Column Optimization for Amine Based Acid Gas Removal Processes

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given to help me. Besides my advisor, I would like to thank the rest of my thesis committee .......... and I would like also to thank Professor Filipa Ribeiro for all the support.

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“Success is to measured not so much by the position that one has reached in life as by the obstacles which he has overcome while trying to succeed”

Booker T. Washington
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Abstract

This master thesis consists in process optimization for acid gas treatment using amine solvents. This work is focused on getting a gas within certain specifications and conditions, which are necessary for the gas commercialization and consumption.

Thus, the study performed was made for different sources of natural gas, with different compositions. For all these a preliminary study was made on the absorption column process to determine the possible design that can be used to achieve the required specifications. For all designs, a careful selection was performed in order to select the best and most profitable design to be studied. Additionally, the parameters that change between each design are the column height and solvent flowrate used in the absorber.

For the previous selection economic studies, calculation of the CAPEX and the OPEX are carried out, for each procedural scheme. These studies allow to select which of the situations can ensure greater reliability and viability of the project under analysis.

Additionally, it is performed several sensitivity analysis to the mass transfer parameters in the absorber, this sensitivity study is performed to ascertain the most susceptible factor to be changed to ensure the optimization of the operational conditions and consequently to obtain a project economically more favorable.

Using the most economical packing design it will be studied the influence of changing the packing type in the operational conditions, in the CAPEX and in the OPEX. From different commercial packings, it is selected the one that allows to reduce the columns dimensions in order to reduce the column price, the absorber price is very important because this equipment is the unit with a greater weight in CAPEX calculation.

The results, obtained for natural gas with CO₂ and H₂S and with only CO₂ in the gas composition, allow to conclude that the packing designs are usually more viable economically than conventional trays designs. In addition, processes with lower amine flowrate allow to have processes with better OPEX and better operations yields in the absorber, due to the fact that with lower flows it is possible to work close to the thermodynamic equilibrium of the system under study. Analyzing the results of the sensitivity analysis it can be verified that the most sensitive parameter is the interfacial area, so increasing this area a column will be obtained with lower height, so cheaper. In all the cases the \( k_G \) (gas coefficient of mass transfer) variation in \( \pm 20\% \) don’t have a sizeable impact in the CO₂ and H₂S removal. Although the \( k_L \) (liquid coefficient of mass transfer) variation could be interesting.

Concluding, the packings that fit better with our requirements are the PACKING 6, PACKING 3, PACKING 4 and PACKING 2.

Keywords: Absorption, Absorber, Regenerator, Packing, Trays, Process design and optimization, Acid gas, Economic analysis, Mass Transfer
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Resumo

Esta tese de mestrado consiste no estudo da otimização de processos para remoção de gases ácidos do gás natural usando aminas como solvente. Este trabalho tem como foco a obtenção de gases dentro de certas especificações e condições necessárias para a comercialização e consumo do gás natural.

Deste modo, o estudo efetuado foi realizado para diferentes fontes de gás natural com diferentes composições, para todos estes foi efetuado um estudo preliminar à coluna de absorção do processo, para determinar quais são as possíveis configurações que podem ser utilizadas para atingir as especificações requeridas. Dentro de todas as configurações possíveis é efetuada uma seleção de modo a filtrar quais os melhores “designs”, cada “design” varia em termos de tipo de enchimento, altura da coluna e quantidade de solvente usado para a extração dos componentes ácidos.

Com os casos anteriores são realizados estudos econômicos ao CAPEX e OPEX para cada esquema processual, sendo que estes permitem selecionar qual a situação que garante maior fiabilidade e viabilidade do projeto.

Adicionalmente são efetuadas análises de sensibilidade aos coeficientes de transferência de massa na coluna de absorção, esta análise é realizada para se determinar quais são os fatores mais susceptíveis a alteração para garantir uma otimização nas condições processuais.

Após a seleção da configuração mais econômica para a coluna de enchimento é examinado qual a influência da alteração do tipo de enchimento nas condições operatórias, no CAPEX e no OPEX. Como tal é selecionado qual o enchimento comercial que permite diminuir as dimensões da coluna e reduzir os custos da coluna de absorção. Este é o equipamento que representa o maior peso na determinação do CAPEX.

Os resultados obtidos realçam que os designs em que se utiliza enchimento permitem obter projetos economicamente mais viáveis, para além disso, processos onde o caudal de amina é inferior proporcionam um OPEX mais baixo e melhores rendimentos no funcionamento da coluna de absorção, pois com menos caudal é possível trabalhar mais perto do equilíbrio termodinâmico do sistema. Das análises de sensibilidade efetuadas é possível verificar que os parâmetros de transferência de massa são de extrema importância na remoção de CO2, pois como a amina usada é seletiva na remoção de H2S este componente é removido com mais facilidade tornando assim o CO2 o componente limitante no processo de absorção. Na maioria dos casos o fator mais sensível para ser modificado é a área interfacial entre o gás e o líquido sendo que em alguns casos o aumento do valor do coeficiente de transferência de massa do líquido também é uma boa abordagem para melhorar as dimensões da coluna. Finalmente, dos diferentes tipo de enchimento comercial é possível selecionar alguns que permitem uma redução significativa no preço da coluna, tais como os packings: PACKING 6, PACKING 3, PACKING 4 and PACKING 2.

Palavras-Chave: Absorção, Absorvedor, Regenerador, Enchimento, Pratos, Optimização e dimensionamento de processos, Gás ácido, Análise econômica, Transferência de mass
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Nomenclature

Geral

\(a_i\) \hspace{1cm} \text{Interfacial area} \hspace{1cm} m^2/m^3

\(C_i^i\) \hspace{1cm} \text{Concentration of the component } i \text{ at the interphase} \hspace{1cm} \text{mol/m}^3

\(C_i^b\) \hspace{1cm} \text{Concentration of the component } i \text{ at the bulk of phase} \hspace{1cm} \text{mol/m}^3

\(C_i^*\) \hspace{1cm} \text{Concentration of a component } i \text{ in equilibrium with bulk phase} \hspace{1cm} \text{mol/m}^3

\(C_i^\infty\) \hspace{1cm} \text{Concentration of the component } i \text{ at the interphase} \hspace{1cm} \text{mol/m}^3

\text{CAPEX} \hspace{1cm} \text{Capital Expenditure} \hspace{1cm} k\€

\text{CO} \hspace{1cm} \text{Cape Open}

\text{CCC} \hspace{1cm} \text{Correlative factor}

\(D\) \hspace{1cm} \text{Diameter}

\(H_i\) \hspace{1cm} \text{Henry's coefficient for a component } "i" \hspace{1cm} m^3/Pa.mol

\(H_{\text{packing}}\) \hspace{1cm} \text{Packing height} \hspace{1cm} m

\text{HETP} \hspace{1cm} \text{Theoretical plate}

\text{HMB} \hspace{1cm} \text{Heat and Material Balance}

\text{HTU} \hspace{1cm} \text{Height of transfer units} \hspace{1cm} m

\text{IEA} \hspace{1cm} \text{International Energy Agency}

\text{ISBL} \hspace{1cm} \text{In Side Battery Limits}

\(k_G\) \hspace{1cm} \text{Coefficient of mass transfer for the gas} \hspace{1cm} m/s

\(k_L\) \hspace{1cm} \text{Coefficient of mass transfer for the liquid} \hspace{1cm} m/s

\(K_G\) \hspace{1cm} \text{Overall mass transfer coefficient for the gas} \hspace{1cm} m/s

\(K_L\) \hspace{1cm} \text{Overall mass transfer coefficient for the liquid} \hspace{1cm} m/s

\text{LNG} \hspace{1cm} \text{Liquified natural gas}

\(m_i\) \hspace{1cm} \text{Partition coefficient}

\(N_i\) \hspace{1cm} \text{Absorption rate} \hspace{1cm} \text{mol/m}^2.s

\text{OPEX} \hspace{1cm} \text{Operational Expenditure} \hspace{1cm} k\€/year

\text{OSBL} \hspace{1cm} \text{Out Side Battery Limits}

\(P_i\) \hspace{1cm} \text{Partial Pressure of a component } "i" \hspace{1cm} \text{bar}

