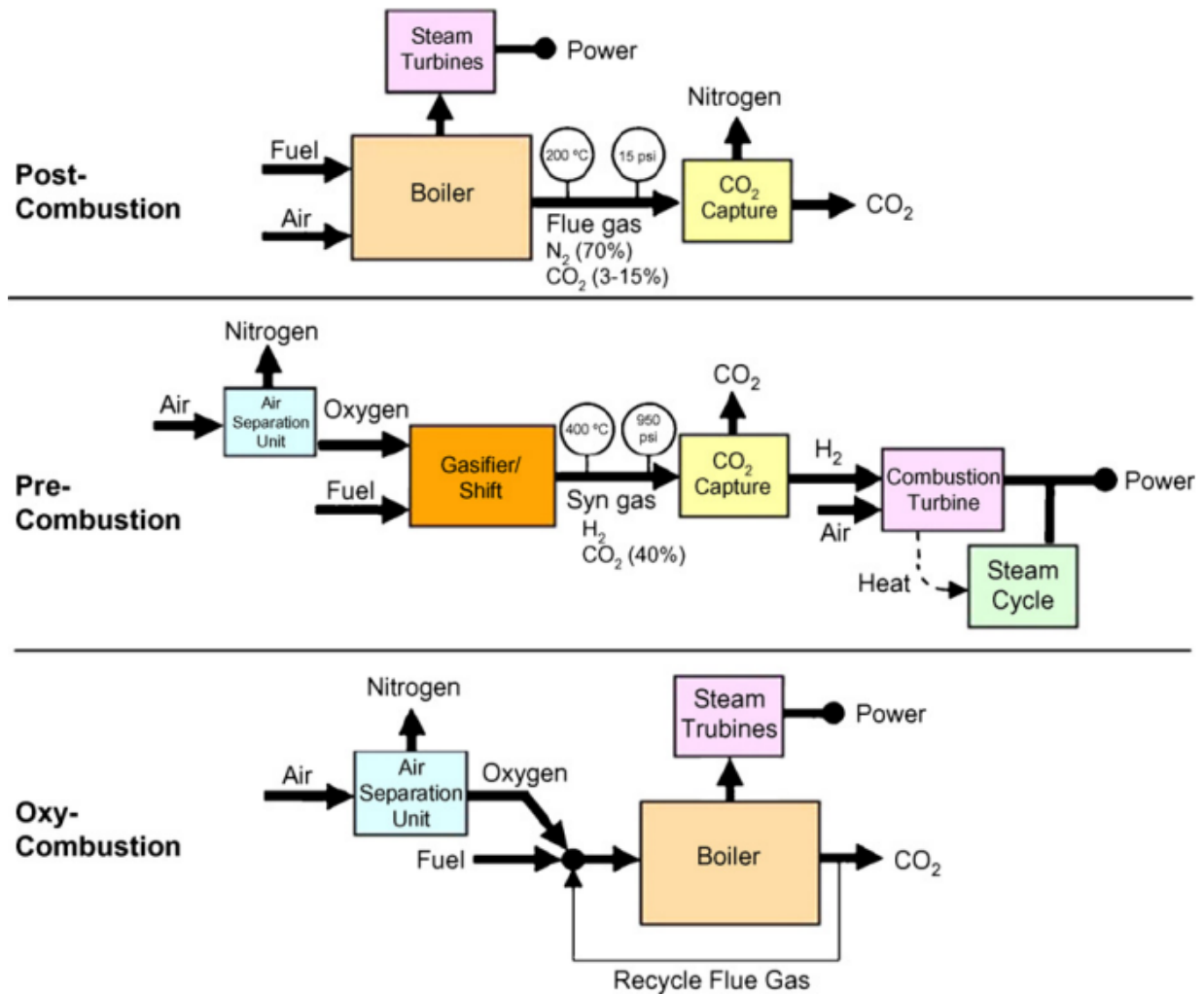


Figure 3.2: Schematic representation of the 3 different processes used for CO_2 capture [11]

The 3 processes may use the 3 techniques described in the section 3.1 and each case has its own advantages and disadvantages. A really important point is the degree of maturity of each technique so it will also be presented thanks to the different Technology Readiness Level (TRL) defined in Table 3.4. These are provided by the Electric Power Research Institute and give us a good idea of the maturity of the technology. The higher the TRL, the more mature is the technology.

	TRL	Description
Demonstration	9	Normal commercial service
	8	Commercial demonstration, full-scale deployment in final form
	7	Sub-scale demonstration, fully functional prototype
Development	6	Fully integrated pilot tested in relevant environment
	5	Sub-system validation in relevant environment
	4	System validation in laboratory experiment
Research	3	Proof-of-concept tests, component level
	2	Formulation of the application
	1	Basic principles observed, initial concept

Table 3.4: TRL level defined by the Electric Power Research Institute [32]

3.2.1 Pre-combustion

In pre-combustion capture, carbon is removed from the fuel before combustion. This can be achieved through steam reforming of gas or gasification of fuel as can be seen in Figure 3.3.

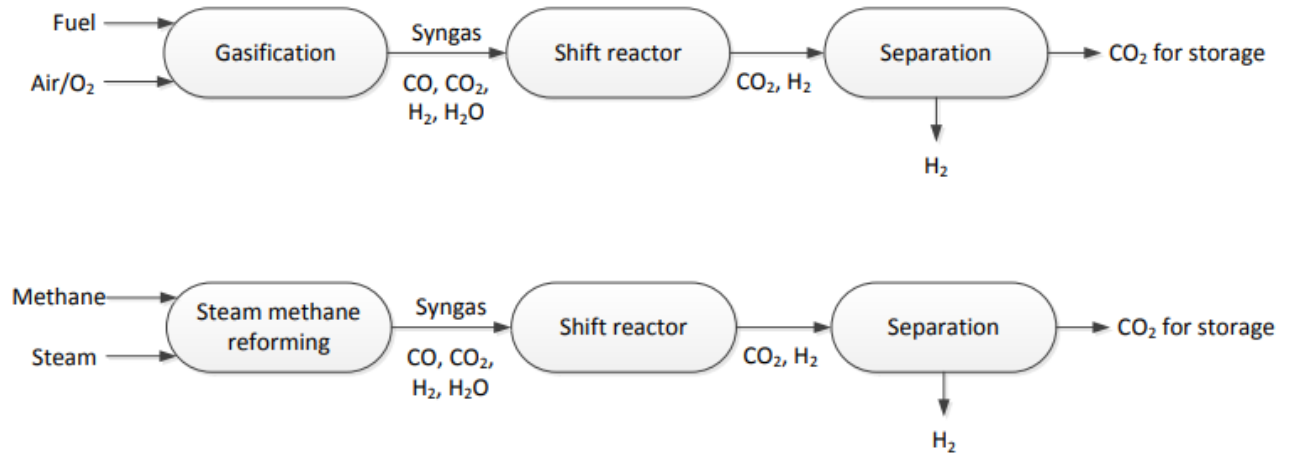


Figure 3.3: Pre-combustion CO_2 capture process via gasification and steam-methane reforming [32]

The idea is to produce a gas mainly composed of H_2 and CO_2 that can be further separated in order to obtain hydrogen that can be used as a fuel for electricity generation or to power hydrogen cars for example (see Figure 3.4).

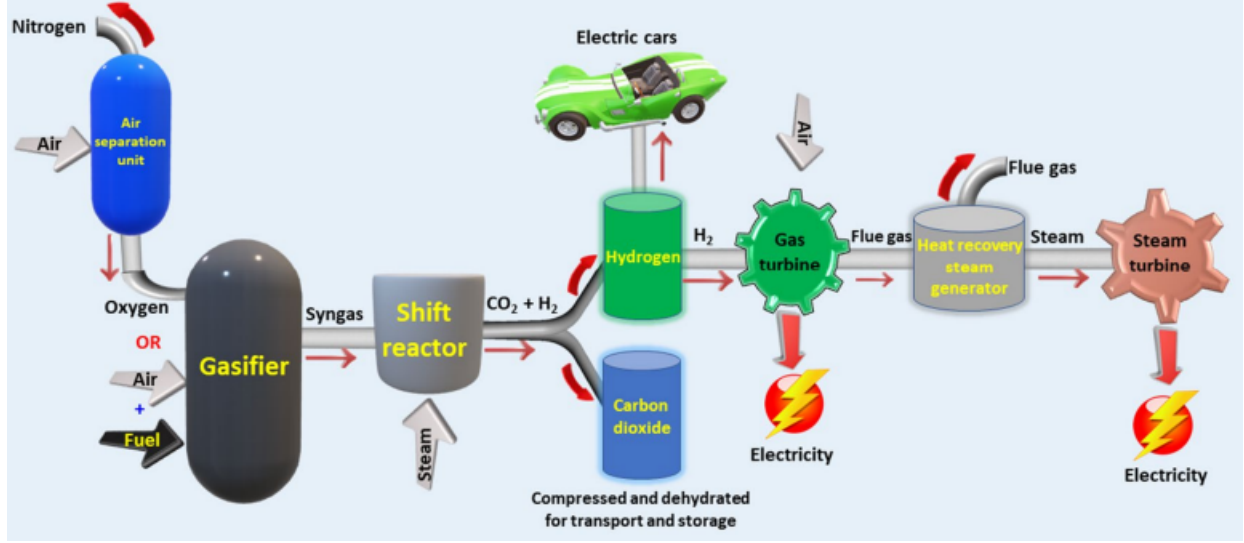


Figure 3.4: Precombustion carbon capture process and reuse [30]

The syngas is a mixture of CO , CO_2 , H_2 , CH_4 , H_2 and H_2O with other contaminants depending on the source fuel. First the mixture is cleaned to remove toxic impurities and then shifted via the well-known water-gas shift reaction ($CO + H_2O \rightleftharpoons CO_2 + H_2$) to generate a stream of H_2 and CO_2 visible in Figure 3.4. Then, the separation of CO_2 and H_2 is made by physical absorption and is facilitated by the high pressure of the H_2/CO_2 gas stream. A typical application of this technique is for IGCC plant where coal is transformed into syngas before combustion.

The interest of pre-combustion capture technology mainly comes from the higher efficiency to produce power via IGCC compared to pulverised coal combustion. Indeed, the CO_2 is separated at pressure higher than ambient pressure reducing compression requirements and as the partial pressure in syngas is higher than in combustion flue-gas streams, the efficiency of pre-combustion CO_2 capture processes is higher than their post-combustion counterparts.

TRL are given in Table 3.5 for the different techniques used for pre-combustion capture (more information about these techniques are available in the IEAGHG report (2019 [32])). The numbers are not so high with numbers between 4 and 6 so it can be concluded that improvements for pre-combustion are still necessary.

Technology	Current TRL	Development trajectory
H_2 separation membrane	5-6	→
CO_2 separation membrane	5-6	→
Solid sorbent	5	→
Chemical liquid absorbents	5	→

Table 3.5: Pre-combustion capture processes : Overview of development[32]

3.2.2 Oxyfuel combustion

The second process is oxyfuel combustion and has three main steps: Air separation (Nitrogen is removed from the air prior to combustion), combustion with pure oxygen (95-97%) producing mainly CO_2 and water and finally CO_2 compression and purification. The CO_2 (60-75% wet) produced still contains impurities (SO_x and NO_x) which will be removed through classical processes as can be seen in Figure 3.5.

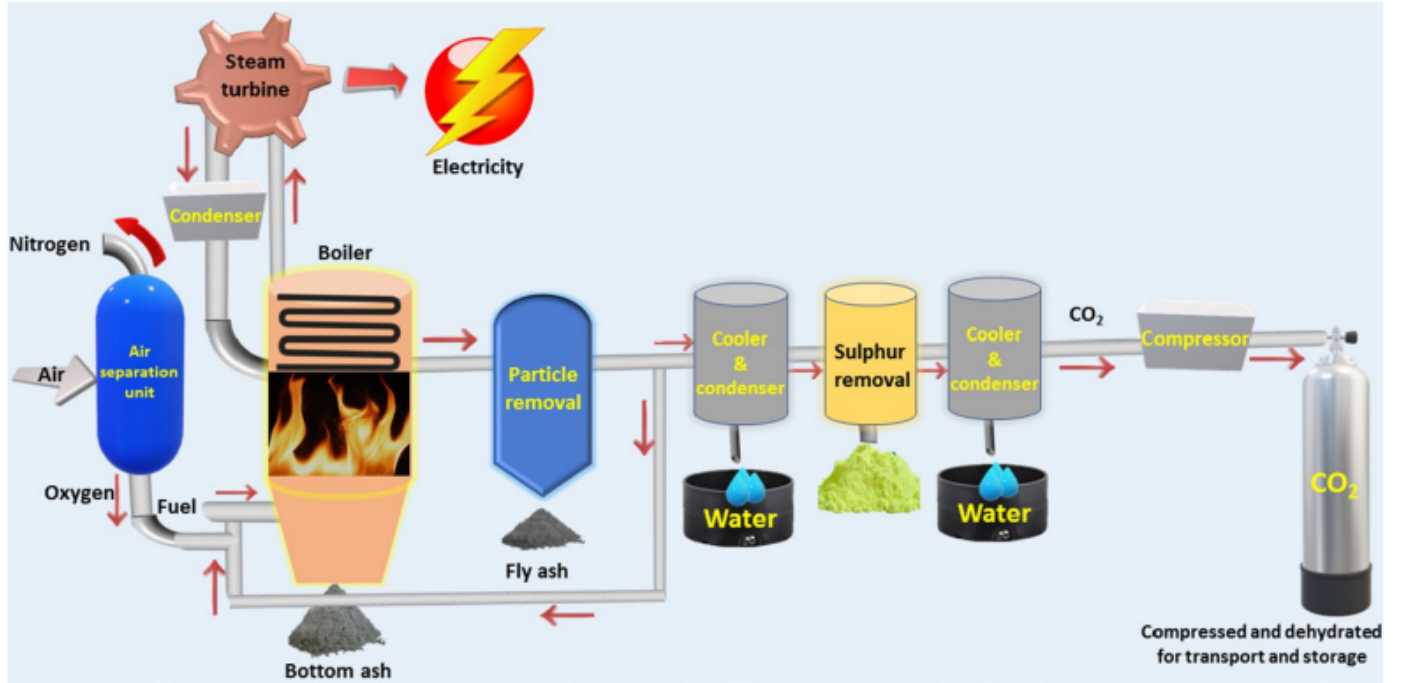


Figure 3.5: Oxyfuel combustion carbon capture process [30]

In oxy-combustion, the fuel is burned in an oxygen stream that contains little or no nitrogen. This leads to have mainly CO_2 and H_2O as gaseous products of the coal combustion. Then, water can be easily condensed so that the oxyfuel combustion produces a flue gas stream composed of CO_2 only and so further gas separation step is not always required for the flue gas depending on the desired purity.

In most of the cases, a cryogenic air separation unit (ASU) (unique commercially available technology) is used to meet the large volume of moderate purity (95%) oxygen required. This constraint of large O_2 production requirement can be cost prohibitive.

Table 3.6 presents current development progress for oxy-fuel combustion and it is obvious that TRL for this process are also not high enough.

Technology	Current TRL	Development trajectory
Pressurized oxyfuel combustion	5	→
Oxyfuel gas turbines	2-5	↑
High-T° air-separation membranes	4-7	→
Chemical-looping combustion	4-5	→

Table 3.6: Oxyfuel and chemical-looping combustion processes : Overview of development [32]

3.2.3 Post-combustion

In post-combustion capture, the CO_2 is separated from other flue gas constituents either originally present in the air or produced by the combustion. More precisely the CO_2 is absorbed into a chemical solvent which can be of different types.

Post-combustion capture process involves absorption-regeneration loop with amine-based solvent. The exhaust flue gas (with CO_2 concentration of about 10%) enters in the absorber and is put in contact with the solvent which will absorb the CO_2 at low temperature (around 50°C).

The rich solvent (loaded in CO_2) is pumped to the stripper via a heat-exchanger to increase its temperature around 110°C. Once in the stripper, the solvent is regenerated through the reverse chemical reaction that happened in the absorber because the equilibrium is displaced due to the higher temperature.

The regenerated solvent is fed back to the absorber once at the right temperature. After being separated from water in the condenser, the final product may reach a CO_2 -purity of 99% by volume and is ready to be transported by pipeline after compression (Chao et al.,2021 [6]).

This process is detailed in Figure 3.6 below with the use of monoethanolamine as solvent.