\(P\) \hspace{1cm} \text{Pressure} \hspace{1cm} \text{bar}

\text{PME} \hspace{1cm} \text{Process Modeling Environment}

\(Q\) \hspace{1cm} \text{Flowrate} \hspace{1cm} S m^3/h

Components

\(H_2S\) \hspace{1cm} \text{Sulfure d'hydrogène}

\text{CO}_2 \hspace{1cm} \text{Carbon dioxide}

\text{MDEA} \hspace{1cm} \text{Monoethanolamine}

\text{DEA} \hspace{1cm} \text{Diethanolamine}

\text{TEA} \hspace{1cm} \text{Triethanolamine}

\text{DIPA} \hspace{1cm} \text{Diisopropanolamine}

\text{DGA} \hspace{1cm} \text{Diglycolamine}

\text{MEA} \hspace{1cm} \text{Methydiethanolamine}

\text{COS} \hspace{1cm} \text{Carbonyl sulfide}

\text{CS}_2 \hspace{1cm} \text{Carbon disulfide}

\text{RSH} \hspace{1cm} \text{Thiol}

\text{H}_2\text{O} \hspace{1cm} \text{Water}
\[ N_2 \quad \text{Nitrogen} \\
CH_4 \quad \text{Methane} \\
C_2H_6 \quad \text{Ethane} \\
C_3H_8 \quad \text{Propane} \\
iC_4 \quad \text{Iso-Butane} \\
NC_4 \quad \text{N-Butane} \\
iC_5 \quad \text{Iso-Pentane} \\
NC_5 \quad \text{N-Pentane} \\
C_6^+ \quad \text{Hexane and compounds with a larger number of carbon atoms than hexane}

\textbf{Subscripts}

\begin{align*}
G & \quad \text{Gas phase} \\
L & \quad \text{Liquid phase}
\end{align*}
1 Introduction

1.1 Motivation

Natural gas market is growing due to the global demand for energy. In the oil sector, the use of resources richer in acid gases, contributed to the changing of the environmental constraints and therefore of the targeted specifications, and this leads to the need of developing new treatments; also the technologies and the treatment used are constantly changing due to technical and economical issues.

The H$_2$S and CO$_2$ removal processes have great interest in today’s industry so the motivation of this work is the development and improvement of the technical aspects in the processes for gas treating for removal of acid gas using amines. The importance of this study is to ensure that this component must be captured either to achieve imposed legislation limits or to meet required specifications and ensure the best profitable situation for the industry. There are diverse types of amine solvents and several structures of packing that the industry can use so it is relevant to make a study of what is the best operational and technical conditions to achieve the different gas specifications for transport and processing, and at the same time ensure the lowest CAPEX and OPEX for the absorber and for the regenerator.

1.2 Objectives

This internship is a part of an industrial project, where the objective is to optimize an amine based gas treatment process. This focuses on the research of more adapted packings (in terms of capacity and mass transfer) to optimize the design of the absorption and regeneration columns and to study how to minimize CAPEX and OPEX. In this internship these are the more important stages:

- Perform a sensitivity analysis on market representative cases studies;
- Analyze the behavior of absorption and stripping columns in different case studies;
- Find for each case the key parameters driving the mass transfer and define targets;
- According to the previous results, identify commercial packings that could help to reach these targets using literature and in-house data;
- Perform technical-economic studies with the selected packing’s and compare with existing technologies.

1.3 Master Thesis Outline

This master thesis can be divided in four distinct sections:

1) **The State of Art**: this section is the synthesis of the bibliographic study. This chapter describes the importance of the gas natural for the world energy demand, the processes that can be used for treating and conditioning the natural gas, and the absorption process by amine solvents (chemical reactions, mass transfer theory, etc.).

2) **Methodology**: in this section it is explained the methods applied for the design and optimization of acid gas treatment using amine solvents to achieve the wanted specifications and to obtain a more economical and reliable process.

3) **Results and Discussion**: the results for each feed gas studied are presented and discussed to ensure the CO$_2$ and H$_2$S specification in the treated gas. For each situation the most economical and reliable process was chosen using the economic results, the sensitivity analysis carried out and by the attempt of optimize the absorber using different commercial packing.
4) **Conclusion** - final conclusion where the most important results are featured.
2 State of art

2.1 Global Vision

Natural gas is a key energy resource, whose reserves are abundant and which also supplies petrochemicals and heavier compounds for the gasoline pools; plants for these products must be flexible, both in technical and economic terms, so that they can react quickly to demand peaks, and are ideally twinned with intermittent renewable options such as wind power. They can also provide a back-up electric generating capacity needed as more variable renewable capacity comes online. When replacing other fossil fuels, natural gas can also lead to lower emissions of greenhouse gases and local pollutants. [1] [2]

This gas can help to diversify energy supply as it is possible to see in the Figure 1, in this figure it’s evident that the demand for gas is increasing and is expected to continue to increase; it can be observed that between 2008 until 2035 there is a predicted increase of the demand of the natural gas of 62% so that the average rate of increase in the gas demand is expected to be nearly 2% per year. [3]

![Figure 1. World primary energy demand by fuel in the GAS scenario. [3]](image)

The statistics from IEA predicts that around 2020 the demand of natural gas will overtake the demand of coal, this overtaking makes the natural gas the second-largest fuel in the primary energy mix. [3]

According to the International Energy Agency “The future for natural gas is bright”. With mounting concerns over energy security and global climate change, and renewed debate surrounding the future role of nuclear power, these developments merit a deeper investigation of the prospects for, and the implications of, a “golden age of natural gas”. [1]

Additionally, in the world there is a considerable number of natural gas reserves; however its geographic disposition presents some complexity because they are scattered across the globe but there are regions with higher amounts of natural gas, this fact can be seen in Figure 2. So the strong geographic disparity of these reserves leads to the classification of three families of natural gas (Raw gas comprising CO₂, crude gas comprising H₂S, raw gas comprising CO₂ and H₂S), for each family we need to implement different types of technologies. The choice of treatment technologies can therefore be also conditioned by the initial content in the raw gas in heavy hydrocarbons, in particular aromatics and by the initial H₂S/CO₂ ratio, in order to limit the solubility of the hydrocarbons and to maximize the H₂S/CO₂ selectivity. [3] [2] [4]
Natural gas can enhance security of supply for the world energy demand because looking at the Figure 3. and consulting the IEA statistic it is observable that the total global resources of natural gas exceed 250 years of current production while in each region, these resources exceed 75 years of current consumption. [3]
This statistics uses a combination of conventional and non-conventional gas resources, the unconventional natural gas is constituted by shale gas, tight gas and gas hydrates, the gas resource base is vast and geographically diverse. [3] [6]

One of the big bets in natural gas market is the liquefied natural gas or LNG. LNG plants are complex and as such their economics thrives on economics of scale. [2]
The liquefied natural gas is predominantly methane that has been converted to liquid form for ease of storage or transport. Hence the LNG industry is growing which is boosting significantly the share of LNG in global trade, this growing will allow to enhance the supply security and give to the market more flexibility. During the last decade, several companies have invested in LNG terminals in different regions of the world. [3] [7]
Through the analysis of Figure 4 it is observable that looking further ahead to the period between 2015 and 2020, projects with a total over 500 bcm of additional liquefaction capacity are being evaluated. The Australia, Russia, Nigeria and Iran account for three-quarters of this capacity for 2020.
The LNG facilities will mostly likely be incorporated into an existing regasification terminal to take advantage of mooring facilities and tankage. [3]

In short it is predicted the increasing of the global demand of natural gas so there is the need of ensuring that the gas is within the legislated standards concerning the transportation, storage and usage of this energy.

In order to ensure that specifications are fulfilled, the gas processing facilities should seek to optimize the processes and seek for new technologies to be possible to treat gases with ever larger quantities of carbon dioxide, so with more quantities of CO₂ and H₂S. In the next subchapters it will be explained the importance of removing these two components.

2.2 Gas Treating

Gas treating requires different process plants depending on sour gas composition and treated gas specifications. Undesirable components should be removed from gas streams to ensure the security and good operating conditions, since these compounds can be responsible for these different constraints: [2] [6]

- Contamination of the final product;
- Catalyst poison;
- By-product production;
- Corrosion;
- Dew point, unwanted condensation downstream;
- Environmental considerations.

Nowadays the big challenges are related with the emission reduction of carbon dioxide and sulfur to the atmosphere. Each day that goes by the governments apply more severe environmental legislation so it is important to reduce the percentage of these components in gas stream before being transported or used. So the objective of gas treating facilities is trying to find the most effective solutions in order to make the process more profitable. Having said that, it must be remembered that operational costs and any lost production are also factors related with the reliability and profitability of the process. There is always competition and the operator with the best profit margin will be better off in the longer term. [4] [2] [4]

The Figure 5 gives the global diagram for a natural gas processing, the section that is directly related with this report is the amine sweetening gas unit.
The goal of these units/processes is to reduce the acid gases concentrations, like $\text{H}_2\text{S}$ and $\text{CO}_2$ to achieve the required specifications allowing the natural gas to be commercialized. Additionally, it is possible to use the acid gas obtained in the sweetening process to produce solid sulphur in a Claus Unit (see Figure 5). When commercialization of the natural gas is made there are two possible applications, one is the LNG production and other the transportation through pipelines of natural gas. The specifications required in terms of acid gas concentrations are different for each type of application, so in Table 1 the compositions for each application are specified.

<table>
<thead>
<tr>
<th>Acid Gas Components</th>
<th>Natural Gas Pipeline Transport</th>
<th>LNG Production</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2\text{S}$</td>
<td>4 ppm</td>
<td>4 ppm</td>
</tr>
<tr>
<td>$\text{CO}_2$</td>
<td>20 ppm</td>
<td>50 ppm</td>
</tr>
</tbody>
</table>

Table 1. Specifications for each gas application. [2]

The gas treating line is affected by the composition of the natural gas and by the application that the gas will have. One should notice that the gas composition (light and heavy hydrocarbons, impurities, metals, water, $\text{H}_2\text{S}$, $\text{CO}_2$, etc.) is related with the geographic area where the natural gas reserve is located, and with the time of exploration of the well [4].
Figure 6. Percentage of CO\textsubscript{2} and H\textsubscript{2}S in natural gas by geographic area. [4]

In the Figure 6 it can be observed different compositions of acid gas for different places in the world, in some places like Europe the gas is majority composed by CO\textsubscript{2} while the natural gas in North America is composed by H\textsubscript{2}S and CO\textsubscript{2} almost in the same percentage (% mole). While gas composition can vary significantly, gas treatment has common objectives like: [6] [2] [4]

- Sweet the raw gas (removal of CO\textsubscript{2} and H\textsubscript{2}S) to meet the specifications required for use (pipelines, liquefaction, sulfur production, etc.);
- Removing sulfur compounds such as mercaptans, carbonyl sulfide (COS) and carbon disulfide (CS\textsubscript{2}) which are present in low levels but contribute to the total sulfur content in the gas;
- Dehydrate the gas;

As previously discussed the raw gas can have different composition so it is necessary to use different contactor technologies and/or different type of solvent to ensure that the quantity of CO\textsubscript{2} and H\textsubscript{2}S desired in the treated gas is reached. Then it is essential to understand and to know the different types of processes that can be used and what are the processes and solvents that turn the processing unit more profitable.

2.3 Overview of different types of processes

As referred in the previous text there is a need for different sweetening processes. Currently, there are three main families of acid gas treatment: [2] [4] [6]

- Adsorption processes, which aim to eliminate H\textsubscript{2}S or other minor sulfur compounds (COS, RSH, CS\textsubscript{2}, light sulfides) suitable for gas with low H\textsubscript{2}S levels;
- Redox processes, which aim to eliminate the H\textsubscript{2}S, suitable for low to moderate H\textsubscript{2}S concentration in the gas, and which have the advantage of removing sulfur directly under solid form;
- Absorption processes, which aim to eliminate the CO\textsubscript{2} and H\textsubscript{2}S, and which use chemical solvents, physical or hybrid. Depending of the gas characteristics can be selected the most appropriate technology to deal with it.

In order to choose between one of the three families of technologies the quantity of sulfur per day (kg S/day) should be analyzed; if the gas stream has between 50 – 100 kg S/day an absorption processes can be used but
if the feed gas has up to 10 \( \text{ton/day} \) it is better to use redox processes. However if the gas has more than 10 \( \text{ton/day} \) the best technology is the absorption processes. [4]

Furthermore other parameters should be considered for choosing the most adequate technology. For example, the elimination of \( \text{CO}_2 \) can’t be performed with the adsorption processes or oxidation-reduction since these two technologies can only eliminate the \( \text{H}_2\text{S} \). For such cases, the removal of \( \text{CO}_2 \) requires the use of absorption, alone or in sequence with one another technology. The choice of the absorption method (chemical solvent, physical or hybrid) will depend on other criteria such as acid gas content, \( \text{CO}_2 + \text{H}_2\text{S} \), the presence of sulfur impurities (RSH, COS, CS\(_2\), sulfides), application of the heavy oil content and in particular aromatics, the required specifications [2] [4].

The adsorption processes were developed to respond to a need for selective removal of \( \text{H}_2\text{S} \) against \( \text{CO}_2 \), for a gas with low levels of \( \text{H}_2\text{S} \) and \( \text{CO}_2 \). The main applications are the processing of natural gas and lightly loaded \( \text{H}_2\text{S} \) gas storage. The adsorbent masses or liquid implemented are largely non-regenerable and therefore the amount of \( \text{H}_2\text{S} \) to be treated should be limited because these processes induce high OPEX costs, the OPEX is an ongoing cost for running a product, business, or system. [9]

The main advantage of these processes are:

- The low CAPEX, the CAPEX represents the cost of developing or providing non-consumable parts for the product or system. [9]
- The low OPEX, because in this process it is necessary less regeneration energy to regenerate the solvent used.

### 2.4 Absorption Processes

The technology family that we will apply in this master thesis is the absorption process, so it is essential to understand the basis of this technology. Absorption is a widely used process for separating gases, removing undesired gas components or to prevent pollution from stacks. The mass transfer process is generally rate controlled. Inside the column the mass transfer phenomena occurs between the gas and the liquid. Mass transfer rates and mass transfer coefficients may differ between the components that are involved in the absorption process [6] The objective of this process is to capture gaseous acids, as \( \text{CO}_2 \) and \( \text{H}_2\text{S} \), and also to remove the COS and mercaptans. [10] [4] [2]

Absorption processes use solvents to remove undesirable components. [11] There are three types of solvents that can be used:

- Chemical solvents that react with acid gases;
- Physical solvents which don’t react with the acid gases;
- Hybrid solvents consisting of a reactive molecule and a physical one, it is a mixture of the last two types.

The partial pressure of acid gas in the treated gas and in the raw gas are fundamentals for the solvent selection (Figure 8). It is evident that the amine solvent is very diverse and it can have several applications.
Since the absorption rate is driven by mass transfer then the gas liquid contact is critical to ensure good performances. The most efficient contactors are those who develop the largest interfacial area between the two fluids and which retain as much as possible the dispersed phase, while remaining within acceptable pressure loss values. To have a large interfacial area, it is necessary to disperse one phase into another creating turbulence to improve the transfer. [12]

For the acid gas processing, the gas and solvent are usually set in contact in a column equipped with trays or with packings (random or structured). The advantage of using packing is that this creates a larger interfacial area while the void fraction is higher than 90%, then packed columns generate small pressure drops and increase capacity compare with columns trays. [2] [4] [10]

The contactor capacity is critical for a pressurized column. A capacity increase allows to reduce the column diameter, then to decrease significantly the CAPEX, especially due to the thickness of metal necessary for sustain under pressure. It should be noticed that when the capacity decreases the efficiency usually increases. Then, the choice of a contactor is fundamental, and it is important to maintain a compromise between efficiency and capacity in an absorption column. [4] [6]

The column pressure is the driving force of the mass transfer but the design of the absorber depends on the gas volume, inlet concentration, outlet specification, pressure, temperature, liquid circulation rate, solubility of the gas in liquid, number of trays, height, contact time, diameter of column and the presence of other components in the gas. [2]