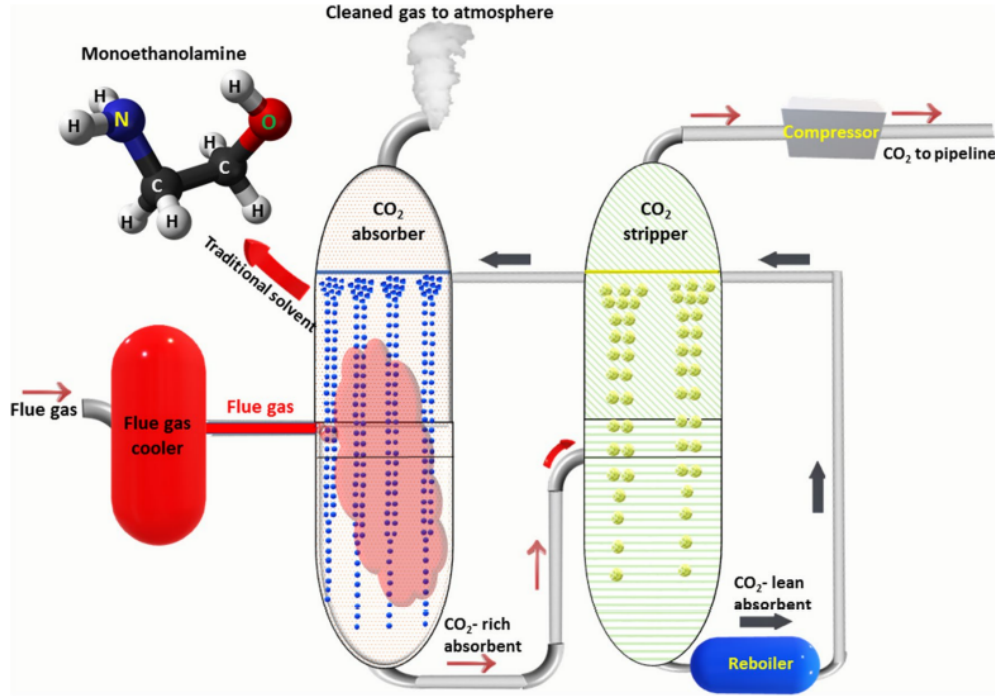


Figure 3.6: Post-combustion carbon capture process with chemical solvent [30]

Several research groups confirmed that absorption is the most mature post-combustion capture process: Among the assessment of post-combustion capture process, 57% apply absorption, 14% rely on adsorption, 8% use membranes, and 21% apply mineralization or bio-fixation (Chao et al., 2021 [6]). These results were expected since absorption gas separation has been largely applied in various petrochemical industries. The other systems need further development before being applied at a large scale.

A summary diagram of the 4 most famous techniques (absorption, adsorption, membrane and micro-algae) used for post-combustion CO_2 capture is shown in Figure 3.7. These are more detailed in Osman et al.(2021 [30]) and Chao et al. (2021 [6]).

A description of the advantages and drawbacks of these techniques are also available in Table 3.7. The use of solvent is the most interesting for our application. Membrane and solid sorbents are quite interesting alternatives but further developments are still necessary to consider large-scale developments. Micro-algae suffers from a big drawback which is a very low capture rate.

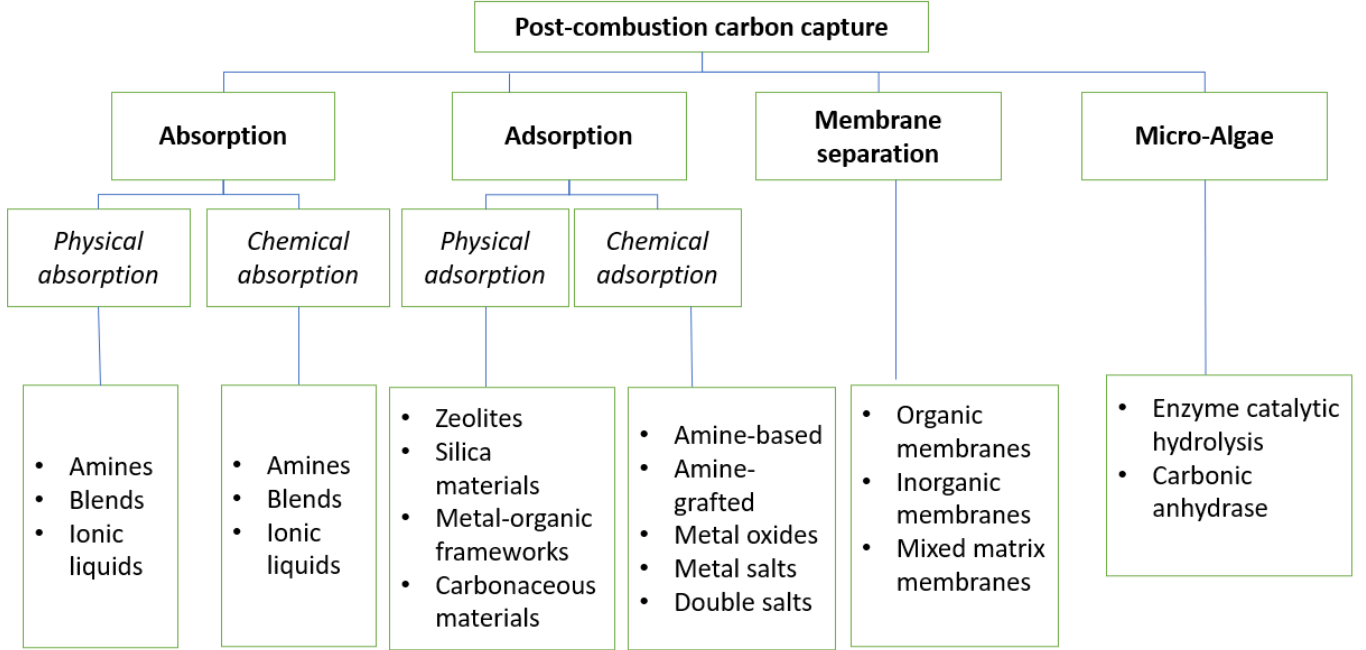


Figure 3.7: Post-combustion carbon capture technologies summary [30] and [6]

Capture technology	Advantages	Disadvantages
Solvent	<ul style="list-style-type: none"> • High chemical potential or driving force necessary for selective capture from streams with low CO_2 partial pressure • Ease of heat management 	<ul style="list-style-type: none"> • Significant amount of steam required to reverse chemical reactions and regenerate the solvent • Energy required to heat, cool, and pump nonreactive carrier liquid
Solid sorbent	<ul style="list-style-type: none"> • High capacities on a per mass or volume basis • Enabling capture from streams with low CO_2 partial pressure 	<ul style="list-style-type: none"> • Heat management more difficult • Sorbent attrition • Pressure drop can be high
Membranes	<ul style="list-style-type: none"> • No steam load nor chemicals • Simple design 	<ul style="list-style-type: none"> • More suitable for high-pressure processes • Difficulties to have both high recovery rate and high purity • High selectivity required • Poor economy of scale
Algae	<ul style="list-style-type: none"> • Highly efficient in a wide range of CO_2 concentration • Co-production of food, feed, bio-fuel and value-added products 	<ul style="list-style-type: none"> • Significant area required (Very low CO_2 capture rate)

Table 3.7: Post-combustion technology advantages and challenges [18]

The main advantage of this post-combustion configuration is its potential to be retrofitted to an existing plant without making big modifications to the current process, if enough space is available at the site. This makes post-combustion carbon capture the most researched and applied capture method today. This explains the fact that it can reach a TRL between 6 and 9 today (see liquid absorbents with aqueous amine in Table 3.8).

Table 3.8 shows different TRL for some technologies used for post-combustion. It can be noticed the value of 6 for membrane and solid sorbents and the value of 4 for micro-algae which is in link with what was previously said.

Technology		Current TRL	Dvpment trajectory
Liquid absorbents	Aqueous amine	6-9	→
	Amino acid and mixed salts	6	↑
	Ionic liquids	4	↓
	Water-lean absorbents	5	↑
	Precipitating	4-6	→
	Liquid-liquid separating	4-5	↑
	Catalysts	6	↑
Membranes	Polymeric membranes	6	↑
	Membrane contactors	5-6	→
	Hybrid processes	6	↑
Solid sorbents	Pressure-swing adsorption	6	→
	Temperature swing adsorption	6	↑
	Ca looping	6	→
Cooling liquefaction		5	→
Electrochemical separation		4	↑
Algae-based capture		4	↓
Direct air capture		5	→

Table 3.8: Post-combustion capture and high-temperature solids-looping processes: Overview of development[32]

3.2.4 Comparison

As a conclusion of this introduction, a lot of different techniques were presented and the choice of CO_2 capture method considerably related to the type of the plant which is producing CO_2 and the type of fuel utilized.

In the next parts of this work we will focus on the post-combustion with chemical solvent because it is the most mature technology as demonstrated previously. One thing more, post-combustion is directly applicable to the majority of existing power plants.

Nowadays, there are a lot of researches trying to develop other techniques like direct air capture, micro-algae, high-temperature solid-looping processes or cryogenic separation and other many examples but it is not the scope of this work. Further detailed information about these techniques can be found in the IEAGHG report (2019 [32]).

3.3 Transport and storage

Once the CO_2 is captured thanks to one of the techniques described above, it is interesting to know what can be done in the next steps of the process of CCUS. A short introduction of the last two steps of the CCUS process, which are transport and storage, is presented below.

CO_2 can be transported by 2 ways (G.Leonard, 2020 [17]):

- By ship with special tankers in liquefied state ($-30^{\circ}C$, 15 bar). It represents 100,000 tons transported/year (1000t CO_2 /ship).
- By pipeline in supercritical state (100 bar). Water and oxygen must be removed to prevent corrosion.

There also exist mainly 3 sites to store CO_2 with their own advantages and drawbacks (G.Leonard, 2020 [17]):

- In saline aquifers : Large capacity but reservoir properties under study and geology less well-known.
- In depleted oil and gas fields: Geology is well-known and storage safety has been proven but limited capacity.
- In coal seams : Possibility to recover methane but low permeability and limited capacity.

The re-use of CO_2 is also a really interesting subject but it is not the scope of this thesis so more information about re-use and storage are available in Osman et al.(2021 [30])

Chapter 4

Solvent choice: From MEA to AMP+PZ becoming the new benchmark

For several years, the benchmark technology for CO_2 capture application was chemical absorption with 30 wt% MEA but progresses in amine-based PCC have shown that current commercially technologies will have significantly better performance. One way of improvement is to use another solvent than MEA like AMP+ PZ paying attention to energy, environmental and economic performances.

In this project, post-combustion CO_2 capture is used because it is the most mature technology. The first idea was to use MEA as solvent because as it is the conventional benchmark but after extensive researches on alternative solvents, other solvents such as AMP+PZ proved to have better performance compared to conventional MEA. This choice will be explained in this chapter.

The available solvents used for CO_2 capture processes possess a number of drawbacks such as solvent degradation, high corrosivity, solvent loss and high regeneration energy requirement. Different ways to decrease costs or energy penalties and to improve the whole process can be listed (Tohid et al.,2019 [28]):

- Use alternative solvents
- Optimize the process flowsheet and process configurations
- Integrate energy with other sections of the power plant

This thesis is inspired by these different approaches to reduce energy penalties to make the PCC process more feasible to implement. The first step in this regards is to find an alternative solvent.

4.1 Characteristics of a good solvent

As explained previously, the main disadvantage of the post-combustion CO_2 capture with chemical solvent is the high energy requirement to regenerate the solvent so the key to have a good energy performance for the plant is having solvents where the equilibrium CO_2 loading changes substantially with temperature. We have also to take into account many constraints like the corrosivity of the solvent, the solvent degradation rate, HSE (health, safety and environment) related properties, viscosity and cost (Hoff et al., 2013 [14]). In fact, there are many other factors to take into account to choose the most suitable solvent.

A good solvent should also have a very low absorption enthalpy so that the regeneration is easier. Its loading capacity should be high and its reaction with the CO_2 should be rapid. Furthermore, it should possess a large loading cycle so that high CO_2 -recovery rates are possible at the absorber. It should also be cheap and stable at the process temperature. Novel solvents for carbon absorption are currently under development and tested (G.Leonard, 2008 [23]).

A synthesis about what was mentioned can be done by making a list of a combination of many parameters to take into account to help making comparison between different chemical solvents:

- Reaction with CO_2 : Mechanism, kinetic
- Physico-chemical properties of the CO_2 solvent system: Density, viscosity, diffusivity, solubility.
- Industrial availability of the solvent
- Cost of the solvent
- Solvent degradability: Reaction with other components (SO_x , NO_x ..) of the flue gas, irreversible reactions with CO_2 , effects on equipment.
- Regeneration of the solvent: Regeneration energy and efficiency

The main challenge of this technology is to reduce the energy consumption which has a dramatic effect on the global efficiency. For instance, the power generation efficiency of a typical 500 [MWe] hard-coal power plant is around 44% without PCC process. When the carbon capture process is added, the power generation efficiency can be reduced by 9.4–10.6% (Li et al., 2021 [21]). A second example is the case of a NGCC plant: An efficiency penalty of 7%-points reducing the efficiency from 58.3% to 51.2% is noticed when a capture process is added (Ystad et al., 2012 [38])

As shown in Figure 4.1, in next years it is expected to have a decrease in energy requirement thanks to the development of new alternative solvents.

The use of single conventional amine (e.g., MEA) to capture CO_2 , corresponds to a significant amount of energy of approximately 4.1 GJ/ t_{CO_2} . The current solvent used reduces the energy requirement by more than 30% to approximately 2.6 GJ. With development of mixed solvents (sometimes more than 5 compounds), the energy requirement of PCC is expected be reduced to 2.0 GJ. One of the main issues is to keep the solvent highly effective over long time periods and keep its composition constant (Liang et al., 2015 [22]).

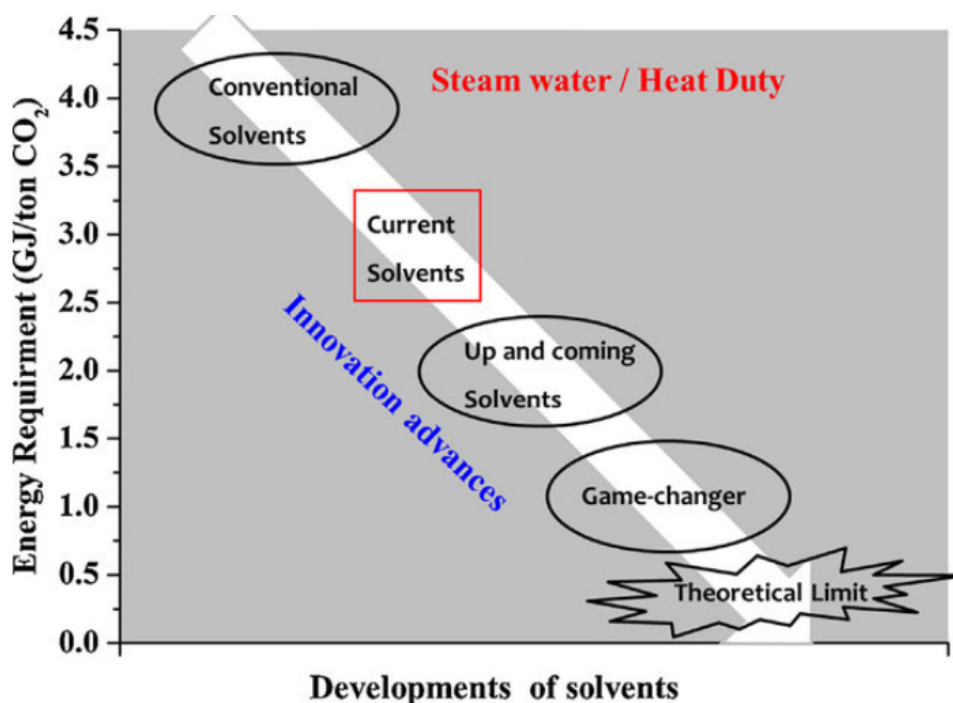


Figure 4.1: Energy requirement of post-combustion capture technologies from the past, present and the future developments when we have to capture one tonne of CO_2 (Liang et al., 2015 [22])

4.2 Chemical absorbents in pilot plants

A wide range of chemical solvents exists, like single amine solvents, amine-based blended solvents, ammonia based solvents, amino acid salt based solvents and carbonate salt based solvents. Some of them were used and tested within different pilot plants (Mumford et al., 2015 [27]).

A lot of information about chemical absorbents, their exact names, the companies involving in the researches and the future development work can be found in the paper of

Mumford et al. (2015 [27]). The most important information were synthesized in Table 4.1 with their corresponding advantages and disadvantages.

Type	Advantages	Disadvantages
Advanced amine	Extensive operational/design experience available; Freedom to determine the compositions of amine mixtures to optimise its performance	Corrosion; Solvent degradation; Stable salts formation; Amine emission; Viscous
Amino acid salt	Low vapour pressure; Low oxidative degradation; Low environmental impact and low emission; Reactive towards CO_2 ; Similar rate constants to MEA	Forms heat stable salts with SO_2 and NO; High heat of regeneration; difficult to produce in large quantities
Carbonate system	Low vapour pressure; Low toxicity; Low regeneration energy; Low environmental impact and low manufacture cost ; Non-volatile; No oxidative degradation; Multi-impurity capture; FGD unnecessary	Reduced kinetics
Aqueous ammonia	Does not decompose; High capacity and purity product; Competitive heat of regeneration	High ammonia vapour pressure; Slower kinetics than MEA; Solid ammonium bicarbonate formation; Ammonia emission; Harsh conditions due to low operating temperature
Immiscible liquid	Low regeneration energy; Non-aqueous environment to mitigate corrosion, formation of salts and degradation	Mechanism and chemistry unsure; Low maturity
Ionic liquid	High thermal stability; No water evaporation in regeneration nor vapour pressure, Tailorable	Expensive; High viscosity; High selectivity to water

Table 4.1: Chemical solvents comparison (Mumford et al.,2015 [27])

The most important thing to note is that advanced amines are already usable at large scale and their disadvantages can be compensated by finding new mixtures of amine. This is why a big interest from several companies for this kind of solvent can be noticed. In the followings of this work, this type of solvent will be used. Other chemical solvents lack of experimental data and/or maturity to be developed on a large scale.