2.5 Global absorption Process by Amines

As previously discussed, the design of the absorber depends on the gas volume, inlet concentration, outlet specification, pressure, temperature, liquid circulation rate, solubility of the gas in liquid, number of trays, height, contact time, diameter of column and the presence of other components in the gas. [2]. In some cases, mass transfer must be enhanced by chemical reactions, this is called reactive absorption processes. For gas treatment, amines are widely used to react with undesirables acid gases. A typical process based on an amine solution is shown in the Figure 9. These processes can support large quantities of H2S economically, and CO2 may also be controlled if necessary.
Explaining the process shown in the Figure 9 it can be seen that initially the raw gas enters into an absorber column but normally first it is admitted into a gas-liquid separator where the gas is free of any liquid trace to prevent the strong foaming or flooding of the column, this unit isn’t represented in the Figure 9. After the feed gas pass through the separator it enters into the bottom of the absorber where the current contacts with the regenerated solvent, lean solvent, which enters at the absorber head. The absorber can be filled with packings or plates and usually operates at high pressures between 50 until 100 bar. The treated gas, without acid gas, exits in the top of the absorber and it is cooled in a heat exchanger, air cooler, and next it passes through a gas-liquid separator for the treated gas stream to be free of any liquid trace, then the gas stream can be sold, transported or storage. The amine-rich acid gases and processed gas condensates are sent to the ball flash operating at medium pressure, the relaxation allows the majority of light hydrocarbons to be vaporized, this step isn’t performed if the gas that enters in the unit is at a pressure near to atmospheric pressure, such as in the case of biogas. [2] [6] [4]

The solvent rich in acid compounds is then preheated in an amine-amine heat exchanger using the regenerated solvent, and then it enters the regeneration column operating at low pressure, about 2 bar, where it is thermally regenerated by stripping. As the absorber, the regenerator can be filled or fitted with trays. The acid gas is released in head, and the existent water in the acid gas is condensed by a heat exchanger and then separated in the reflux drum. [2] [6] [4]

The separated water is called reflux and it is reintroduced in the head regenerator. In the bottom of the regenerator, enters the amine reboiler, often type Kettle, where amine is heated and in here the vapor generated returns to the regenerator and the regenerated amine leaves the column and it goes to amine-heat exchanger to be cooled. 10% of the amine flow is led into the filter device and all of the regenerated solvent is cooled and pressurized so it can be reused in the absorber. [6] [4]

2.6 Amine-Based Process

During the 19th and early 20th century, the elimination of H₂S gas was usually achieved by methods employing solid adsorbents such as iron oxide or solutions of inorganic salts but the discovery by Bottoms, in 1930, of a regenerative method using alkanolamines contributed to the rapid increase in the use of natural gas. Since that time, many gas acidification processes have been developed. However, the process of absorption using amines still is the most accepted and widely used. The technology that Bottoms patented used triethanolamine, TEA, but today in the market exists a wide range of amines solvents that can be used. In the Table 2 is represented the three family of amine solvents that can be used e some proprieties of these amines. [13] [6]
Table 2. Different kind of amines and their characteristics. [2] [6]

<table>
<thead>
<tr>
<th>Primary Amine</th>
<th>Secondary Amine</th>
<th>Tertiary Amine</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_2\text{N} - \text{OH} )</td>
<td>( \text{HO-CH}<em>{2}-\text{NH-CH}</em>{2}-\text{OH} )</td>
<td>( \text{HO-CH}_{3}-\text{OH} )</td>
</tr>
<tr>
<td>Monoethanolamine (MEA)</td>
<td>Diethanolamine (DEA)</td>
<td>Triethanolamine (TEA)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Characteristics</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>+basic; +reactive; Not selective elimination of CO(_2) and H(_2)S; +corrosive; Regeneration energy more important.</td>
<td>It is a middle ground between Primary Amines and Secondary Amines</td>
<td>-basic; -reactive; Selective elimination of the H(_2)S vs CO(_2); -corrosive; Regeneration energy less important.</td>
</tr>
</tbody>
</table>

These amines have different properties and applications therefore it is relevant to explain and talk a little bit about these: [2] [4] [13] [6]

- **MEA or Monoethanolamine** was the earliest amine used for sweetening sour gas. This amine is a primary amine. It is a colorless, viscous liquid with an odor reminiscent to that of ammonia. MEA is the strongest base when compared with the other amines, so it reacts very quickly with the acid gas. Furthermore it is considered a non-selective amine between the H\(_2\)S and the CO\(_2\), therefore MEA can remove these two acids to low levels. MEA forms no non-regenerative (degradation) compounds so this is a disadvantage of using MEA, also the compounds formed by degradation are a disadvantage for this amine, so these compounds must be removed periodically to lessen the corrosion rate. A reclaimer is usually incorporated in a MEA sweetening train to periodically remove the degradation products from the solution by distillation.

- **DGA or Diglycolamine**, It has been applied in some of the world’s largest sour gas treating plants. The advantage of DGA over MEA appears to be the lower solution circulation rate owing to the higher solvent concentration, resulting in higher acid gas pickup per volume of solution circulated. Disadvantages appear to be degradation of the chemical with CO\(_2\) and greater solubility of heavier hydrocarbons in the solution, as compared to MEA.

- **DEA or Diethanolamine**, it became a popular sour gas treating solvent in the 1960s after it was developed for such application in France. It can be used at higher concentrations than MEA. DEA has the advantage of picking up more acid gas per solution volume circulated, so it means saving some energy in circulation and regeneration. It doesn’t form the non-regenerative products with COS and CS\(_2\) as is the case with MEA, which is another advantage over MEA. DEA is also generally less corrosive than MEA. Basically the aqueous DEA process is similar in principle and operation to the MEA process.

- **DIPA or Disopropylaniline**, this secondary amine isn’t used by itself as a sweetening solvent but is part of the Sulfinol solvent formulation by Shell.
- **MDEA or Methydiethanolamine**, during the 1980’s this amine received a lot of attention due to the lower energy costs for regeneration, degradation resistance, low corrosion and because of its capability for selective reaction with H₂S in the presence of CO₂. This is an attractive feature in cases where it isn’t necessary to remove all the CO₂ from the gas stream. By leaving some of the CO₂ in the natural gas, the circulation rate of the solution can be reduced, or the treating capacity of an existing unit can be increased when compared the MDEA with the DEA.

- **TEA or Triethanolamine**, in a global way, it isn’t used for gas sweetening.

- **Mixture of amines**, basically it is a solvent composed by a primary or a secondary amine and a tertiary amine, it is interesting to couple high reaction rates and low regeneration energies and losses. By optimizing the quantities of each solvent in the solution, the same removal results can be obtained with a less costly solution, by introducing less quantities of amine make-up and by furnishing less quantities of heat to the regeneration column.

Basically, amines are organic bases with pH greater than 7 and the amines will react with acids like H₂S and CO₂ and these acids have pH less than 7 so for amines to remove the acids the reaction that will occur is an acid-base reaction. The equilibrium reactions in the system amine/gas can be summarized in seven independent reactions and all of them are exothermic so these will increase the temperature of the contactor/absorber. The seven kind of reactions that occurs are in the following table:

<table>
<thead>
<tr>
<th>Name of the reaction</th>
<th>Reactions</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionization of water</td>
<td>[2\text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^+ + \text{HO}^-]</td>
<td>Equation 1</td>
</tr>
<tr>
<td>Dissociation of H₂S</td>
<td>[\text{H}_2\text{O} + \text{H}_2\text{S} \leftrightarrow \text{H}_3\text{O}^+ + \text{HS}^-]</td>
<td>Equation 2</td>
</tr>
<tr>
<td>Dissociation of the HS⁻</td>
<td>[\text{H}_2\text{O} + \text{HS}^- \leftrightarrow \text{H}_3\text{O}^+ + \text{S}^{2-}]</td>
<td>Equation 3</td>
</tr>
<tr>
<td>Dissociation of CO₂</td>
<td>[2\text{H}_2\text{O} + \text{CO}_2 \leftrightarrow \text{H}_3\text{O}^+ + \text{HCO}_3^-]</td>
<td>Equation 4</td>
</tr>
<tr>
<td>Dissociation of carbonate</td>
<td>[2\text{H}_2\text{O} + \text{HCO}_3^- \leftrightarrow \text{H}_3\text{O}^+ + \text{CO}_3^{2-}]</td>
<td>Equation 5</td>
</tr>
<tr>
<td>Dissociation of protonated amine</td>
<td>[\text{H}_2\text{O} + \text{R}_1\text{R}_2\text{R}_3\text{NH}^+ \leftrightarrow \text{H}_3\text{O}^+ + \text{R}_1\text{R}_2\text{R}_3\text{N}]</td>
<td>Equation 6</td>
</tr>
<tr>
<td>Hydrolysis of carbamate</td>
<td>[\text{H}_2\text{O} + \text{R}_1\text{R}_2\text{NCOO}^- \leftrightarrow \text{HCO}_3^+ + \text{R}_1\text{R}_2\text{NH}]</td>
<td>Equation 7</td>
</tr>
</tbody>
</table>

About the Table 3 it is relevant to refer that the last equation only occurs for primary and secondary amines.