4.2.1 Amines as solvent

As mentioned before, the most mature chemical solvent is advanced amine but there is still quite a lot of different amines that can be used for CO_2 capture. In this subsection, a direct comparison between these different amines will be performed.

Alkanolamines are the most well-known solvents used for CO_2 absorption (Tohid et al., 2019 [28]). Over the years, a lot of studies on different aspects from chemistry and kinetic reactions to thermodynamic analysis and process modelling in the different type of unit operations were done, hence a lot of data is available in the literature.

The amine absorbents studied in the literature are classified into primary amines, secondary amines, tertiary amines, sterically hindered amines and polyamines in link to to their molecular structures as can be seen in Figure 4.2.

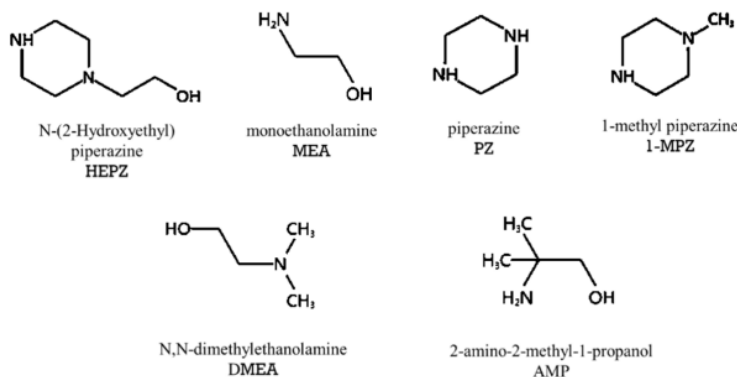


Figure 4.2: Molecular structure of famous alkanolamines used for chemical absorption of CO_2 (Li et al., 20121 [21])

Some important characteristics of these different alkanolamines can be specified: Primary (MEA and 1-MPZ), secondary amines and diamines (PZ) have all three a fast reaction rate, high absorption heat and low absorption capacity. Sterically hindered amines (AMP) and tertiary amines (DMEA) have high circulating absorption capacity, low heat of absorption and slow absorption rate (Li et al., 2021 [21]). These families of amine are also described in the paper of Tohid et al.(2019 [28]).

In a recent study, Li et al. (2021 [21]) compared the performance difference (based on the energy consumption, cyclic absorption and absorbent loss) between HEPZ and all the different molecular structures visible in Figure 4.2. Simulation results of this interesting study can be seen in Table 4.2 and more information about the development and results about these 5 new amines are available in Li (2021 [21]). It can be noticed the lowest reboiler duty for AMP and HEPZ and the highest value of cyclic capacity for AMP.

Absorbent	MEA	PZ	1-MPZ	DMEA	AMP	HEPZ	Unit
Q_{reb}	3.415	4.657	3.316	3.207	3.168	3.018	GJ/ t_{CO_2}
Cyclic capacity	1.5234	0.7247	2.0575	1.0839	2.2883	1.1938	mol CO_2 / kg solv
Solvent loss	0.342	0.142	2.177	29.212	2.466	0.087	mol/s 10^{-3}
Loss/Solv rate	0.14	0.1	0.98	3.23	0.52	0.02	%

Table 4.2: Regeneration energy, solvent loss and cyclic capacity of different solvents [21]

The last researches focus on having a mixed system of alkanolamines with different reaction mechanisms to combine the advantages of 2 different amines to have typically a high

circulating absorption capacity with a rapid absorption rate. This is what will be used later and deeper explained in this work in section 4.3.

4.2.2 Disadvantages of MEA and comparison with AMP+PZ from literature

Conventionally, MEA is the most commonly used absorbent in the process of absorbing CO_2 by amines. Due to the accumulated process experience and performance, it is often considered as the reference solvent for new absorbents. Nevertheless, the regeneration energy needed for the MEA solvent to capture CO_2 is very high and MEA degrades during desorption operation with high temperature. This leads to an increase in the cost of overall carbon capture plant and is unacceptable for long-time, large-scale carbon capture deployment (Li et al., [21]). In addition, AMP, PZ, and MDEA are found to have better oxidative and thermal stability than MEA which is really important in PCC applications (Voice 2013 [33]).

Different interesting studies which directly compared performances of MEA and AMP+PZ on different point of view can be presented briefly through their main results and conclusions:

A first interesting result comes from Bruder et al.(2011) [5], experimental data and a simplified model for the absorption of CO_2 into aqueous solutions of AMP and PZ are reported. If the maximum loading found in tests for AMP/PZ (3+1.5 M) and for 30 wt% MEA systems is considered, the AMP/PZ system has twice the CO_2 partial pressure at 120°C compared to MEA and 128% higher specific cyclic capacity when the temperature of operation is between 40 and 80°C.

Mangalapally et al.(2011 [24]) compared MEA (0.3 g/g monoethanolamine+0.7 g/g H_2O) to two new solvents, CESAR1 (0.28 g/g AMP +0.17 g/g PZ + 0.55 g/g H_2O) and CESAR2 (0.32 g/g 1,2-ethanediamine+0.68 g/g H_2O) which were developed in an EU-project. The two new solvents and MEA were studied in the same way in the pilot plant and detailed experimental results are reported for all solvents.

In this thesis, interest is focus on CESAR1 and results from this study indicate similar kinetics for CESAR1 and MEA so it is relevant to directly compare the pilot plant results for these 2 solvents. CESAR1 shows improvements compared to MEA with a reduction of 45% in the solvent flow rate and 20% in the regeneration energy (Mangalapally et al.,2011 [24]). This work will be used later in Chapter 6 for the validation of our model.

A third important comparison study was achieved by Sanchez Fernandez et al.(2014 [10]). This paper examines the performance of natural gas combined cycle (NGCC) power plants and advanced supercritical (ASC) pulverised coal with two post-combustion CO_2 capture units. The capture unit used is chemical absorption with the same advanced amine solvents

for the comparison: The aqueous solution called CESAR-1 (AMP and PZ) and the conventional MEA solvent.

The comparison between the mentioned technologies is based on the technical assumptions and method provided by the European Benchmarking Task Force (EBTF) methodology in order to establish a common European Standard for comparative studies (Sanchez et al., 2014 [10]). Initially, the resulting net electric efficiencies for the power plants without CO_2 capture were 58.3% and 45.25% for the NGCC and ASC PC cases respectively. When a CO_2 capture system is applied, it is known that the efficiency of a plant decreases as it was previously mentioned. In this case, for the ASC power plant, the CESAR-1 capture unit decreases the efficiency of the plant by 9.4% points while the MEA capture unit decreases the efficiency by 11.7% points. Similarly for the NGCC power plant, the reductions are 8.4% points for the MEA and 7.6 for CESAR-1 when capture is applied.

To sum up, the evaluation of CESAR-1 under the EBTF standards shows a reduction on power production penalty of 12% for the gas fired plant and 25% for the coal fired plant compared to MEA capture units (Sanchez et al., 2014 [10]).

The results for the fourth study come from process simulation model of Van Der Spek et al. (2016 [36]) and show that AMP/PZ post-combustion technology performs better than MEA technology from another aspect : The specific cooling water requirement is reduced from 4.1 to 3.4 GJ/t CO_2 when using AMP+PZ instead of MEA and the specific reboiler duty is also reduced from 3.6 to 2.9 GJ/t CO_2 . The coal power plant net efficiency with AMP/PZ capture unit is 37.2%LHV and 36.2%LHV with MEA. Initially, it was 46.1%LHV without CCS (Van der Spek et al., 2016 [36]).

Finally, a very interesting recent techno-economic assessment for two different types of power plant (An ultra-supercritical coal-fired power plant and a natural-gas combined-cycle power plant) was achieved in the IEAGHG report (2019 [32]) and the results are very clear: The use of 40 wt% formulation of AMP/PZ in a 1:2 molar ratio instead of 30 wt% MEA improves the generation efficiency for both power plants.

The main conclusion is that the costs of capture for the NGCC were reduced by 15% and for the coal-fired power station by 22% by using AMP/PZ instead of MEA. The detailed results of these studies are shown in Table 4.3.

In conclusion, for many years the benchmark solvent for post-combustion CO_2 capture was MEA 30%. Nowadays AMP + PZ becomes the new benchmark. Indeed many researches have been made to find a better solvent than MEA because of all the disadvantages it presents. The different comparison studies clearly shown the interest to focus on AMP+PZ as new benchmark solvent.

	Ultra-supercrit coal-fired PP			NGCC PP		
	W/O PCC	MEA	PZ/AMP	W/O PCC	MEA	PZ/AMP
Technical Performance						
Gross power output MW	900	900	900	890	890	890
Auxiliary power MW	83	266.1	215.6	12	161.8	128.2
Net plant HHV efficiency %	42.5	32.97	35.59	52.66	43.91	45.94
Net plant LHV efficiency %	44.4	34.48	37.23	58.25	48.57	50.82
CO_2 generation (t/h)	604	604	603.3	310	310	310
CO_2 emissions (t/h)	604	61	59.1	310	31	31
CO_2 emissions (t/MWh)	0.739	0.095	0.084	0.353	0.042	0.04
CO_2 capture (t/h)	0	543	544	0	279	279
Equiv E_{cons} (MWh/ t_{CO_2})	-	0.337	0.244	-	0.506	0.423
Economic Performance						
Total capital (million€)	1342.8	1681.1	1659.5	835.7	1172.8	1166.3
Specific capital (€/kW)	1647	2654	2424	939	1611	1531
Fixed OPEX (million€)	37.7	46.3	45.9	29.2	39.7	39.5
Variable OPEX (million€)	7.54	20.1	17.8	3.41	11.9	9.1
LCOE (€/MWh)	51.6	87	79.5	52.9	77.6	73.8
CO_2 -avoided cost (€/t $_{CO_2}$)	-	55	42.8	-	79.3	67.1

Table 4.3: Overview of technico-economic assessment for two types of power plants without PCC, with MEA 30 wt% and with capture using a AMP/PZ blend (IEAGHG report 2019 [32])

4.3 AMP+PZ as a new benchmark solvent

It is known that solvent-based absorption process presents a series of drawbacks, such as high energy requirement for solvent regeneration, solvent losses due to thermal and chemical degradation, evaporation, corrosion, reduced absorption capacity due to impurities. This is why new effective solvents are crucial to be developed for lower energy consumption and acceptable solvent degradation and corrosion. The use of mixed solvents may be the right approach towards this direction.

Today it is important to update the benchmark technology in the domain of CO_2 capture because it is crucial to ensure that any benefit coming from future researches and technology developments are visible against the current commercial offerings (IEAGHG report, 2019 [32])

As already mentioned, the goal of this work is to focus on a mixture of AMP+PZ because this mixture has already shown improvements compared to conventional MEA, according to

the studies presented in section 4.2.2.

In this section, focus will be kept only on AMP+PZ: First AMP and PZ will be more precisely defined through their own characteristics. Then, different modelling studies and recent data collected will be mentioned. Finally, some existing pilot plant examples will be briefly described through their location, their related power plant and/or their goal in the research domain.

4.3.1 Characteristics/definition of AMP+PZ

The solvent AMP+PZ is typically a mixture that combines 2 different amines to take advantages of both. Indeed, AMP/PZ is an interesting solvent for CO_2 capture owing to relatively low stripping heat requirement of AMP and high reactivity of PZ.

AMP is a sterically hindered amine meaning that they are based on primary or secondary amines with alkyl groups attached to the amino group. This group is inhibited from reacting with CO_2 because of steric hindrance. It has in many ways similar thermal properties as tertiary amines but in contrast to tertiary amines, it can react with CO_2 to produce carbamate (minor product) and bicarbonate/carbonate (major products) and reducing regeneration energy. AMP also increases absorption capacity by releasing free amine molecules to react with CO_2 (Mumford et al., 2015 [27]). It has also a better resistance to oxidation and thermal degradation (Li et al., 2014 [19]). However, the reaction kinetics of this system is slower compared to MEA.

AMP has shown high CO_2 equilibrium temperature sensitivity in aqueous solution so it is a good substitute for a tertiary amine (Hartono et al., 2021 [12]).

PZ is a cyclic diamine with two secondary amine nitrogens. It has a faster reaction rate, higher absorption capacity and higher resistance to thermal and oxidative degradation than MEA (Mumford et al., 2015 [27]). PZ is like an additive, often call an "activator", used to increase reaction rate and compensate the low reaction kinetics of AMP with CO_2 .

4.3.2 Modelling studies and recent data using software (Aspen, PPS)

Despite the recent interest for this blend, still today there is few information about all the reactions happening in the mixture AMP+PZ+ H_2O + CO_2 so it is interesting to note what is available in the literature about reactions evolving all these components.

In the work of Van der Spek et al. (2016 [36]), a process model of an AMP/PZ PCC plant was developed using Procédé Process Software (PPS). Its package contains the electrolyte-

Margules model for prediction of activity and it predicts fugacity thanks to the Peng–Robinson Equation of State. The model uses the gamma-phi formulation to describe VLE and it also includes reaction kinetics and mass transfer limitations for rigorous assessment of column performance.

The used physical property (sub)models were based on existing AMP+ H_2O + CO_2 and PZ+ H_2O + CO_2 ternary systems. Additional binary interaction parameters were fitted to describe binary interactions between AMP and PZ where needed, giving a model that represents the blend of the two solvents in a physically consistent way.

Dash et al.(2014 [7]) simulated a CO_2 capture from the flue gas stream of a coal fired power plant using RadFrac-RateSep block in Aspen Plus software. They used the absorption/regeneration process to conduct a rigorous simulation using an e-NRTL thermodynamic model that was regressed based on their own experimental data and performed a parametric study of model variables.

To conclude this part, a recent study published new data comprising CO_2 partial pressure, total pressure and the heat of absorption of CO_2 for over aqueous solutions of 3 M AMP and 1.5 M PZ and also total pressure and heat of absorption for different molar contents of AMP/PZ (3.0/0.0, 0.0/1.5, 0.5/4.0, 1.5/3.0, 2.25/2.25, 3.0/1.5, 4.0/0.5) as functions of CO_2 loading and temperature (Hartono et al.,2021 [12]).

4.3.3 Pilot plants studies

In the last decade , several pilot plant studies were made to study the influence of using AMP+PZ instead of other conventional solvent.

3.3.3.1 Esbjerg

In Esbjerg in Denmark, a 1 ton/h CO_2 capture test facility operating on a flue gas from a coal-fired power plant was performed. The pilot plant has been used to evaluate the performance of novel solvents developed under the CASTOR project aiming to reduce the cost of post combustion CO_2 capture through process optimizations and the development of more energy efficient solvents (Knudsen et al.,2011 [15]).

Test campaigns of approximately 1000 hours duration have been conducted with three different amine solvents: 30% MEA, CESAR 1 and CESAR 2. This study has shown that a minimum Specific Reboiler Duty (SRD) of around 3 GJ/t CO_2 was needed when absorbing CO_2 from a coal flue gas stream (12 vol% CO_2) when using AMP/PZ (Van der Spek et al.,2016 [36]).

3.3.3.2 Kaiserslautern

In Kaiserslautern, a gas-fired absorption/desorption pilot plant to remove CO_2 from flue gases was used. The plant was initially in operation at the University of Stuttgart and has later been transferred to operate in the University of Kaiserslautern in Germany. This pilot rig is used by the researchers to test the solvent under different flue gas conditions and different flue gas and solvent flow rate to achieve further progress in the development of economic PCC.

Kaiserslautern's plant was part of the integrated European Union project CESAR in 2011. Within this project, solvent candidates were first analysed and ranked and then, selected promising solvents were tested in pilot plants. Knowing the performances of a solvent in a laboratory scale, it can be decided whether this solvent should be tested in larger pilot plants or not (Mangalapally et al., 2013 [37]).