The reactivity differences between different classes of amine explains the selective nature of tertiary amines. These amines react according to a rather slow kinetics with CO₂ because they can’t do the hydrolysis of the carbamate. Additionally for secondary amines that are very congested the reactions with CO₂ are very slowly because the steric hindrance prevents the CO₂ molecule to reach the nitrogenous group. Primary amines and secondary amines react very quickly with CO₂ and form a stable carbamate so these aren’t selective and allow complete removal of CO₂ and H₂S. [4] [2] [6]
However it is possible to remove the acid of the gas using physical absorption and many commercial processes rely on this principle. The absorption results of physical contact by solubility without chemical reaction between the gas to be treated and a mixed solvent of a pure product. Therefore it isn’t necessary to set up an addition of water in processes to physical absorption. These absorption is strongly dependent on the gas pressure load and more particularly to the partial pressure of acid gas to eliminate. Most often, the solvents used have a high affinity with water so this method permits simultaneous to deacidify and to dehydrate the gas but in return it is necessary to strip the solvent to remove absorbed water. To choose a good physical solvent it is important to look at the main proprieties that a good solvent needs to have, like: [2] [6]

- Low vapor pressure at the operating temperature to limit solvent losses;
- Low solubility of hydrocarbons;
- No deterioration in working conditions;
- No chemical reaction between the solvent and the compounds of feed gas;
- No corrosion on base metals.

As has already been seen for the gas treatment can be used physical or chemical absorption processes but each one of them have different advantages and disadvantages, so the physical absorption has the following advantages in relation to chemical absorption: [4] [2] [6]

- Low energy for regeneration;
- Reducing corrosion to carbon steel equipment’s so installation less expensive.
- Solubility of acid gases to achieve higher filler content and thus cover a wide range of application;
- Pick pushed mercaptans and other sulfur contaminants.

However, this method also has some disadvantages:

- Need for a high acid gas partial pressure in the load and a low temperature operation;
- Some solvents require the implementation of a regenerator;
- High co-absorption of hydrocarbons including heavy and aromatic hydrocarbons, which is detrimental in the case of implementation of a Claus plant downstream.

In this section the physical absorption process will be described and explained. The chemical process is already represented in Figure 9, and it was already explained in the last subchapter. [4] [2]

The physical absorption process is very similar to the diagram in the Figure 9, except for the regeneration section which can be done by flashing the charged solvent at low pressure with some preheating. However some physical absorption processes can use the same type of regeneration as other processes, as re-boiler, condenser and stripper. The efficiency of the physical absorption decreases as the temperature increases. The absorption step is often operated at low temperature, which may require the implementation of a cooling cycle and it can penalize the process in terms CAPEX and OPEX and the gain on energy regeneration. [10] [6] [2]

Now that has already been analyzed the physical and chemical absorption processes it is interesting to analyze the hybrid solvents process, this process uses a chemical solvent formulated with a physical solvent. This mixture allows the combination of the benefits of both solvents and reduction of the disadvantages. When the companies make these mixtures it can be possible to achieve a complete or moderate removal of CO2 while guaranteeing the desulfurization performance of an amine unit. The removal of mercaptans (or other sulfur compounds) can be improved by increasing the diluent flow rate in circulation or the number of the absorber plates. The hybrid solvent processes let us have the following advantages, when we compare this method with the chemical and physical processes: [4] [2] [6]

- Low energy regeneration;
- Low foaming tendency;
  - Removal of mercaptans and other sulfur contaminants.
- Reducing corrosion.
However, the disadvantages are:

- High co-absorption of hydrocarbons and in particular of heavy aromatic hydrocarbons;
- Some solvents require the implementation of regenerator;
- The costs of chemical products are higher than in the others processes.

The diagram flow of a hybrid process is similar to the general process diagram for absorption with amines but a step of low pressure flash may intervene between the flash drum and the medium pressure regeneration column.

![Diagram](image)

*Figure 10. Diagram of an acidification process by physical absorption with regeneration by successive flashes.* [4]

### 2.7 Absorption Column

Absorption is a unit operation that it is used for gas-liquid process. The liquid that is used to pick up the components must be chosen with care to provide to the best possible medium to effect the targeted separation. [10] [6]

The liquid used to bring about absorption is referred to as an “absorbent” and the gas absorbed is called the “absorbate”. The absorbent enters in the top of the column and contains little amount of absorbate and is usually referred to as “lean absorbent” while the exiting absorbent with its higher load of absorbate is usually referred to as the “rich absorbent”. The application area for absorption is wide. It covers acid gas removal in gas treating where the amount of gas to be removed may vary from a few percent to 50%. For gas to pipelines the end specification for CO$_2$ is typically 2–4% while H$_2$S is removed to 2–4ppm. A liquefied natural gas for transportation would require CO$_2$ content to be lowered down to 50ppm. Water removal from natural gas on the other hand is a relatively easy separation where the column could be as low as four trays or 3m of packing. [10] [6] [2]

Furthermore the design of an absorber is based on the selection of certain key parameters to obtain a correct design, such as: [6]

- Select the absorbent;
- Choose the column hardware;
- Determine the required column height;
- Determine the diameter that will promote mass transfer and minimize pressure drop.

In gas treating with amines there is a need to filter the solution for maintenance but that is done externally to the column as we have already see in the “Global absorption Process by Amines” section. [10] [6] [2] [14]

The column’s function is to provide a gas-liquid contact area to facilitate the required separation, this contact area can be ensured by sprays, packing’s or trays. The best choice depends on the situation and the specifications that the gas needs to have. [15]
The gas and the liquid can flow in counter-current flow or in co-current flow; for easy separations co-current flow is worth considering. The liquid must naturally always be fed from the top unless a liquid-continuous bubble column is used, but this situation is rare.

The absorption can be represented by the flux equations for mass absorption and these can be written in terms of the gas, Equation 8, and in terms of the liquid, Equation 9. [6] [14] [16]

\[ N_i = k_G a_i \left( C_i^{gb} - C_i^{gi} \right) \]  \hspace{2cm} \text{Equation 8}

\[ N_i = k_L a_i \left( C_i^{li} - C_i^{lb} \right) \]  \hspace{2cm} \text{Equation 9}

The legend of the previous equations is:

- \( N_i \) – Absorption rate
- \( k_G \) or \( k_L \) – Coefficient of mass transfer for the gas or for the liquid
- \( C_i^{(G \text{ or } L)i} \) – Concentration of the component i at the interphase in the gas or liquid phase
- \( C_i^{(G \text{ or } L)b} \) – Concentration of the component i at the bulk phase of gas or liquid phase
- \( a_i \) – surface area where occur the mass transfer

Using the interface values isn’t convenient to solve this problem. That is why the overall mass transfer coefficients, that will allow us to use the bulk values in the flux equations, are usually preferred. [6] [14] [13]

The inverse of the mass transfer coefficient for a mass transfer region is the mass transfer resistance. The resistances in the gas and liquid sides are in series. They may not be directly summed since one also must consider the gas/liquid interface. At the interface it is supposed to be at thermodynamic equilibrium. Then, the concentrations of the component “i” in the gas and in the liquid phases are linked. The partition coefficient defines this equilibrium and it is given by the Equation 10.

\[ m_i = \frac{C_i^G}{C_i^L} \]  \hspace{2cm} \text{Equation 10}

Models are used to described the mass transfer phenomena and. To develop that models it is customary to pick a so-called control volume, make all the appropriate mass and energy balances over that volume. This will give one equation, or a set of equations, which may be solved to have the mass transfer parameters associated to the mass transfer process. [14] [13] [16]

Figure 11. Double-film theory in mass transfer for absorption.
The mass transfer in the absorber can be modelled by different theories: penetration theory, surface renewal theory, etc. This work uses the double-film theory (Figure 11). Basically, there is a boundary between the gas phase and the liquid phase in contact and it is presumed to be composed of two films, one film for the gas other for the liquid, these are separated by the interface. [14] [6]

For the double-film theory some assumptions are needed, these assumptions are:

- Fick law’s ➔ Linear concentration profile through stagnant film;
- Stationary state conditions;
- No gradient concentration in the bulk of the phases – perfectly stirred;
- The solutes in the interface between the phases are in equilibrium;
- Instantaneous equilibrium;
- Transport by bulk diffusion is not limiting;
- Dilute solutions, therefore apply Henry’s Law.