Using an AMP/PZ blend, they found SRD's between 3.2 and 5.0 GJ/ t_{CO_2} for a flue gas containing 10 vol% CO_2 which is higher than the values in the Esbjerg plant. This can be explained by the fact that the Kaiserslautern rig has smaller columns leading to insufficient time to react and to reach full chemical equilibrium (Van der Spek et al., 2016 [36]). It can be noticed that the maximum gas flow rate through the absorber was limited to approximately 100 kg/h

3.3.3.3 Loy Yang

In Australia, the pilot plant was initially designed to capture CO_2 from real flue gases at a rate of 50 kg/h using 30 wt% MEA. The flue gas treated (11–13 vol% CO_2) comes from a brown coal-fired power station and is captured by a solution of 25 wt% AMP and 5 wt% PZ for their study. The SRD's were between 4.9 and 6.4 GJ/ t_{CO_2} . The higher values were explained by different reasons: A low PZ content, too small absorption columns and the use of random packing instead of structured packing. In an optimized process, the same order as the Esbjerg pilot plant can be expected (Van der spek et al., 2016 [36]). More details about the design of the capture pilot plant at Loy Yang are available in the paper of Artanto et al. (2014 [3]).

3.3.3.4 Nideraussem

The most interesting recent pilot plant study was realised in a 18 month test in Nideraussem taking into consideration factors like specific solvent regeneration energy, flue gas quality, solvent recirculation rate, plant design, special operational conditions, vapor- and aerosol-based emissions, transient behavior and the chemistry of the solvent degradation (Moser et

al.,2021 [26]).

The post-combustion capture pilot plant at Niederaussem was constructed by Linde and commissioned in 2009 and has an accumulated operating time of more than 85,000 hours. The pilot plant (operated in a 24/7 mode) can capture up to 7.2 t of CO_2 per day at a flue gas flow of 1,550 kg/h (supplied by a 965 MWnet raw lignite-fired power plant) and a CO_2 content of the flue gas at the absorber inlet of approximately 15.2 vol.-%.

This test took part of the ALIGN-CCUS project (started on 08.04.2019 until 30.11.2020 for an amount of 12,275 operating hours) and aimed at accelerating the transition of current industry and power sectors into a future of continued economic viability and low-carbon emissions.

The main idea of the ALIGN-CCUS project is to understand the key mechanisms that are responsible for low solvent consumption and effect mechanisms to achieve the low emissions observed in the long-term testing and transmitting this knowledge to other capture plants and solvent systems.

It is important to note that a previous long-term testing over 13,000 hours with 30wt% aqueous MEA at the post combustion capture pilot plant at Niederaussem in 2011 was achieved and provided a unique data source for the further development of advanced solvent management and provided also better models for solvent degradation in amine-based CO_2 -capture (Moser et al., 2011 [25]).

A comparison between the 2 tests is possible: CESAR1 has shown that it has a significant lower specific solvent regeneration heat demand than MEA (CESAR1: 2,970 MJ/ t_{CO_2} ; MEA: 3,450 MJ/ t_{CO_2}). The second point is that CESAR1 is more stable to degradation. Indeed, during the testing campaign, CESAR1 showed only a linear degradation behavior which is not the case for the MEA-based solvent. Fresh CESAR1 solvent was refilled into the capture plant a total of four times (after 79 (1,896 h), 280 (6,720 h), 315 (7,560 h) and 458 days (10,992 h)) to compensate solvent losses by degradation, emissions and sampling. For comparison, the solvent consumption of MEA has linear degradation regime until 220 days, followed by exponential regime (After 55 days 0.21 kg/ t_{CO_2} , after 228 days 0.35 kg/ t_{CO_2} , and after 328 days 0.66 kg/ t_{CO_2}). This shows a significantly increase over the testing time due to non-linear degradation behavior. The solvent had to be replaced after 334 days because the concentrations of the degradation products of MEA increased so fast that the capture rate decreased rapidly (Moser et al., 2021 [26]).

In conclusion of this part, CESAR1 shown no self-accelerating degradation behavior but has a slow linear degradation rate. Compared to MEA, CESAR1 is also less corrosive, ammonia emissions are lower due to the higher amine resistance against oxidation but the level of AMP emissions requires the application of additional emission mitigation measures.

3.3.3.5 Future

Li et al. (2021 [21]) studied N-(2-Hydroxyethyl) piperazine (HEPZ) which has a chemical structure similar to PZ and has less volatility. It is studied to replace PZ as an "activator" to increase the CO_2 capture rate. However, only a part of the kinetic related research and CO_2 solubility of HEPZ/ H_2O has been studied. Up to now there is a lack of process simulation and thermodynamic modeling of the system HEPZ/ H_2O / CO_2 .

Chapter 5

Sart-Tilman cogeneration plant presentation

The plant studied in this thesis is the CHP plant of University of Liège supplying energy and heat to the University Campus through a heating network of 10 km total length. This network supplies heat to buildings like classrooms, administrative offices, research centres, laboratories but also a hospital which represents about 25% of the total heated area (Sartor et al., 2014 [34]).

During many decades the heat was generated by natural gas boilers but for 2012 a biomass CHP plant whose purpose is to feed the base heat demand of the campus was installed in order to limit CO_2 emissions.

The CHP allows a significant saving in terms of CO_2 emissions because the remaining part of thermal power needed by the network is provided by two natural gas backup boilers. More information about the plant is available in the paper of K.Sartor et al. (2014 [34]).

Developed by Cofély, this biomass cogeneration plant has a maximum rated electrical power of 3.25 MW and a thermal power of 7 MW. The amount of heat produced annually is estimated at 42 378 MWh. It also corresponds to roughly 70% of the heat requirements of the campus of Sart Tilman (University and hospital). Electricity generation is estimated at 10 321 MWh corresponding to about 30% of electricity requirements (University only) [9].

A schematic of the plant configuration is given in Figure 5.1. The biomass feeding system is a moving grid in a simple combustion chamber without staged-air combustion supply. As wood pellets are the constituents of the biomass fuel, flame temperature is too high and exhaust fumes must be recirculated and introduced after the secondary air injection. To keep grid temperature in acceptable ranges, high excess air is also required. The flue gas at the exhaust of the furnace goes successively through an evaporator (platten), screen tubes,

two super-heaters, one evaporator and four economizers. Before being directed to the stack, exhaust gases are filtered. The steam cycle is representative of a traditional cycle with extraction turbines (K.Sartor et al., 2014 [34]).

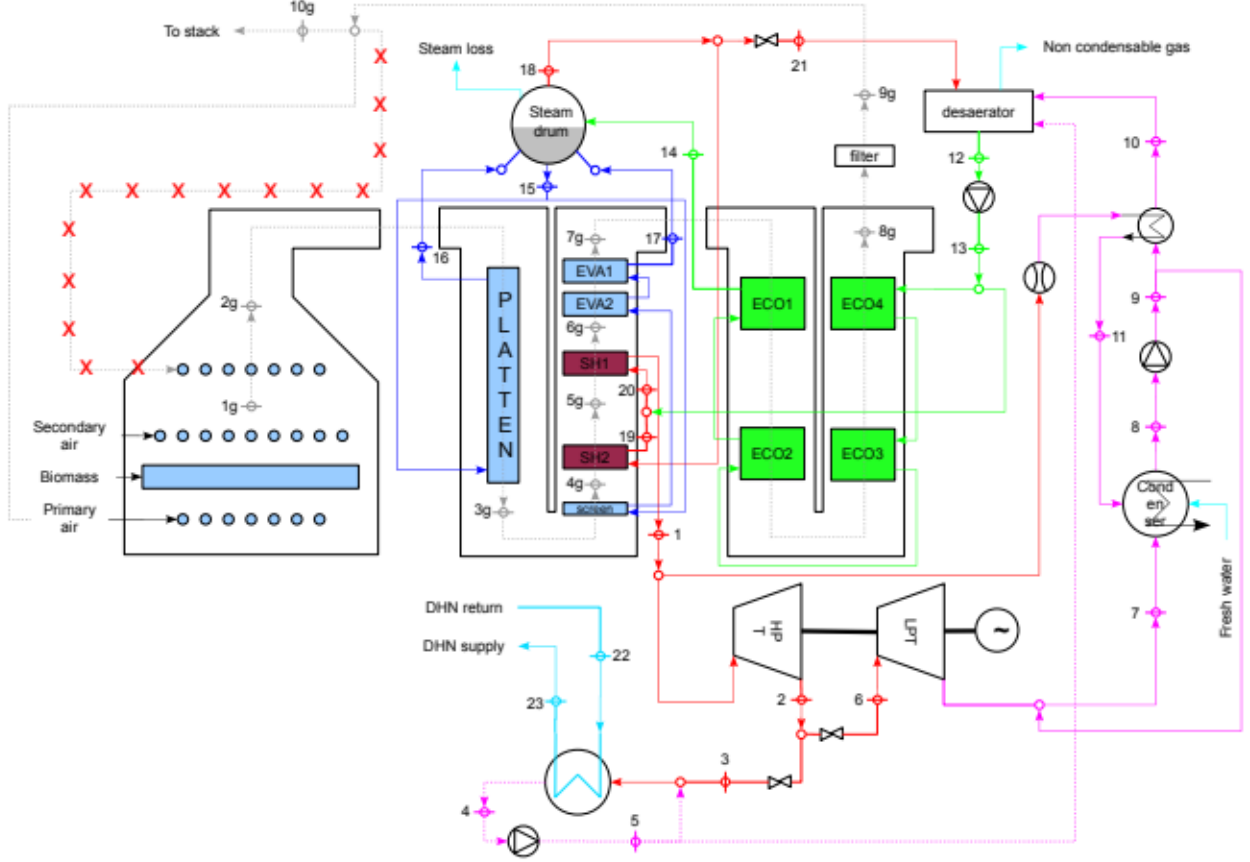


Figure 5.1: Schematic of Sart Tilman CHP plant [34]

A typical flue gas composition and flow rate coming directly from data collected in the CHP plant were furnished by K.Sartor which is involved in monitoring CHP plant management. The composition of the flue gas from the CHP plant of Sart Tilman is available in Table 5.1 and the corresponding flue gas flow rate is 23121 kg/h.

Component	CO_2	H_2O	N_2	O_2
% vol	11.54	11.19	70.51	6.753

Table 5.1: Typical flue gas composition of CHP plant

Chapter 6

Modelling of the PCC plant

Our model was constructed using the software Aspen Plus V11 and the process flow diagram is presented in Figure 6.1.

In section 6.1, the process will be described and the roles of the different blocks will be explained. In section 6.2, the thermodynamic and the reactions used in the model will be described in detail and in section 6.3 the validation of this model will be presented.

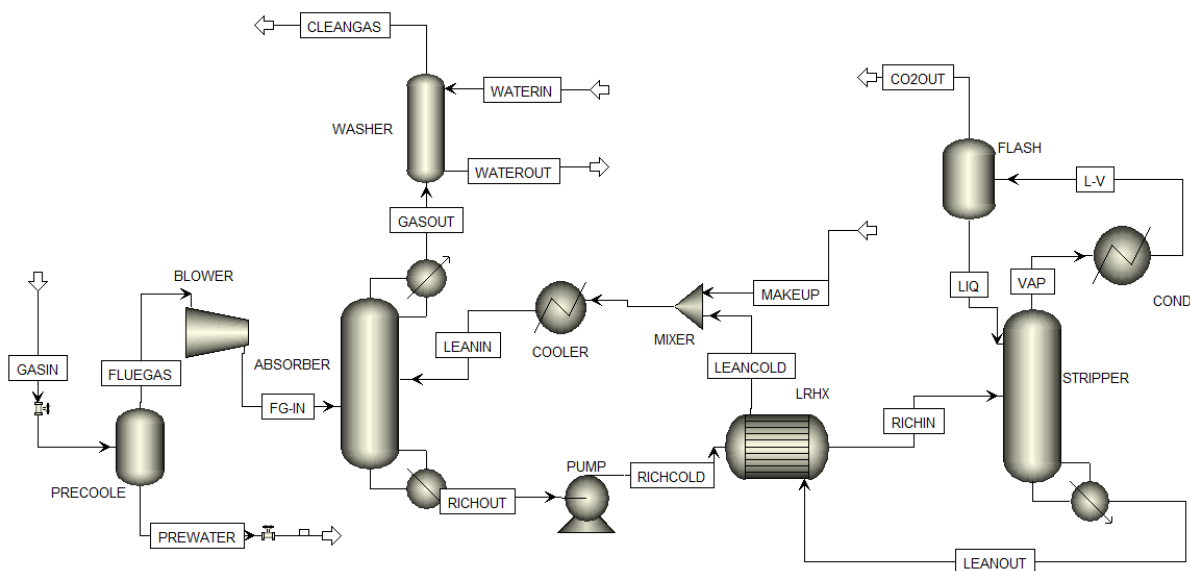


Figure 6.1: PCC model flowsheet

6.1 Process description

The flue gas coming from a power plant (brought to a temperature around 50 °C) enters the pre-cooler which will still decrease the temperature to decrease water contents of gas (the

composition of the PREWATER stream is more than 99% water). Then FLUEGAS stream enters the blower to increase flue gas pressure to 1.08 bar (and the temperature also slightly increases at the same time) to compensate for the pressure drops in the absorber.

After that, the gas (FG-IN) enters the bottom of the absorber while the amine solvent (LEANIN) is introduced at the top. CO_2 is selectively absorbed into an aqueous solution of amine via a reversible chemical reaction which is exothermic and occurs at a temperature around 60°C. The absorption column works at atmospheric pressure.

The GASOUT stream enters the washer to be purified to prevent sending some toxic components in the atmosphere and to recover the solvent because some components of the solvent are lost during the absorption. Indeed, water is also introduced in the washer to recuperate the solvent that could be lost in the GASOUT stream.

Using the equilibrium mode parameters of Table 7.10, if a water flow rate of 1000 kg/hr is injected in the washer, roughly no solvent loss happen in the process. The solvent recuperated in the washer is mixed in water (WATEROUT) and could be reused if the process configuration is improved but it is not represented in this case. The amount of solvent content in the different streams involved in this part of the flowsheet is given in Table 6.1 and can be compared to the solvent mass flow content in the loop (LEANIN). The amount of AMP and PZ recuperated in WATEROUT corresponds to respectively 0.2 and 0.08 % of the AMP and PZ mass flow evolving in LEANIN. In the long term, a non negligible amount of solvent can be saved.

The treated fumes (CLEANGAS) are released into the atmosphere with a very small solvent content as can be seen in Table 6.1 so the recuperation of solvent operates in a right away. It is still possible to increase the amount of WATERIN mass flow to prevent more solvent to escape in the atmosphere in order to meet environmental constraints.

Stream	Leanin	Waterout	Cleangas	Unit
AMP content	19130.7	37.9144	0.1	kg/h
PZ content	9246.06	7.133	1;5E-4	kg/h
Total mass flow	70000	1063.3	20554	kg/h

Table 6.1: Stream content in AMP and PZ with a WATERIN mass flow of 1000 kg/h

The RICHOUT stream loaded with CO_2 after absorption leaves from the bottom of the absorber and goes through a pump before entering the lean-rich-heat exchanger (LRHX). The pump increases the pressure of the rich solvent to 2.2 bar.

In the LRHX, the rich cold stream (RICHCOLD) exchanges heat with the lean hot stream coming from the stripper (LEANOUT). This allows the rich stream to be heated and the lean stream to be cooled down. The pitch point of this heat exchanger will be discussed later

but initially, the LRHX performed to get 110°C for RICHIN.

Before coming back to the absorber, the LEANCOLD stream goes through a cooler (LHX) to bring its temperature down to 40°C. Indeed, the lean solvent is still too hot after passing through the heat exchanger to perform an efficient absorption.

The rich stream from LRHX enters the stripper which is a packed column with a kettle reboiler. The rich amine enters the second stage of the stripper and flows down the column. The temperature inside is higher (around 120°C) so the equilibrium of the reaction between amine and CO_2 is displaced and the CO_2 is released. The influence of the stripper pressure will be discussed later.

Finally, the temperature of the stream (VAP) leaving the stripper is decreased to 40°C through the condenser giving a liquid-gas equilibrium (L-V stream). Water is condensed and can be separated from CO_2 in FLASH. The CO_2 can be collected at the exit of the process at a concentration around 98% (CO2OUT) and the water goes back to the stripper (LIQ).

To be complete, the role of the MAKEUP stream can be explained: It ensures mass balances of water and solvent components between what goes in the model (GASIN+MAKEUP) and what leaves the model (CLEANGAS+CO2OUT). It prevents water accumulation in the process and compensate losses. Solvent also suffers of degradation (not modeled here) and a small part can be lost in the gas so it has to be counterbalanced.

Different fixed parameters and specifications that were mentioned in the process description are given in Table 6.2 below. Parameters like number of absorber and stripper stages, solvent mass flow, stripper pressure and temperature approach will be detailed later.

Parameters	Unit	Data
Flue gas mass flow	kg/hr	23121
Solvent mass flow	kg/hr	70000
Absorber inlet flue gas temperature	°C	47
Absorber inlet flue gas pressure	bar	1.08
Absorber inlet solvent temperature	°C	40
Absorber top pressure	bar	1.01325
Model for absorber and stripper	-	RadFrac
Packing type for absorber and desorber	-	BX 400 by Sulzer
Model LRHX	-	HeatX in Aspen
Pump pressure	bar	2.2
Water flow in washer	kg/hr	1000

Table 6.2: Main specifications of PCC model

6.2 Thermodynamics and reactions

In this work, reaction kinetics are combined with a thermodynamic model based on the electrolyte NRTL theory (ENRTL). The kinetic reactions describing the AMP/PZ/ H_2O / CO_2 system with their corresponding kinetic parameters (k_0 is the pre-exponential factor and E is the activation energy in (MJ/kmol)) used in the simulations are given in Table 6.3 below.