In this theory, the diffusional resistances only exist in fluids, which means that in the interface there isn’t any resistance to the solute transference. In each phase there is one driving force which leads to mass transfer, for the solute transfer in the gas phase is given by Equation 11 and for the liquid phase the driving force is represented by Equation 12.

\[ \text{Driving Force}_{\text{gas phase}} = C^g_i - C^g_{i*} \] \hspace{1cm} \text{Equation 11}

\[ \text{Driving Force}_{\text{liquid phase}} = C^l_i - C^l_{i*} \] \hspace{1cm} \text{Equation 12}

Looking at the equations that give the rate of the mass transfer for liquid and gas phase, since in this theory steady state is assumed, the rate of transfer of mass in the gas film is equal to the rate of transfer of mass in the liquid film and with that the general equation of mass transfer may be represented as:

\[ N_i = k_L^g a (C^g_i - C^g_{i*}) = k_G a (C^l_i - C^l_{i*}) \] \hspace{1cm} \text{Equation 13}

The values of \( C^g_{i*} \) and \( C^l_{i*} \) are difficult to find in practical cases, so considering a new thought about the subject, considering that the absorption involving highly soluble solutes, the driving force usually is the partial pressure of the solute in the gas phase minus the vapor pressure of the solute above the liquid phase. It is relevant to refer that the concentration in gas phase can be represented by the pressure using the equation of the perfect gases.

Writing the gas concentration in the Equation 13 in terms of pressure, the result will be:

\[ k_L^g a (C^g_{i*} - C^g_{i*}) = k_G a (P^b_i - P^l_i) \] \hspace{1cm} \text{Equation 14}

Furthermore, it is possible eliminate the partial pressure using the Henry’s Law:

\[ P^b_i = HC^L_i \] \hspace{1cm} \text{Equation 15}

\[ P^l_i = HC^L_i \] \hspace{1cm} \text{Equation 16}

Where the:

\( H \) – Henry’s coefficient
$C_i^L$ — Concentration of a component in equilibrium with bulk gas partial pressure

The goal is to eliminate the interfacial concentration, $C_i^{Lb}$, because this quantity is essentially impossible to determine. For that, it is made a substitution of the Equation 15 and Equation 16 in the Equation 14 and considering that Henry’s coefficient is dimensionless, Equation 17, it is achievable to obtain an equation that solves the $C_i^{Lb}$ problem.

$$H = \frac{M}{RT} \quad \text{Equation 17}$$

$$k_L^0 (C_i^L - C_i^{Lb}) = k_G \{ H C_i^L - H C_i^G \} \quad \text{Equation 18}$$

Equation solves for $C_i^L$.

$$C_i^L (k_L^0 + k_G H) = k_G H C_i^L + k_L^0 C_i^{Lb} \quad \text{Equation 19}$$

Putting the function as a function of $C_i^L$ and substitute this in the Equation 9, it is obtained:

$$N_i = k_L^0 \left( \frac{k_G H C_i^L + k_L^0 C_i^{Lb}}{k_L^0 + k_G H} - C_i^{Lb} \right) \quad \text{Equation 20}$$

Developing the equation we obtain:

$$N_i = \frac{k_L^0}{k_L^0 + k_G H} (C_i^L - C_i^{Lb}) \quad \text{Equation 21}$$

Now let:

$$K_L = \frac{k_L^0}{k_L^0 + k_G H} \quad \text{Equation 22}$$

Where $K_L$ is the overall mass transfer coefficient, so we get for the liquid the correlation given by the Equation 23 and applying the same relationship to the gas liquid. It is acquired the next two equations:

$$N_i = K_L (C_i^L - C_i^{Lb}) \quad \text{Equation 23}$$

$$N_i = K_G (P_i^L - P_i^G) \quad \text{Equation 24}$$

Where $P_i^G$ is the partial pressure of a component “i” in gas in equilibrium with bulk liquid concentration.

2.8 Packing or Trays Absorption Column

A column could simply be an empty shell with nozzles to spray the liquid as droplets that would fall in contact with the gas. This arrangement tends to provide one equilibrium stage as a maximum, while for gas treating several stages are usually needed. That is why the industries use in their columns trays or packings. Both of these two types of internals have been used for a long time, and there are no signs that one will oust the other. [17] [18]
The choice between the two types of internals is basically an economic question. The two types of column have different properties that will represent different advantages and disadvantages depending on the application and the specification required. [15]

For a particular application a decision can only be made with complete assurance of the cost for each design. However, this will not always be worthwhile, or necessary, and the choice can usually be made on the basis of experience by considering the main advantages and disadvantages of each type, which are listed below: [18] [19]

- Plate columns can be designed to handle a wider range of liquid and gas flow-rates than packed columns.
- Packed columns aren’t suitable for very low liquid rates.
- The efficiency of a plate can be predicted with more certainty than the equivalent term for packing (HETP or HTU).
- Plate columns can be designed with more assurance than packed columns. There is always some doubt that good liquid distribution can be maintained throughout a packed column under all operating conditions, particularly in large columns.
- It is easier to make provision for cooling in a plate column; coils can be installed on the plates.
- It is easier to make provision for the withdrawal of side-streams from plate columns.
- If the liquid causes fouling, or contains solids, it is easier to make provision for cleaning in a plate column; manways can be installed on the plates. With small diameter columns it may be cheaper to use packing and replace the packing when it becomes fouled.
- For corrosive liquids a packed column will usually be cheaper than the equivalent plate column.
- The liquid hold-up is appreciably lower in a packed column than a plate column. This can be important when the inventory of toxic or flammable liquids needs to be kept as small as possible for safety reasons.
- Packed columns are more suitable for handling foaming systems.
- The pressure drop per equilibrium stage (HETP) can be lower for packing than plates; and packing should be considered for vacuum columns.
- Packing should always be considered for small diameter columns, say less than 0.6 m, where plates would be difficult to install, and expensive.

2.8.1 Packings

Packed columns are used for distillation, gas absorption, and liquid-liquid extraction. Stripping (desorption) is the reverse of absorption and the same design methods will be applied. The gas liquid contact in a packed bed column is continuous, not stage-wise, as in a plate column. The liquid flows down in the column over the packing surface and the gas, counter-currently, flows up in the column. In some gas-absorption columns co-current flow is used. [19] [17] [20]

The performance of a packed column is dependent on the maintenance of good liquid and gas distribution throughout the packed bed, and these are an important consideration in packed-column design. A packed distillation column will be similar to the plate columns however the trays [18]

The main requirements that a packing should have are: [18]

- Provide a large surface area: a high interfacial area between the gas and liquid.
- Have an open structure: low resistance to gas flow.
- Promote uniform liquid distribution on the packing surface.
- Promote uniform gas flow across the column cross-section

There are several types and shapes of packing, these have been developed to satisfy new requirements and needs. They can be divided into two broad classes: [18] [6]
- **Structured Packing**: packing with a regular geometry, such as stacked rings and grids.
- **Random Packing**: rings, saddles and proprietary shapes, which are dumped into the column and take up a random arrangement.

Both types of packings require specific liquid and gas distributors, collectors, redistributors and supports. [18] [6]

The choice of material will depend on the nature of the fluids and the operating temperature. Ceramic packing will be the first choice for corrosive liquid, but ceramics are unsuitable for use with strong alkalis. Plastic packings are attacked by some organic solvents and they can be used up to moderate temperatures, so are unsuitable for distillation columns. Where the column operation is likely to be unstable metal rings should be specified, as ceramic packing is easily broken. [18] [20]

### 2.8.1.1 Random Packings

The principal types of random packings are expressed in the annex 7.1.