Kinetic reaction	k_0	E (MJ/kmol)
$CO_2 + OH^- \longrightarrow HCO_3^-$	4.32E13	55.4709
$HCO_3^- \longrightarrow CO_2 + OH^-$	7.61E14	106.512
$AMP + CO_2 + H_2O \longrightarrow H_3O^+ + AMPCOO^-$	1.0E9	34.3401
$H_3O^+ + AMPCOO^- \longrightarrow AMP + CO_2 + H_2O$	1.52E20	53.1431
$PZ + CO_2 + H_2O \longrightarrow H_3O^+ + PZCOO^-$	4.14E10	33.6548
$H_3O^+ + PZCOO^- \longrightarrow PZ + CO_2 + H_2O$	7.94E21	65.9756
$CO_2 + H_2O + PZCOO^- \longrightarrow PZCOO^{-2} + H_3O^+$	3.62E10	33.6548
$PZCOO^{-2} + H_3O^+ \longrightarrow CO_2 + H_2O + PZCOO^-$	5.56E25	76.9199

Table 6.3: Kinetic parameters of the system ($CO_2 + AMP + PZ + H_2O$) used in the Aspen model

Different techniques were used to find binary interaction parameters for the E-NRTL model: The E-NRTL binary interaction parameters available in Aspen databank are outdated for some interactions (more information about the results obtained due to these outdated parameters are available in Appendix A.1), so in order to get latest parameters, regression was performed to find the parameters for interactions between $AMP + H_2O$ and between $PZ + H_2O$. The Binary VLE data of components was imported utilizing NIST Thermo Data Engine, which is a Search Engine available in Aspen, and then regressed using the regression tool available in ASPEN plus to obtain binary interaction parameters for E-NRTL model. The data used for the regression are available in the Appendix A.2 and the resulting parameters are available in Table 6.4 with their respective references.

Furthermore, the E-NRTL binary interaction parameters for $AMP + PZ$ mixture were acquired from Hartono et al.,(2013 [13]) and the per default values in ASPEN databank were enough precise for interactions between $CO_2 + H_2O$ and between $H_2O + HPZCOO$. This regression calculation was made with the collaboration of Salman Muhammad who helped me to achieve this difficult part of the work. Thanks to its help, it was possible to note great improvement and better results for the validation part. Even if it is not perfect, these results are satisfying for this thesis but some further improvements may still be needed.

Component i	Component j	A_{ij}	A_{ji}	B_{ij}	B_{ji}	α_{ij}	References
AMP	PZ	7.0567	-2.4095	4.1687	1.8764	0.3	[13]
AMP	H_2O	-3.35076	6.08124	693.235	-1432.42	0.3	[2]
PZ	H_2O	-12,1288	- 2,90873	6474,42	-1913,95	0.3	[16]
CO_2	H_2O	0	0	0	0	0.2	Aspen databank
H_2O	$HPZCOO$	0,29335	0,0748454	0	0	0,3	Aspen databank

Table 6.4: Coefficients of molecule-molecule binary interaction parameters for E-NRTL model

6.3 Model validation with pilot plant data

In section 4.3.2, different modelling studies were presented. For the validation of our model, the experimental study of Mangalapally and Hasse (2011) is used. This work used the complete absorption/desorption process to treat gas from a gas-fired pilot plant and compared 2 new solvents with MEA (Mangalapally et al., 2011 [24]). The solvent composition reused in our validation is the following : (0.28 g/g 2-amino-2-methyl-1-propanol + 0.17 g/g piperazine + 0.55 g/g H_2O). This composition was called CESAR1 in their paper.

The main specifications of the pilot plant used in their study are available in Table 6.5 and the operating conditions of the PCC experimental plant are summarized in Table 6.6.

Parameters	Unit	Data
Flue gas source	-	Natural gas burner
CO_2 content in the flue gas	vol%;dry basis	3-14
Flue gas mass flow	kg/h	30-100
Solvent mass flow	kg/h	20-350
Type of packing in the absorber and desorber	-	BX 500
Total height of packing in the absorber	m	4.25
Total height of packing in the stripper	m	2.55
Inner diameter absorber and desorber	m	0.125
F-factor in absorber	$Pa^{0.5}$	0.6-2.1
Liquid load in absorber	m^3/m^2 h	2-28.5

Table 6.5: Main specifications of PCC pilot plant used for validation [24]

The validation was performed in 3 ways: First, the capture rate has been verified, next the reboiler duty for different L/G ratio and finally the rich and lean CO_2 loading also for different L/G ratio.

	Unit	Mangalapally
CO_2 partial pressure in flue gas	mbar	102
Flue gas mass flow	kg/h	80
Solvent mass flow	kg/h	75-275
Ratio of solvent to flue gas mass flow (L/G)	-	0.94-3.5
CO_2 mass flow in flue gas	kg/h	11.6
CO_2 mass flow captured	kg/h	10.5
Solvent temperature at absorber inlet	$^{\circ}C$	40
flue gas temperature at absorber inlet	$^{\circ}C$	47
F-factor in absorber	$Pa^{0.5}$	1.8
Liquid load in absorber	m^3/m^2h	17.5

Table 6.6: Conditions of the experiments [24]

6.3.1 Capture rate validation

The way used to validate the capture rate is described in this section:

Without putting any constraint on capture rate in our model, the idea is to reproduce the exact same conditions of partial pressure, flue gas and solvent mass flow and the corresponding reboiler duty for which the amount of CO_2 captured was 90% in the study of Mangalapally; and to calculate the amount of CO_2 captured in our model expecting to be close to the 90% observed experimentally.

	Unit	Mangalapally	Aspen Model
CO_2 partial pressure in flue gas	mbar	102	102
Flue gas mass flow	kg/h	80	80
Solvent mass flow	kg/h	232	232
Reboiler duty	MJ/h	41.67	41.67
CO_2 mass flow in flue gas	kg/h	11.6	11.6
CO_2 mass flow captured	kg/h	10.5	10.672
Capture rate	wt %	90	92

Table 6.7: Capture rate validation

In Table 6.7, the same operating conditions for both cases can be observed and the value of CO_2 captured using our model is 92% which is close enough to 90%. It can be concluded that the validation of the capture rate is verified.

6.3.2 Reboiler duty validation

The second step was to focus on the reboiler duty at the stripper:

Figure 6.2 shows the regeneration energy as a function of the ratio of solvent mass flow rate ($\dot{Q}_{solvent}$) to flue gas mass flow rate ($\dot{Q}_{fluegas}$) defined in equation 6.1. For this case, the solvent mass flow rate was varied and the flue gas mass flow rate was kept constant. The L/G ratio has its importance to evaluate the functioning of the absorber.

$$\frac{L}{G} = \frac{\dot{Q}_{solvent} [kg/h]}{\dot{Q}_{fluegas} [kg/h]} \quad (6.1)$$

In the simulations, L/G ratio was varied from 1.57 to 2.9 as can be seen in Figure 6.2 and the higher the L/G ratio, the higher the reboiler duty. This can be explained because at higher solvent mass flow, more energy is required to heat up the solvent at the right temperature to perform the stripping in a right way.

Results from Figure 6.2 are in good agreement with results from Mangalapally and have the same trend so it can be concluded the validation of the reboiler duty was performed in a right way.

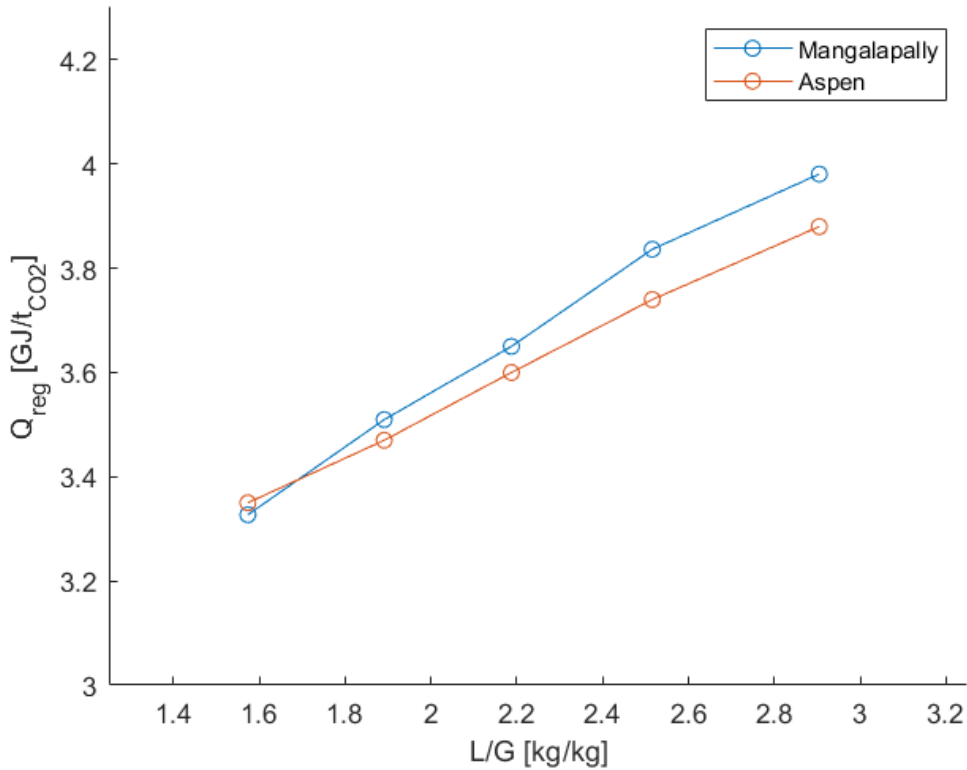


Figure 6.2: Reboiler duty validation

6.3.3 CO_2 loading VS L/G ratio validation

The last step is dealing with rich and lean loading. This concept can be defined by the capacity of the solvent to absorb carbon dioxide. The loading is defined as the ratio between the mole number of CO_2 in the solvent flow (rich or lean) by kilogram of solvent.

The lean loading is the loading of the solvent stream after its regeneration (LEANIN). The rich loading is the loading of the solvent after the absorption (RICHOUT). If the difference between the rich and the lean loading is large, the utilization of the solvent is efficient.

As in the previous subsection, L/G ratio was varied from 1.57 to 2.9 during the simulations. First, the evolution of the lean loading can be analyzed and it can be seen in Figure 6.3 that lean loading increases when L/G ratio increases. This can be explained because if the solvent mass flow increases, the solvent has more capacity to absorb CO_2 . At higher L/G ratio, there is no need to strip all the CO_2 and it explains why lean loading is higher.

For the rich loading, it is logical to get the inverse trend than for lean loading in Figure 6.3 because the inverse reasoning can be applied. At lower L/G ratio for example, less solvent is in circulation so the rich loading will be higher at the exit of the absorber to achieve the unchanged 90% CO_2 captured.

Once again, results from Figure 6.3 are in good agreement with results from Mangalapally and have the same trend so it can be concluded the validation of the rich and lean loading was performed in a right way.

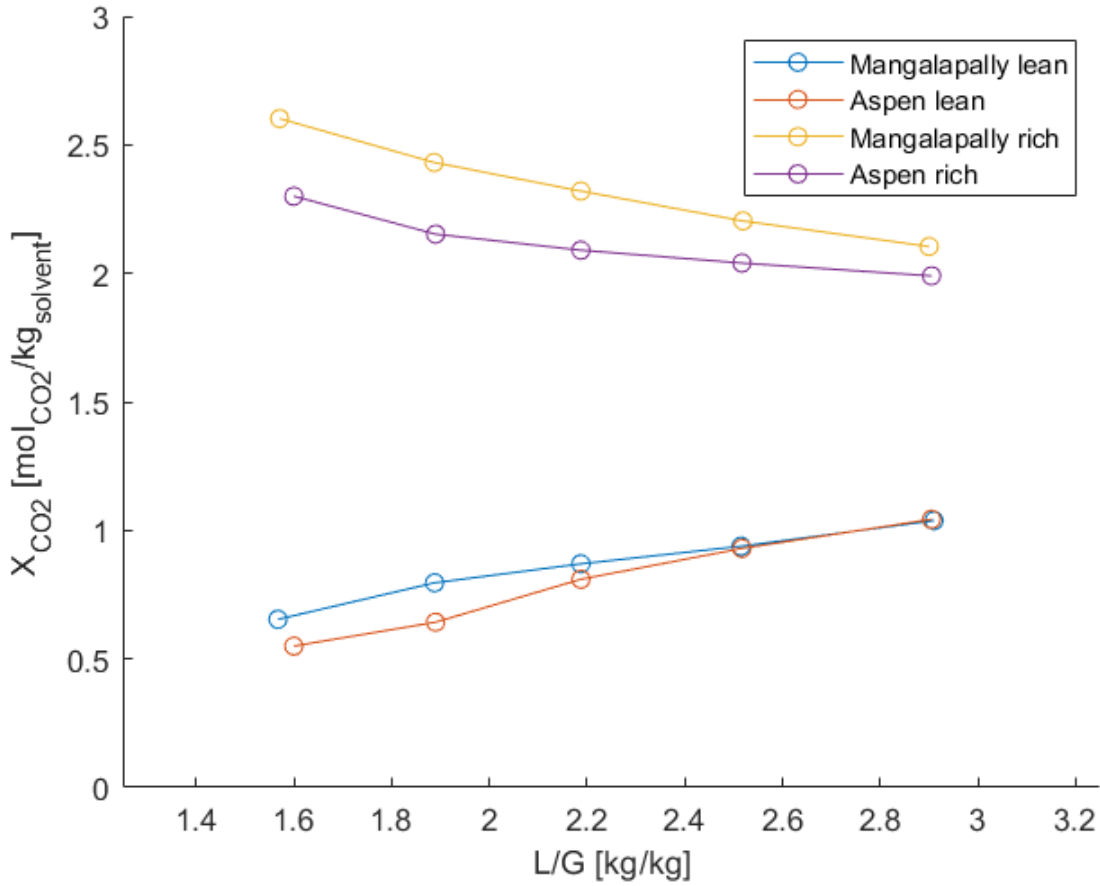


Figure 6.3: Lean/rich solvent loading validation

6.3.4 Comparison of simulation results with experimental results

In conclusion of this validation part, the Absolute Average Relative Deviation can be calculated thanks to equation 6.2 with N the number of calculated points. It gives a good idea to know how close are the simulation results compared to the experimental results. The results obtained for all the validation parts are satisfying because the AARD values are quite small as can be seen in Table 6.8.

$$AARD = \frac{1}{N} \sum_{i=1}^N \left| \frac{x_{i,sim} - x_{i,exp}}{x_{i,exp}} \right| \quad (6.2)$$

Performance indicator	AARD
Capture rate	0.0222
Reboiler duty	0.02
Lean loading	0.087
Rich loading	0.091

Table 6.8: AARD between Aspen results and experimental results of Mangalapally

Chapter 7

PCC parametric optimisation for CHP plant in Sart Tilman

Now that the model is validated, it will be used to have a first idea about variation in different parameters (like stripper pressure, number of absorber/stripper stages, temperature approach of the heat exchanger..) that should be used in the PCC of the CHP plant in Sart Tilman described in Chapter 5.

The main idea of this work is to see how the model adapted for the CHP plant in Sart Tilman will react while using the new benchmark composition of solvent which is 40 wt% of PZ/AMP in a 1:2 molar ratio (typically 3.0 molar AMP and 1.5 molar PZ with respectively 26.74 wt% and 12.92 wt. % [32]).

The exact composition of the solvent used in the simulations of this chapter is available in Table 7.1 and the composition of the flue gas was given in Chapter 5. These parameters will be kept constant all over this chapter and a 90% of CO_2 captured will always be applied.

Component	AMP	PZ	H_2O
% (wt)	27	13	60

Table 7.1: Solvent composition in LEANIN

A last important thing to note is that this chapter will be separated in 2 sections. In section 7.1 equilibrium mode as calculation type will be used in absorber and stripper column to make the convergence easier. In this configuration, each theoretical stages in absorber and stripper are at a chemical and thermodynamic equilibrium state meaning that mass and energy balances are respected for each stages. The rate-based mode will be studied in section 7.2 to further calculate the total height and the inner diameter of the 2 columns. This model will take into account the mass transfer limitations unlike the previous model.

7.1 Sensitivity analysis

There are many ways to analyse the sensitivity of our model with different parameters but it is always important to keep in mind that the solvent regeneration energy requirement has to be as low as possible because the energy penalty at this step of the process can be very high. Indeed it was already mentioned that it is the biggest challenge for post-combustion capture so the parameters will be adapted in order to have a low reboiler duty to keep a good efficiency for the power plant.

The heat supply at the reboiler of the stripper column to regenerate the solvent clearly represents the main part of the total energy consumption of the whole process. This is why thermal energy consumption at the stripper is often used as reference to evaluate the effect of a process modification on the total energy consumption of the process, neglecting the other energy consumption in the process like pump or blower consumption.

The flue gas treated is now much higher than before so the first step in the optimisation will be to optimize the number of stages in the absorber and stripper. To do this, arbitrary values for the stripper pressure and solvent flow rate will be given and these two values will be optimized in later steps. Finally, the sensitivity analysis of the temperature approach at the lean-rich heat exchanger will also be performed.

7.1.1 Number of equilibrium stages in absorber

First, the sensitivity analysis to find an ideal number of absorber stage (N_T) is performed. In table 7.2, initial values are given for parameters studied in the following.

Specification	Capture rate	N_T stripper	P_{strip}	Solvent mass flow	RICHIN T°
Value	90 %	11	2 [bar]	70000 [kg/hr]	110°C

Table 7.2: Specifications for sensitivity analysis of absorber stages

Our obsession is to save a maximum of energy to keep the efficiency of the plant the highest as possible. As can be seen in Figure 7.1 it is obvious that 6 or 7 stages are not enough. However, it can be noticed that the benefit of increasing the number of stage becomes less and less important at higher values. Typically by passing from 18 stages to 19 or 20 stages is not very interesting because the benefit is small in term of energy savings. Moreover, the more the number of absorber stages, the more will be the height of the column resulting in increase in the equipment cost. In conclusion, 14 stages will be kept in the following because it seems to be a good trade-off.

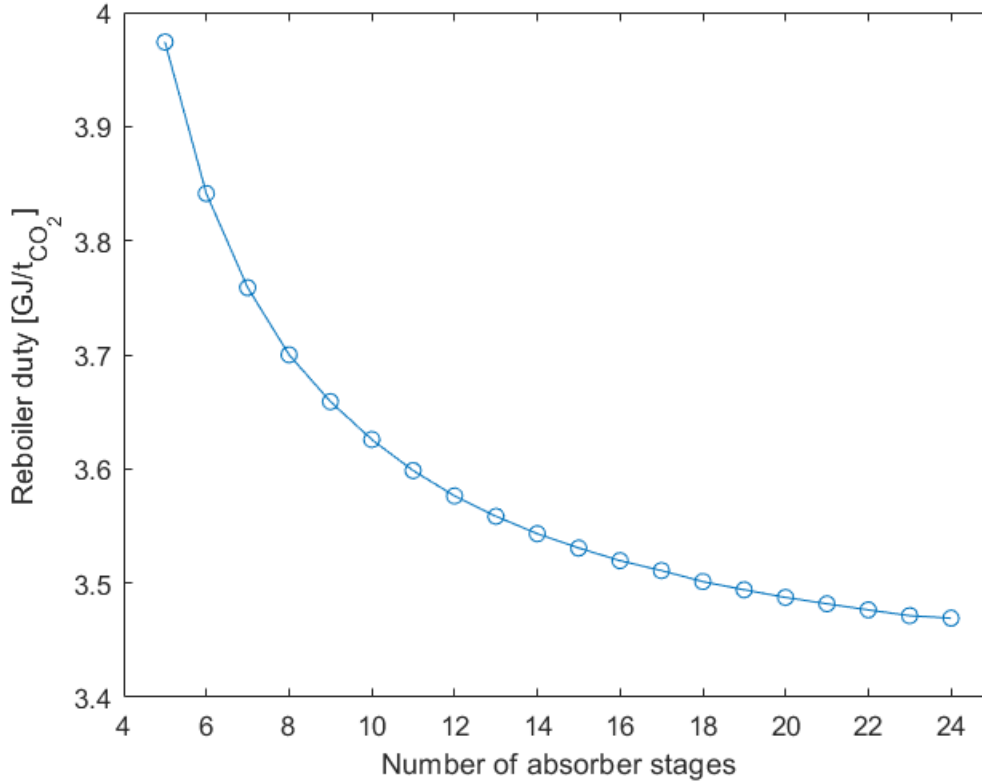


Figure 7.1: Influence of the number of stages in the absorber on the reboiler duty

7.1.2 Number of equilibrium stages in stripper

The second step is to study the sensitivity of the number of stripper stages. Same initial values are given in Table 7.3 except the number of absorber stages which is updated from the previous analysis.

Specification	Capture rate	N_T absorber	P_{strip}	Solvent mass flow	RICHIN T°
Value	90 %	14	2 [bar]	70000 [kg/hr]	110 °C

Table 7.3: Specifications for sensitivity analysis of stripper stages

The analysis to find an optimized value for the number of stripper stage is quite clear. Indeed Figure 7.5 shows the presence of a minimum at 10 stages and it tends to increase a little bit after this value. If the number of stages increases, a better regeneration of the solvent is performed but at the same time more stripping steam to avoid to have insufficient steam at the top of the column is needed. At one point, it is not possible to capture more CO_2 with a better regenerated solvent but more energy for the stripping steam still need to

be provided so the specific reboiler duty increases.

As discussed previously, the reboiler duty difference between 10 and 8 stages is very small so at first sight it's not interesting to increase the number of stages too much because it will increase the equipment cost. This is why 8 stages will be used in the following.

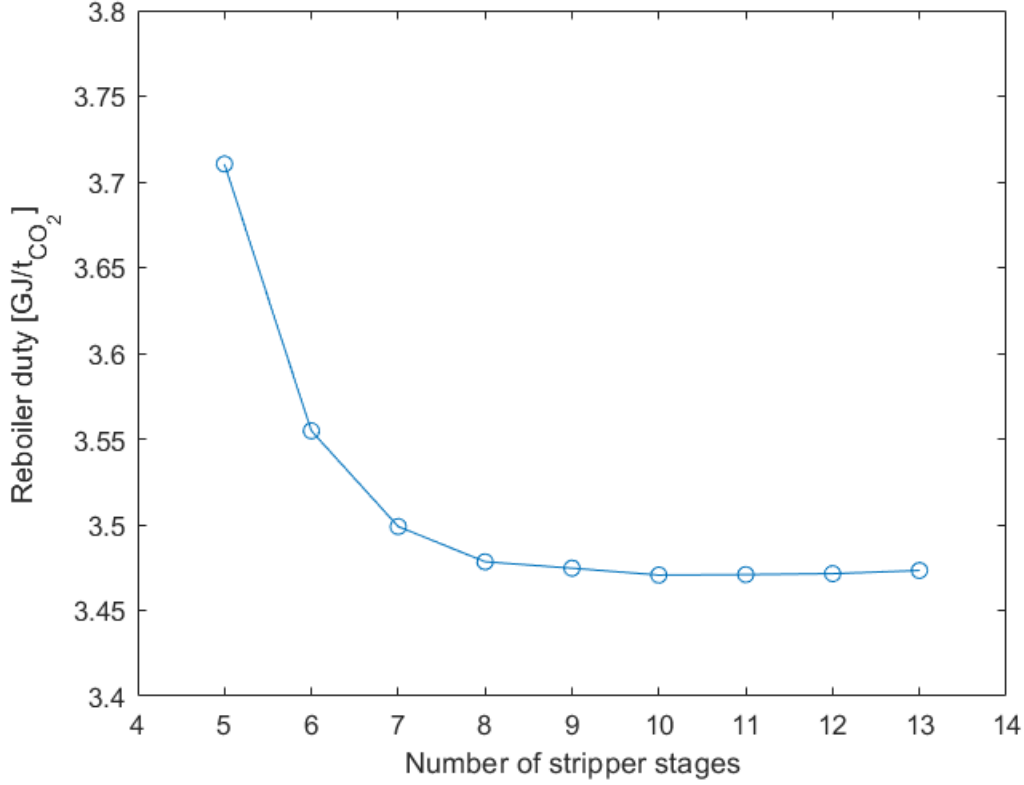


Figure 7.2: Influence of the number of stages in the stripper on the reboiler duty

7.1.3 Solvent mass flow

Third step is to study the effect of varying the solvent mass flow and the different input parameters used are available in Table 7.4.

Specification	Capture rate	N_T absorber	N_T stripper	P_{strip}	RICHIN T°
Value	90 %	14	8	2 [bar]	110 °C

Table 7.4: Specifications for sensitivity analysis of solvent flow rate

It is known that a minimum in the thermal energy consumption of the process will be observed when varying the solvent mass flow at a fixed flue gas rate so it is easy to determine

an ideal value.

In Figure 7.3, a minimum around 70000 kg/h of solvent mass flow can be detected. This minimum can be explained because the reboiler divides itself into three contribution: Firstly, energy is required to bring the solvent feed (RICHIN) to the desired regeneration temperature. Secondly, the absorption heat must be furnished for CO_2 to desorb out of the solvent. Thirdly, energy will be consumed to generate steam at the bottom of the stripper (G.Leonard, 2008 [23]).

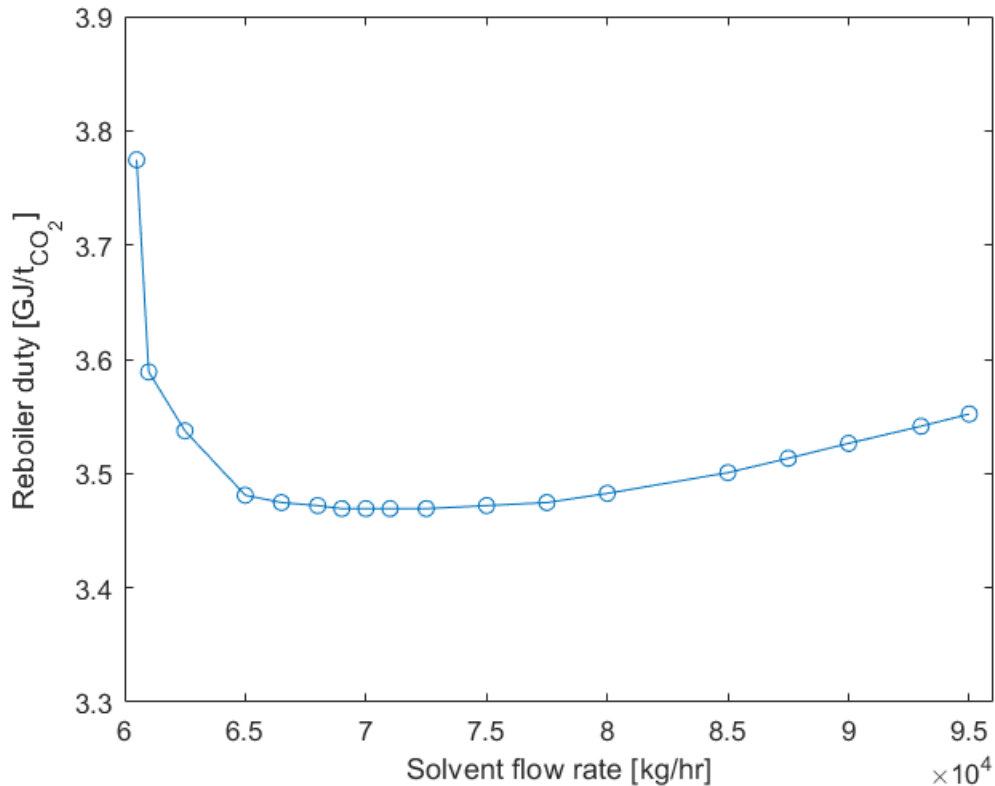


Figure 7.3: Influence of the solvent mass flow on the reboiler duty

At low values of solvent mass flow (and so low values of lean solvent loading), the amount of stripping steam required to achieve this low lean solvent loading is dominant in the thermal energy requirement (left part of the curve). At high values of solvent flow rate (and so high values of the solvent lean loading), it is the heating up of the solvent at this high circulation mass flow that is dominant in the thermal energy consumption (right part of the curve). A 70000 kg/h solvent mass flow will be kept in the following.

7.1.4 Temperature approach

The fourth analysis is in link with the lean-rich heat exchanger temperature approach. First it is important to define what is called temperature approach in this work and the concept of this parameter.

It will be considered that temperature approach is the difference between the lean stream (LEANCOLD) outlet temperature and the rich stream inlet temperature (RICHCOLD). This parameter has a direct influence on the inlet temperature of RICHIN stream. Indeed if the temperature approach decreases, the RICHIN temperature will increase as can be seen in Table 7.5. Previously 110 °C was used to perform all the sensitivity analysis and this value corresponds to a temperature approach between 1 and 2°C. Now RICHIN temperature will be allowed to vary and the influence of this parameter will be studied.

T°C approach	1	2	3	4	5	6	7	8	9	10
RICHIN T°	110.4	110.1	109.85	109.62	109.4	109.15	108.9	108.67	108.43	108.2

Table 7.5: Corresponding temperature between temperature approach in LRHX and RICHIN

As mentioned in section 7.1.3, if the temperature inlet of RICHIN increases, one of the three contributions of the reboiler duty (the sensitive heat) will decrease so the consumption at the stripper will decrease.

The specification used to study the temperature approach are available in Table 7.6.

Specification	Capture rate	N_T absorber	N_T stripper	P_{strip}	Solvent mass flow
Value	90 %	14	8	2 [bar]	70000 [kg/h]

Table 7.6: Specifications for sensitivity analysis of temperature approach

As can be seen in Figure 7.4 reducing the temperature approach is always benefiting because it increases RICHIN temperature and so decreasing the reboiler duty.

However it is important to note we are limited by the size of the heat exchanger. Indeed, the temperature difference between the rich inlet temperature and the lean outlet temperature is directly correlated to the surface of the lean-rich heat exchanger and if the heat exchanger performance is increased, the energy consumption of the process will be improved since more energy will be recuperated. There is a trade-off between the investment of a very efficient heat exchanger to have a lower reboiler duty needed or accepting a higher reboiler duty with a cheaper heat exchanger.

Furthermore, the cooling energy requirement at the solvent cooler will also decrease if more

heat is recovered from the lean solvent so increasing the heat exchanged is an advantage on this point of view.

It is very important to have an ideal lean-rich heat exchanger in CO_2 capture processes because it plays a crucial role. Indeed Figure 7.4 shows that there is a quite significant difference in reboiler duty between each points

A temperature approach of $5^\circ C$ will be kept in the following because it seems to be a good trade-off between high performances and capital costs related to the heat-exchanger. The corresponding streams temperature evolving in LRHX with a temperature approach of $5^\circ C$ are available in Table 7.7.

Stream	Inlet temperature	Outlet temperature
Lean	122.4	58
Rich	53	109.4

Table 7.7: Temperature of streams evolving in the LRHX

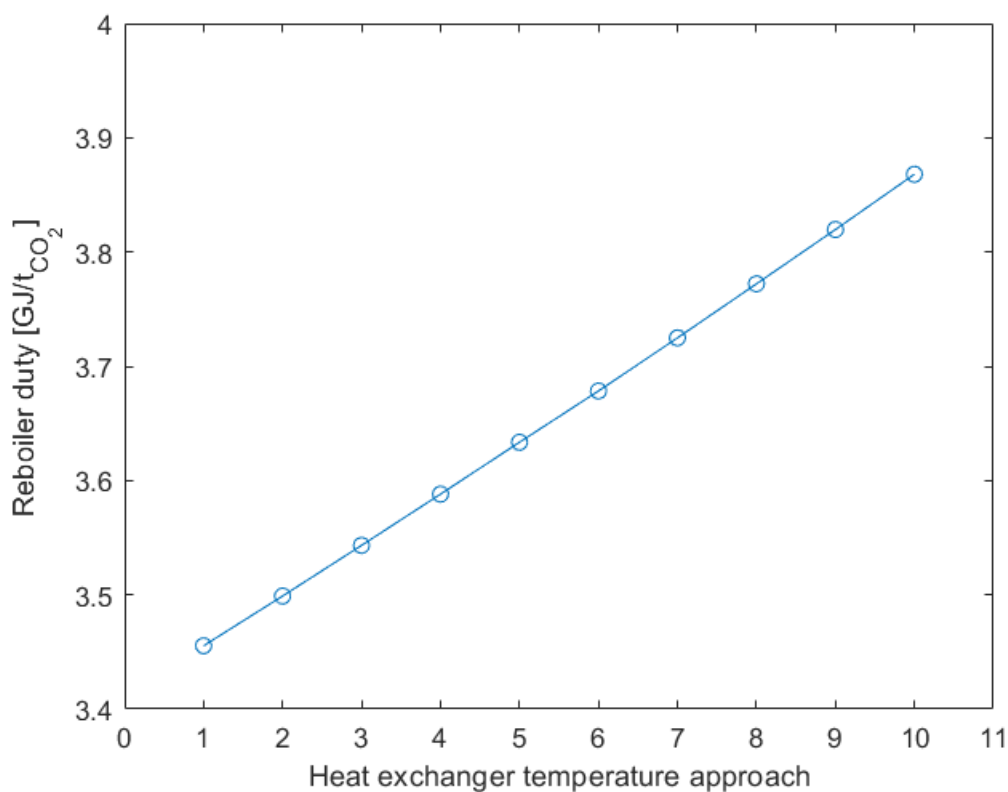


Figure 7.4: Influence of the heat-exchanger temperature approach on the reboiler duty

7.1.5 Stripper pressure

Finally, the last parameter to optimize is the stripper pressure. The input parameters used for this study are given in Table 7.8.