Raschig rings are one of the oldest specially manufactured types of random packing, and they continue to be used and represent the first generation of packings. These are tubes with length equal to their diameter. Sizes typically ranged from 10 to 100 mm, with 50 mm probably the most common size in the chemical industry. [18] [6]

Pall rings are essentially Raschig rings in which openings have been made by folding strips of the surface into the ring. This increases the free area and improves the liquid distribution characteristics. [18] [6]

Berl saddles were developed to give improved liquid distribution compared to Raschig rings, the Intalox saddles can be considered to be an improved type of Berl saddle, their shape makes them easier to manufacture than Berl saddles. These and Pall rings probably belong to what may be referred to as a second packing’s generation. Particularly the plastic variety of the saddles and the Pall rings is addressed to supply the lack of total access to the surfaces of the packing and still providing more drip points compared to the Raschig rings. [6] Later the development of the Pall ring claimed to be more cost effective for a given performance. This is an interesting case as simple corrugations were used to make the ring stiffer allowing the use of thinner metal parts thus reducing the amount of material and more tongues meant more available surface area, which was sacrificed to make the ring bigger, thus saving on the number of rings per unit volume. Hence, less metal, less machining and a lower price. [6] [18]

Third generation of packings (Kister, 1992), could be started with the Mini Rings. They claimed much improved performance over Pall or Hy-Pak by making the height of the ring 1/3 of its diameter. The Hypac and Super Intalox packings can be considered improved types of Pall ring and Intalox saddle, respectively. [18].

Recently one speaks about fourth generation of packings like Raschig Super Packings or Raschig Super Rings. Compared with third generation packings, the fourth generation should increase capacity for a similar efficiency.

### 2.8.1.2 Structured Packings

The term structured packing refers to packing elements made up from wire mesh or perforated metal sheets. The material is folded and arranged with a regular geometry, to give a high surface area with a high void fraction. [18] [17]

These packings are available in metal, plastics and stoneware. The advantage of structured packings over random packings is their lower HETP, typically less than 0.5 m, and lower pressure drop, around 100 Pa/m. They are being increasingly used for the following applications: [6] [18]

- For difficult separations, requiring many stages: such as the separation of isotopes;
- High vacuum distillation;
- For column revamps: to increase capacity and reduce reflux ratio requirements.
The driving force for the use of this packing was the desire for high performance columns needed to distil heavy water, which is very demanding in terms of the number of separation stages needed. [6]

The applications of these have mainly been focused in distillation, but structured packing's can also be used in absorption where the absorption requires high efficiency and low pressure drop. The cost of structured packings will be significantly higher than that of random packings, but this could be offset by their higher efficiency. [18]

2.9 Operational problems

2.9.1 Corrosion

Normally the chemical solvents aren’t corrosive in nature, because they combine both a relatively high pH, 8 to 11, and a low electrical conductivity. However, they become corrosive when they absorb acid gases so the main corrosivity parameters that are important to consider are:

- The nature of the amine, when loaded with acid gases the more corrosive amines are the primary amines and next sequence gives the order of the amines from the more corrosive to the less corrosive: Primary > Secondary > Tertiary amines;
- The concentration of amine;
- Load rate of amine with acid gas, which increases corrosivity of the solution and increases the operating temperature;
- Degradation products concentration;
- The solvent circulation rate which can cause erosion if the circulation rate is too large.

To protect against corrosion the design must be done trying to limit the factors that increase the phenomenon. It isn’t always possible to overcome these problems in the design and control of process conditions. Often it is necessary to select steel grades that can resist corrosion, using less sensitive process areas, high rate of charge and high temperature or using corrosion inhibitors. [2] [4] [6]

2.9.2 Degradation

The degradation products are solvent molecules where the chemical structure was modified by reactions with other compounds; it is supposed that these reactions don’t occur. The degradation products also can be formed under the effect of heat. For some of these products it is possible to occur the reverse reaction. Some of the degradation reactions are irreversible and the generated degradation products have adverse effects on the process such as a drop in performance, which can lead to a gas out of specification, an increase corrosion phenomena or a trend to solvent foaming. [2] [4] [6] [21]

2.9.3 Foaming

This phenomenon is probably the problem more often encountered in the operation of gas acidification processes by absorption. It can reduces the processing capacity, decreases performance, increases the solvent losses and generates problems for downstream units. [2] [6]

New solvent fillers have a tendency for very low foaming formation. However, the presence of contaminants can drive a solvent to form foam. Foaming may have multiple causes, the most common being the presence of solids suspended liquid hydrocarbon, methanol, degradation products of the amine, greases or lubricants or excessive use of anti-foam agents. The foam control is done by eliminating responsible contaminants and guaranteeing effective filtration of the solvent. However, it isn’t always possible to eliminate all foaming sources and, as a last resort, it is possible to destabilize the foam by judiciously injecting, as a shock or continuously, small amounts of antifoam. [4] [6]
3 Methodology

In order to develop the master thesis objectives, several programs were used to perform all the necessary simulations to get the wanted results. So to explain the methodology applied it was necessary to split this chapter in two sub-chapters.

The first sub-chapter presents a short summary and explanation of each program used in the development of the thesis. The other sub-chapter is dedicated to the presentation and explanation of the steps performed during the work, so in this way we can observe the methodology used.

3.1 Programs

3.1.1 Simulation tools

This part will present the tools used to simulate the process scheme. Simulations were performed using in house software models (Thermodynamic and Unit operations) developed in Cape Open standards which allow the models to be used in every compliant process modeling environment, as Pro II, Aspen Plus, ProSim+ and others.

For my master thesis, the simulator is used as a tool to obtain the stream data and determine by sensitivity analysis what type of parameters, like the flow, number of plates and more operational conditions, are the optimum to obtain the desired specifications.

3.1.1.1 PME : PROII 9.1.3

PRO II is a process simulator program for process design and operational analysis for process engineers in the chemical, petroleum, natural gas, solids processing and polymer industries. It includes a chemical component library, thermodynamic property prediction methods, and unit operations such as distillation columns, heat exchangers, compressors, and reactors as found in the chemical processing industries. Additionally it can perform stationary state Heat and Material Balance (HMB) calculations for modeling continuous processes.

In this program A first step is to draw the process flowsheet, where it is necessary to define the inputs related with the streams and the units. However in some cases, it is essential to determine what the process conditions are, by making several sensitive analysis.

For my case, Pro II is used to simulate general equipment, miscellaneous utilities (reporting, calculator and controllers) using the proprietary Cape Open thermodynamic model:

- Flash drum
- Mixers / splitters
- Heat Exchangers / air coolers
- Pumps
- Valves

The columns are simulated using specific Cape Open unit operations.

3.1.1.2 Specific in house models : Program A

Models are dedicated to simulate a mine based processes for gas sweetening. It includes a thermodynamic model (properties package and pure component libraries) and rigorous columns unit operations (for absorption and regeneration) using mass transfer rate-based models for acid gas reactions with liquids. These models are rated
by more than 40 years’ experience of plant operation and process data from on-running gas sweetening units. Each column can be simulated in a rigorous or a short cut method. The rigorous absorber and/or regenerator are used to obtain the right equipment design and obtain the real duties and real product streams data. The short cut absorber and/or regenerator perform for a given specification of heat and material balances considering an equilibrium stage and it is used as a first study, like for example to estimate solvent flowrate or reboiler duty, and for simplify the sensitivity analysis or when all the process scheme is simulated to edit HMB’s.

A launcher is dedicated to perform sensitivity studies. It should only be used to simulate absorbers equipped with packing. Moreover the launcher can automatically launch one or more simulations with one or more parameter sets and recover the following results:

- Acid gas content in the treated gas;
- Profiles in the absorber for operational conditions (Temperature, Composition and others).

Additionally, in this launcher the study will focus in analyzing the influence of changing the mass transfer parameters on the treat gas, for that it is important introduce a new term, “CCC”, which is an adjustment factor that lets the program vary each variable in percentage regarding the standard value defined for the programs used.

3.1.2 Costs estimation tool: Program B

The Program B is designed to quickly and easily assess the cost of a complete process unit from the costs of major equipment requiring a reduced number of data. The program is confidential. It is used as an input in the design parameters of all the equipment’s related with process, the design parameters are obtained with the simulator described previously (HMB) and a proprietary program, Program C, the last one makes the design of equipment’s using the stream data obtained in PRO II.

Additionally to understand the results obtained from Program B, it is essential to know the meaning of “the cost estimate perimeter” (“Class 4” as defined by the AACE (Association for the Advancement of Cost Engineering)) which means that the values obtained and presented in the report are in an accuracy range of -30 % / +50 %. In other words the values obtained aren’t fixed values but rather a range of values, however for this work this type of data won’t damage the results because what it is requested isn’t the real cost of the units but a way to make the choice of the most profitable process.