Specification	Capture rate	N_T absorber	N_T stripper	Solvent mass flow	T_{app}°
Value	90 %	14	8	70000 [kg/h]	5

Table 7.8: Specifications for sensitivity analysis of stripper pressure

The same observation as in the previous subsection can be made in this case because increasing the stripper pressure is always benefiting on a reboiler duty point of view because it always decreases the energy requirement in the ranged considered between 1.8 and 2.35 bar as can be seen in Figure 7.5. It can be easily explained because increasing the pressure is aiding in better stripping: This results in achieving higher temperature easily and thus increasing the RICHIN temperature.

Like previously, a trade-off has to be performed because solvent degradation can occur if too high pressure is applied so other problems could have to be taken into account in the design.

Li et al. (2013 [20]) calculated that for a 2 m PZ, 4 m AMP blend, significant thermal degradation started at temperatures over 127°C. Therefore, this maximum allowable stripper bottom temperature will be considered. As can be seen in Table 7.9, this temperature limit is reached for a stripper pressure equal to 2.3 bar so this value will be used in the final optimised model.

P_{strip}	2.2	2.25	2.3	2.35	[bar]
Corresponding LEANOUT T°	125.3	126.1	126.7	127.3	[°C]

Table 7.9: Variation of LEANOUT T° for different stripper pressure

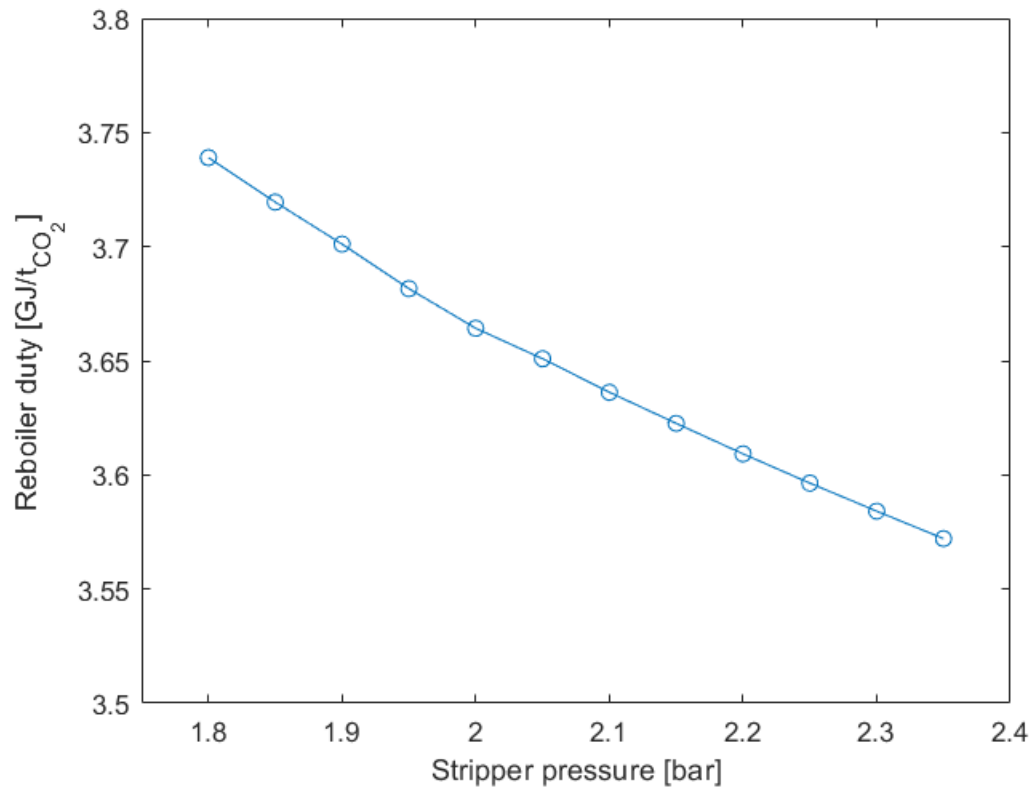


Figure 7.5: Influence of the stripper pressure on the reboiler duty

7.1.6 Final results of the optimized model

The final optimized parameters in equilibrium mode and a summary of the different specifications of the optimized model are available in Table 7.10.

Parameters	Unit	Equilibrium mode
CO_2 partial pressure in FG-IN	bar	0.13
Flue gas mass flow	kg/h	23121
Solvent mass flow (LEANIN)	kg/h	70000
Ratio of solvent to flue gas mass flow (L/G)	-	3
CO_2 mass flow in flue gas	kg/h	4161.8
CO_2 Capture rate	%	90
Number of absorber stages	-	14
Number of stripper stages	-	8
LRHX temperature approach	°C	5
Stripper pressure	bar	2.3
Solvent lean loading	mol_{CO_2}/mol_{AMP+PZ}	0.035
Solvent rich loading	mol_{CO_2}/mol_{AMP+PZ}	0.3
Reboiler duty	GJ/ t_{CO_2}	3.58
Water flow in washer	kg/hr	1000

Table 7.10: Optimized parameters in equilibrium mode

7.2 Rate-based calculation

As mentioned previously, in this section the model will take into account heat and mass transfer limitations because the rate-based calculation type will be used in the 2 columns. This section will be dedicated to obtain dimensions (diameter and height) of the 2 columns (absorber and stripper).

The packing type of the columns is BX from Sulzer as mentioned in Table 6.5. More information are available in a data sheet furnished by Sluzer[35] and more precisely in Figure A.2 in which the corresponding curve is BX 400. This will help to determine the dimensions of the columns.

7.2.1 Absorber dimensions

To perform the calculations in rate-based mode, the same optimized parameters calculated in equilibrium mode and available in Table 7.10 were used and the calculation type was shifted from equilibrium to rate-based mode. A diameter of 2.1 meter was obtained for the absorber in the simulation.

Furthermore, to determine a first guess of the total height of the column, a method based on the Height Equivalent to a Theoretical Plate (HETP) will be used. Indeed, a guess of the total height of the column can be determined by multiplying the amount of stages with the HETP.

To find the HETP, another important parameter will be used: The F-factor. It is an es-

sential parameter in making sure that the packing works in the conditions imposed by the manufacturer. It is defined as the superficial vapor velocity multiplied by the square root of the vapor density (Peeters 2020[31]). The diameter of the column has high impact on the F-factor as it influences the vapor velocity value.

The F-factor corresponding to a diameter of 2.1 meter in the previous simulation was equal to $1.96 \sqrt{Pa}$.

Then, Figure A.2 was used to determine the HETP. This graph gives us a corresponding HETP which is roughly 0.215 m and as the number of stages was calculated before, it is possible to easily obtain a first guess of the total height by multiplying the HETP by 14 so a total height of 3m is obtained for the absorber as first guess. The F-factor is in the optimal range suggested by the manufacturer which is between 1 and $2.5\sqrt{Pa}$.

7.2.2 Stripper dimensions

Exactly the same approach used to determine the dimensions of the absorber is used to determine the diameter and the first guess of the total height of the stripper column. The diameter of the stripper obtained after the simulation in rate-based mode using the optimized parameter of Table 7.10 was equal to 1.2m.

The corresponding F-factor was $1.25\sqrt{Pa}$ and thanks to Figure A.2, it can be seen that it corresponds a value of 0.18 for the HETP. By multiplying by the 8 stages used in the stripper, it gives a first guess for the total height equal to 1.5 m for the column.

Once again, the F-factor for this case is in the optimal range suggested by the manufacturer which is between 1 and $2.5\sqrt{Pa}$.

7.2.3 Sensitivity analysis of the column heights

The ratio between the height and the diameter won't be so small in practice for these two columns. As mentioned before, the data from Sulzer were used to get an initial guess for both heights. It is now interesting to study the influence of the height of the columns on the reboiler duty. The parameters used for theses analysis are available in Table 7.11 and it is important to note that the sensitivity analysis for the absorber height has been performed with a total height of 2 m for the stripper.

Specification	Capture rate	N_T absorber	N_T stripper	Solvent mass flow	T_{app}°	P_{strip}
Value	90 %	14	8	70000 [kg/h]	5	2.3 bar

Table 7.11: Specification for sensitivity analysis of columns height

As can be seen in Figure 7.6, the ideal height is around 7m. Indeed, the same reasoning can be applied as when calculating the number of absorber stages. After 7m, still increasing the height won't lead to big decrease of the reboiler duty. In order to not increasing too much the equipment cost, 7 m will be chosen.

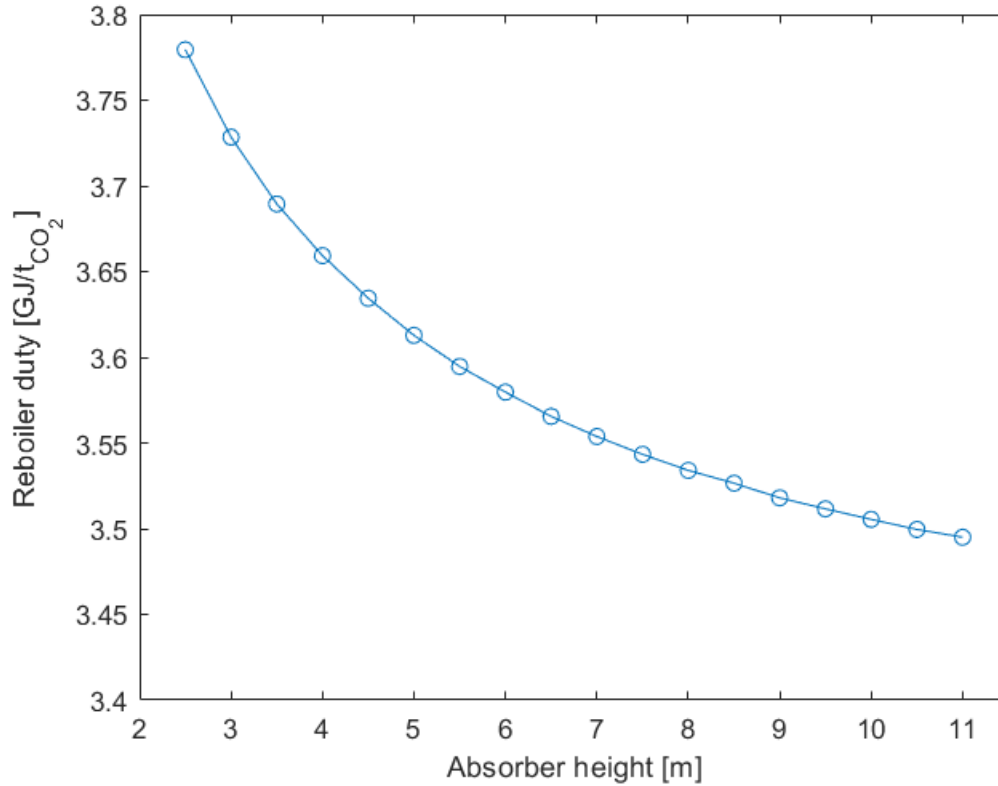


Figure 7.6: Influence of the absorber height on the reboiler duty with a stripper height of 2m

Once again, the same analysis can be made for the sensitivity analysis of the stripper height as can be seen in Figure 7.7. The ideal value determined for the total height of the stripper is around 4m for the same reasons as for the absorber.

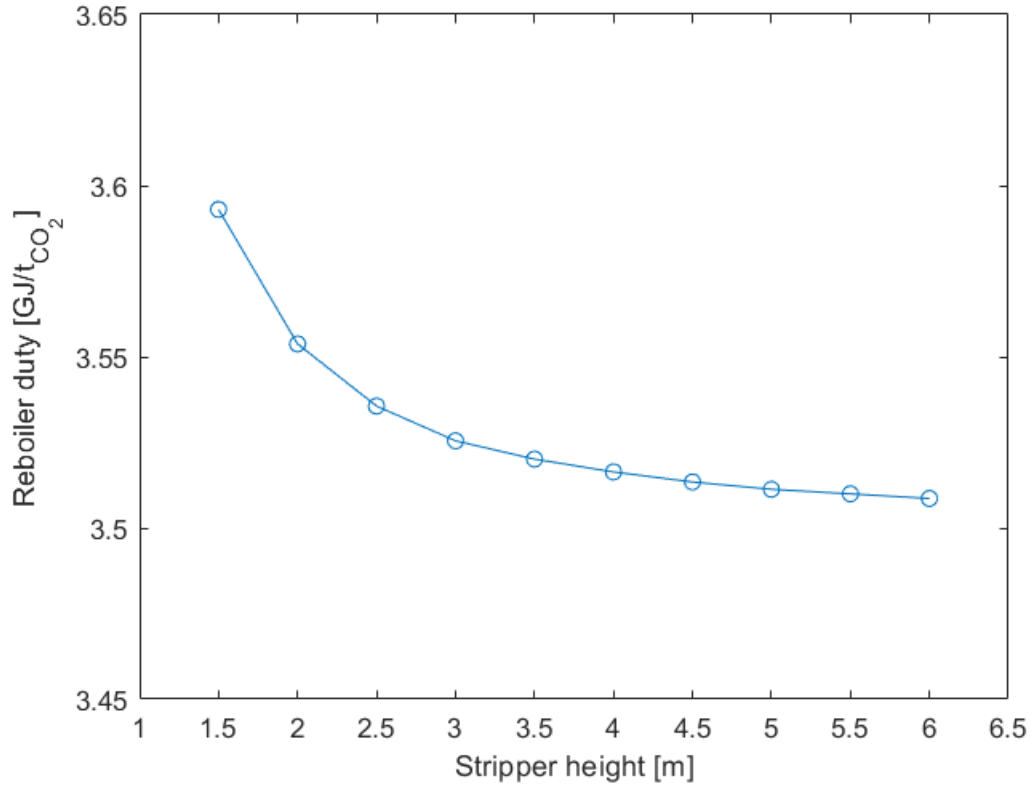


Figure 7.7: Influence of the stripper height on the reboiler duty with an absorber height of 7m

7.2.4 Final results of the optimized model

The final parameters data obtained in rate-based mode with the obtained dimensions from the previous point and the different specifications of the optimized model are available in Table 7.12 and compared with results of the equilibrium calculation mode.

The value of the stripper pressure could be increased until 2.4 bar without that the temperature of LEANOUT exceeds 127°C in rate-based mode. One thing more, the value of the lean loading is higher in the rate-based mode resulting in a decrease in the reboiler duty. Artanto et al. (2014 [3]) suggested that in the case of a lower lean loading, the extra energy required to strip CO_2 from the absorption liquid generates more steam, which in turn makes the absorption liquid leaner. Theses 2 reasons can explain why a lower value for the reboiler duty in rate-based mode was got even when heat and mass transfer limitations are taken into account.

Parameters	Unit	Equilibrium	Rate-based
CO_2 partial pressure in FG-IN	bar	0.13	0.13
Flue gas mass flow	kg/h	23121	23121
Solvent mass flow (LEANIN)	kg/h	70000	70000
Ratio of solvent to flue gas mass flow (L/G)	kg/h	3	3
Water flow rate	kg/h	1000	1000
CO_2 mass flow in flue gas	kg/h	4160.2	4160.2
LRHX temperature approach	°C	5	5
CO_2 Capture rate	%	90	90
Stripper pressure	bar	2.3	2.4
Temperature LEANOUT	°C	126.7	126.86
Solvent lean loading	mol_{CO_2}/mol_{AMP+PZ}	0.035	0.05
Solvent rich loading	mol_{CO_2}/mol_{AMP+PZ}	0.3	0.316
Number of absorber stages	-	14	14
Number of stripper stages	-	8	8
Reboiler duty	GJ/ t_{CO_2}	3.58	3.49
Total height of packing in the absorber	m	-	7
Total height of packing in the stripper	m	-	4
Inner diameter absorber	m	-	2.1
Inner diameter stripper	m	-	1.2
F-factor in absorber	$Pa^{0.5}$	-	1.96
F-factor in stripper	$Pa^{0.5}$	-	1.1

Table 7.12: Comparison of optimized parameters for equilibrium mode and rate-based mode

Chapter 8

Conclusions and perspectives

In this conclusion, observations and results from this work will be summarized. Some process modifications to improve the model will be mentioned in a second time.

This thesis had the objective of delivering a first idea for the design of a post-combustion carbon capture installation with AMP+PZ as solvent for the CHP plant in Sart Tilman. The aim was to see if the use of this new solvent could be a good alternative for this plant.

First, the evolution of the benchmark solvent for this kind of application was studied. This is why a detailed study about the characteristics of an ideal solvent were given. Through a large amount of research of pilot plant studies, it was shown that the official new benchmark based on the current state of the art was a ± 40 wt% formulation of PZ/AMP in a 1:2 molar ratio [32] (3.0 molar AMP (26.74 wt%) and 1.5 molar PZ (12.92 wt. %) (Moser et al.,2021 [26])).

After that the idea was to apply this new solvent benchmark to a concrete case that is CHP plant in Sart Tilman treating a real flue gas composition and flow rate coming from this cogeneration. A description of the plant was made and the exact values for the composition was mentioned. To do this, two main steps were achieved: First of all, build and validate our model and after that optimize different parameters in the process through different sensitivity analysis.

The first step was to build and validate a model. A description of the process was realised defining all the streams and the role of each blocks. Initial values of the important parameters were given.

The validation was performed in 3 step by comparing the model with experimental results [24]. First the validation of the capture rate, then that of the reboiler duty and finally the lean and rich loading were studied. An Absolute Average Relative Deviation of respectively 2.2; 2; 8.7 and 9.1 % was found which was satisfying for this thesis.

The second point was to perform several sensitivity analysis to find optimized parameters suited for the plant studied. Parameters like number of absorber and stripper stages, solvent mass flow, heat-exchanger temperature approach and stripper pressure were studied for both equilibrium and rate-based mode calculation. After performing the analysis, 14 and 8 stages were found for the absorber and stripper respectively; a mass flow rate of 70000 kg/h was determined; the temperature approach was fixed to 5°C and the stripper pressure was allowed to increase to 2.3 bar. The rate-based mode allowed us to determine the dimensions of the columns and these are respectively 7 and 4 meters for the total heights of the absorber and the stripper and the diameters are respectively 2.1 and 1.2 meters.

The results with the use of the optimized parameters for both equilibrium and rate-based mode are summarized in Table 7.12.

The final value obtained for the reboiler duty is 3.58 and 3.49 GJ/ t_{CO_2} in equilibrium and rate-based mode respectively. This small decrease was obtained in the rate-based mode because the lean loading was higher and also because the stripper pressure could be higher without leading to degradation.

Improvements to apply to our the model and perspectives.

To go further, there are still many ways to improve the model and to save energy in the process. Mainly the design of the flowsheet could be modified and also better parameters for the reaction kinetics in the thermodynamic model could be found.

In the model there are different places where it would be possible to recuperate energy to decrease the total energy consumption of the PCC plant:

- At the very beginning because fumes from CHP plant are cooled down to roughly 60°C
- At the solvent cooler
- At the condenser

Modifying the process for example by adding absorption intercooling or lean vapor re-compression were studied in the literature and could be implemented in our model to increase the efficiency of the plant.

Then, studying the cost related to the increase of number of stages in the columns and also studying the investment cost of a heat exchanger performing at lower temperature approach could be interesting. Finally, studying more in details the solvent degradation with the objective of increasing the stripper pressure if possible could also be a way to still decrease the reboiler duty.

The perspectives in the context of building an experimental pilot in the Sart Tilman CHP plant using AMP+PZ as solvent is a way to be explored in depth. Indeed, the better performances of this new solvent composition was demonstrated in the literature (mainly less regeneration energy requirement and less degradation). Furthermore, this work gives satisfying results in term of energy consumption and as mentioned here above there are quite a lot of ways to improve the process and savings energy.

Appendix A

Appendix

A.1 Improvement of the results using an updated thermodynamic model

This section is used to show why the per default Aspen data were not suited as explained in section 6.2. Indeed, when performing the validation (especially for the lean and rich loading in section 6.3.3), very bad results of rich and lean loading were got. Figure A.1 shows the bad results obtained as a first step (light blue for lean loading and green for rich loading). The AARD was also calculated in the same way as described in section 6.3.4 and can be seen in Table A.1. In a second phase, as explained in section 6.2, an updated thermodynamic model was built making regression to obtain updated parameters. The results can be seen in Figure A.1 and are deeper explained in section 6.3.3. The AARD were also calculated and it can be noticed a great improvement in Table A.1.

Performance indicator	Old AARD	Updated AARD
Lean loading	0.4158	0.087
Rich loading	0.1566	0.091

Table A.1: AARD between experimental results of Mangalapally and Aspen results for both old and updated models

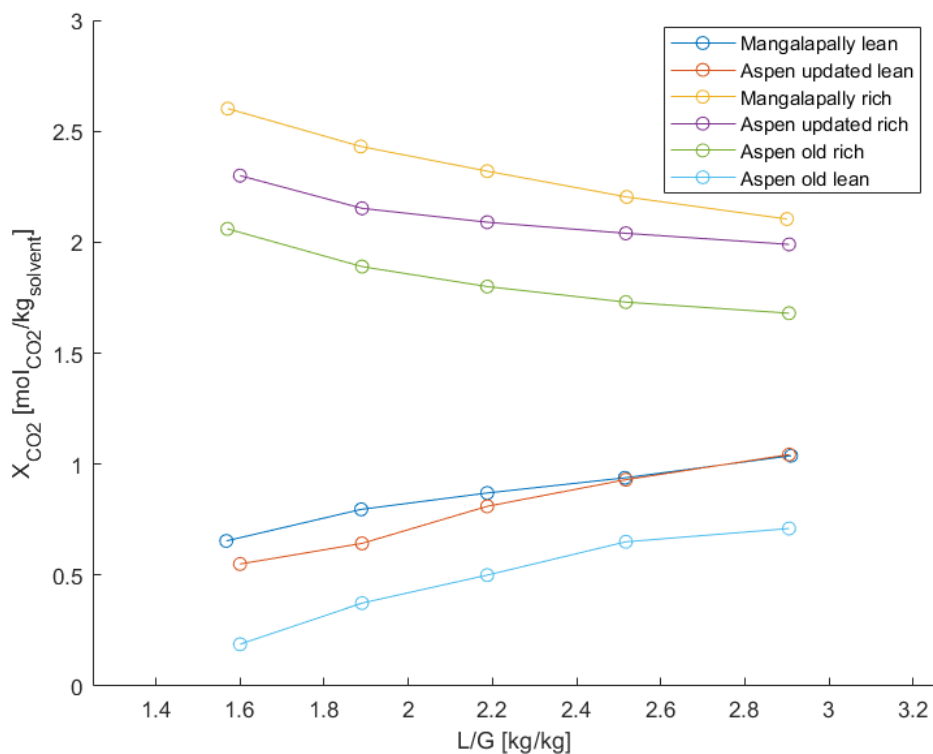


Figure A.1: Lean/rich solvent loading using both old and updated models

A.2 Data used for regression for interactions between $\text{AMP} + \text{H}_2\text{O}$ and $\text{PZ} + \text{H}_2\text{O}$

In this appendix , all the data used to make the regression in order to obtain better binary interaction parameters between AMP and H_2O on the one side and PZ and H_2O on the other side are listed in the tables below.

TEMPERATURE	PRESSURE	X	X	Y	Y
°C	N/sqm	AMP	H_2O	AMP	H_2O
293,15	2283,8	0	1	0	1
293,15	2170,3	0,0498	0,9502		
293,15	2030,5	0,1001	0,8999		
293,15	1976,9	0,18	0,82		
293,15	1669,8	0,2603	0,7397		
293,15	1446,4	0,3598	0,6402		
293,15	1002,7	0,5408	0,4592		
293,15	691,5	0,6692	0,3308		
293,15	362,7	0,8203	0,1797		
293,15	40,5	1	0	1	0
303,15	4147,8	0	1	0	1
303,15	3958,4	0,0498	0,9502		
303,15	3722,5	0,1001	0,8999		
303,15	3528,3	0,18	0,82		
303,15	3038,9	0,2603	0,7397		
303,15	2617,9	0,3598	0,6402		
303,15	1789,8	0,5408	0,4592		
303,15	1226,9	0,6692	0,3308		
303,15	708,1	0,8203	0,1797		
303,15	97,6	1	0	1	0
313,15	7221,9	0	1	0	1
313,15	6912	0,0498	0,9502		
313,15	6530	0,1001	0,8999		
313,15	6080,3	0,18	0,82		
313,15	5326,5	0,2603	0,7397		
313,15	4564,2	0,3598	0,6402		
313,15	3087,2	0,5408	0,4592		
313,15	2107,4	0,6692	0,3308		
313,15	1296,3	0,8203	0,1797		
313,15	217,6	1	0	1	0
323,15	12107,1	0	1	0	1
323,15	11608,1	0,0498	0,9502		
323,15	11012	0,1001	0,8999		
323,15	10148,8	0,18	0,82		
323,15	9023,1	0,2603	0,7397		
323,15	7691,4	0,3598	0,6402		

Table A.2: Regression data AMP+ H_2O

TEMPERATURE	PRESSURE	X	X	Y	Y
°C	N/sqm	AMP	H_2O	AMP	H_2O
323,15	5160,5	0,5408	0,4592		
323,15	3513,8	0,6692	0,3308		
323,15	2244,6	0,8203	0,1797		
323,15	453,1	1	0	1	0
333,15	19615,6	0	1	0	1
333,15	18823,5	0,0498	0,9502		
333,15	17923,9	0,1001	0,8999		
333,15	16451,7	0,18	0,82		
333,15	14817,1	0,2603	0,7397		
333,15	12565,8	0,3598	0,6402		
333,15	8381,7	0,5408	0,4592		
333,15	5700,9	0,6692	0,3308		
333,15	3703,6	0,8203	0,1797		
333,15	888,9	1	0	1	0
343,15	30815,4	0	1	0	1
343,15	29574,5	0,0498	0,9502		
343,15	28257,1	0,1001	0,8999		
343,15	25964,2	0,18	0,82		
343,15	23649,7	0,2603	0,7397		
343,15	19956,5	0,3598	0,6402		
343,15	13259,2	0,5408	0,4592		
343,15	9019	0,6692	0,3308		
343,15	5858,7	0,8203	0,1797		
343,15	1654,4	1	0	1	0
353,15	47073,7	0	1	0	1
353,15	45155,9	0,0498	0,9502		
353,15	43278,5	0,1001	0,8999		
353,15	39980,2	0,18	0,82		
353,15	36776,7	0,2603	0,7397		
353,15	30883,2	0,3598	0,6402		
353,15	20471,3	0,5408	0,4592		
353,15	13939,9	0,6692	0,3308		
353,15	8930,6	0,8203	0,1797		
353,15	2938,6	1	0	1	0

Table A.3: Regression data AMP+ H_2O (following)

TEMPERATURE	PRESSURE	X	X	Y	Y
°C	N/sqm	AMP	H_2O	AMP	H_2O
363,15	70102,2	0	1	0	1
363,15	67178,9	0,0498	0,9502		
363,15	64568,9	0,1001	0,8999		
363,15	60182,1	0,18	0,82		
363,15	55837,7	0,2603	0,7397		
363,15	46668,7	0,3598	0,6402		
363,15	30905,7	0,5408	0,4592		
363,15	21086,3	0,6692	0,3308		
363,15	13174,8	0,8203	0,1797		
363,15	5006,8	1	0	1	0

Table A.4: Regression data AMP+ H_2O (end)

TEMPERATURE	PRESSURE	X	X	Y	Y
C	N/sqm	PZ	H_2O	PZ	H_2O
386,05	157610	0	1	0	1
386,05	139020	0,1023	0,8977	0,00925	0,99075
386,05	125330	0,1606	0,8394	0,0219	0,9781
386,05	113810	0,2079	0,7921	0,03763	0,96237
386,05	103400	0,256	0,744	0,05921	0,94079
386,05	91232	0,3256	0,6744	0,1003	0,8997
386,05	81359	0,3993	0,6007	0,1541	0,8459
386,05	76362	0,4434	0,5566	0,19	0,81
386,05	74921	0,4623	0,5377	0,206	0,794
386,05	66864	0,5517	0,4483	0,2847	0,7153
386,05	59567	0,6515	0,3485	0,379	0,621
386,05	54085	0,7282	0,2718	0,4606	0,5394
386,05	43076	0,8814	0,1186	0,6879	0,3121
386,05	38029	0,9445	0,0555	0,8321	0,1679
386,05	33600	1	0	1	0
471,95	1511700	0	1	0	1
471,95	1454800	0,0481	0,9519	0,0132	0,9868
471,95	1388300	0,1014	0,8986	0,0295	0,9705
471,95	1321000	0,1511	0,8489	0,0464	0,9536
471,95	1243500	0,2085	0,7915	0,068	0,932
471,95	1125600	0,3032	0,6968	0,1095	0,8905
471,95	1071100	0,3488	0,6512	0,1324	0,8676
471,95	1028350	0,3902	0,6098	0,1552	0,8448
471,95	943890	0,4611	0,5389	0,1991	0,8009
471,95	872870	0,5366	0,4634	0,2538	0,7462
471,95	828400	0,5718	0,4282	0,2827	0,7173
471,95	730840	0,6635	0,3365	0,3706	0,6294
471,95	666030	0,7251	0,2749	0,4424	0,5576
471,95	588120	0,8043	0,1957	0,5548	0,4452
471,95	542270	0,8539	0,1461	0,6404	0,3596
471,95	481250	0,9107	0,0893	0,7576	0,2424
471,95	446090	0,941	0,059	0,8304	0,1696
471,95	389140	1	0	1	0

Table A.5: Regression data PZ+ H_2O

A.3 Absorber /stripper type of packing

- Most economical load range: F-factor between $1-2.5 \sqrt{Pa}$

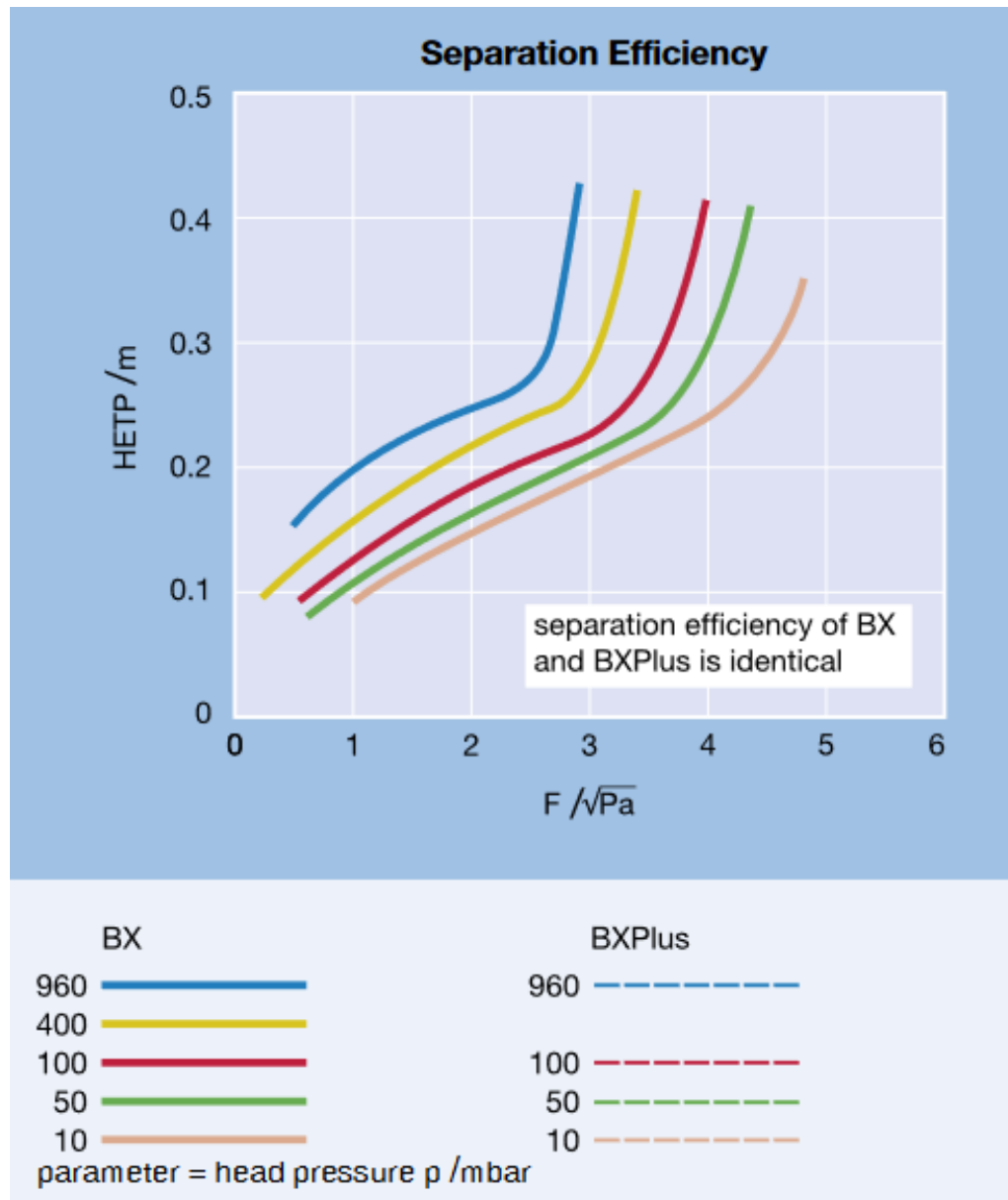


Figure A.2: Data sheet form Sulzer: BX 400 packing type

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