For this comparison, the ISBL (unit total erected cost Inside Battery limits), was used. This cost includes the equipment costs, proprietary equipment’s, piping and valves, instruments & control equipment, electrical power, freight, construction of main equipment items, set-up of piping and valves, instrument installation, electrical power wiring, civil works, steel structure, insulation and painting. However the investment cost excludes the raw & product storages, utilities generation, pipe racks, electrical substation, buildings, DCS system (in control room), site preparation, construction management, Direct Owner’s costs (catalyst, spare parts and etc), Indirect Owner’s costs (licensor’s fees, operators training, commissioning, vendors assistance and etc), legal expenses, insurances, taxes and contingencies.

3.2 Methodology

As already mentioned the main objective in this work is the research of more capacitive and efficient packing to optimize the design of the absorption and regeneration columns and to study what is the most profitable situation in terms of CAPEX and OPEX in sweetening process. Basically the methodology is divided in four steps:

1. Cases Selection – there is the need to select what are the cases that are relevant to the study, so several simulations are done on the process. In these simulations, variations of the amine flowrate and the number of plates or the height of packing are made, that will let us reach the specification of CO2 in the
treated gas and try to find the case that is most close to the equilibrium conditions, the proximity is measure by the ratio $Y_{CO_2}^*/Y_{CO_2}$ when this ratio is more close to one better is the separation.

2. **Economic Analysis**- in this section it is made the study of the CAPEX and the OPEX for each previously case selected. This estimation let us compare the processes and that makes it easier to select the most profitable option.

3. **Sensitivity Analysis to the Mass Coefficients and Superficial Area**- this sub-chapter is related to the study of the sensitivity analysis of the case that was chosen in the section of economic analysis, the case chosen is the one with lower cost and best operational conditions.

4. **Selection of the best type of Packing**- here the objective is to make the computation of commercial packing’s in the previous simulations and see what is the effect of changing the type of packing in the column dimensions, diameter and absorption height, and the influence in the column cost.

For execution of the previous steps it was essential to have two type of simulations on PROII, one related only with the section of the absorber and other related with all the units required for the sweetening process. The first group of simulations have the objective of studying the influence of the amine solvent flowrate and the percentage of CO$_2$ or H$_2$S in the lean stream to ensure that the treated gas is inside the require specifications. The second simulations are fundamental for the economic analysis because it will let us know what is the economic influence of each unit when the absorber design changes.

Additionally, it is required to define several factors to run the simulation, such as:

- The feed gas composition;
- The lean amine composition;
- The operational conditions of the input streams;
- The final specification for the CO$_2$ and/or H$_2$S in the treat gas.

The above steps will be explained and stated in more detail below.

**3.2.1 Cases Selection**

The main objective in this section is the study of which are the best cases for the execution of an economic analysis, the best cases are chosen considering several factors, the amine flowrate, the number of stages, the percentage of CO$_2$ and H$_2$S and if the absorber operational conditions are near to the thermodynamic equilibrium at bottom conditions, so high temperature and loading.

The first step consists in the building of a PROII simulation where only two equipment’s are present: a scrubber to separate condensate (water and hydrocarbon) from the feed gas to optimize the efficiency of the mass transfer in the absorber and avoid foaming. The second equipment is a rigorous absorber. The PROII scheme can be seen in the Figure 12.
Figure 12. Flowsheet for the scrubber and the absorber.

The necessary inputs for the simulation shown in the Figure 12 are the data of the feed gas and lean amine and the operational conditions of the two units. Furthermore, for the scrubber it is considered a pressure drop of 0.5 Bar. For the absorber column analysis it is needed to follow the next procedure:

1) Design an absorber with trays:
   a) Find the number of trays to reach the specification with specific amine flowrate;
   b) Perform sensibility analysis on Trays number and solvent flowrate;
   c) Select the best case.
2) With the selected amine flowrate will be: computed the height of PACKING 1 to reach the specification:
   a) Use the correlation “PACKING 1” to compute transfer coefficient;
   b) Computed absorber in design mode with flooding factor =0.8;
   c) Perform sensibility analysis Packing height vs solvent flowrate.

Posteriorly, all the data obtained in the previous steps give us the variation of the CO₂ and/or H₂S concentration in the treated gas stream between a range of amine flowrates for several number of Trays. Therefore, using the data obtained it was possible to choose which are the most favorable cases for absorbers with trays and with packing. For the absorber, because of high pressure, it is essential to optimize the diameter to reduce the cost.

3.2.2 Economic Analysis

The economic analysis is based on the study of the CAPEX and the OPEX, so it is important to refer once again the meaning of this two economic terms.

The CAPEX is a capital expenditure. It is money invested to acquire or upgrade, physical, fixed, non-consumable assets, such as buildings, equipment’s and/or a new business. There are two types of CAPEX, the first type is the investment to maintain the existing levels of operation and the second one is the capital invested in something new to foster future growth.

The OPEX is the money a company spends on an ongoing, day-to-day basis in order to run a business or system. Depending upon the industry, these expenses can range from the ink used to print documents to the wages paid to employees.

For the thesis’ study, it were made calculations were made of the last two economic parameters, these will be determined by using the simulation for all the acid gas treatment schemes. Running the processes simulations, the composition and the conditions for all the process streams and equipment’s are obtained, these data are important because in the CAPEX calculation it is necessary to design and determine the cost of all the equipment’s and for that the results obtained for the process simulation are necessary. The simulations are done in PRO II and an example of the simulation is represented in the Figure 13. The initialization of all the units in the process, except the absorber and the regenerator, are described in the annex 0.
Then, to be able to determine all the data required for the economic analysis it is needed to add some independent units to help in the calculation of necessary values for the equipment’s design and consequently the calculation of CAPEX. The added units/equipments are:

- **Water Make-up** – In the sweetening processes there are losses of water from solvent during the process by the exiting gas stream (treated gas, acid gas and fuel gas), so it is essential to add water to the process at the stream of lean amine regenerated. So using the tool “Calculator” in PRO II to calculate and a controller to impose the quantity of water that the stream 20 needs to have. The stream 20 represents a make-up of water in the tank of lean amine (could also be added in the reflux drum or in the absorber washing section to reduce amine losses but not considered in this study). The Figure 14 is the PRO II simulation for this unit.

- **New gas- liquid separator** – For sizing calculations it is required to add a virtual gas-liquid separator to compute properties of each phases (for mixed streams) to allow the design of equipment’s, as the condenser or amine /amine heat exchanger for example. The inputs for this unit are pressure loss and heat duty equal to zero.

- **Reboiler** - To simulate and size the reboiler and compute properties from the feed liquid and the vapor to desorber it was necessary to build a simulation with two flash’s where the first flash used is fed with the regenerated lean amine (stream 16bis) and the generated vapor (stream 15) and it is specified a liquid fraction in the stream 14 (stream from regenerator to reboiler) equal to one, and in the second flash it is considered that the duty is equal to the duty calculated in the regenerator. The Figure 15 shows the representation of the reboiler in PRO II.
• STRIPEXCESS - this section is used to determine two types of results needed for the regenerator design. In here it is necessary to create a unit that represents the regenerator with excess of stripping, so using this unit and using a PRO II tool, “calculator”, it can be obtained two results, the Result 1, that represents the excess of stripping, and the Result 2, that gives us the duty in the reboiler. Furthermore these two parameters have the following units, \( \frac{kg}{m^3} \).

Obtaining all the previous data it is possible to make the design of the equipment’s and calculate the price associated to each equipment and consequently get the value of CAPEX.

Concluding the calculation of CAPEX the next step is to start with the OPEX analysis. The OPEX is given by three parcels, the electricity that is used for the pumps and air coolers, the steam used in the reboiler and at last the solvent stock because in the process there are some solvent losses by degradation or simply for solvent losses in several out streams. Furthermore, for the OPEX calculation it is required the prices of the three parts mentioned, different costs for chemicals and utilities are used but these values are confidential, and it is still necessary to take some assumptions, these are described in the following topics:

• Total solvent losses in a year is given by \( X\% \) for the all solvent storage used in the process, so \( X\% \) of solvent losses/year;
• It is assumed 8000h of work/year;
• The solvent price it is given by the pondered average of the prices of each component that the solvent is made.

Using operating system data from simulations and using the prices for each parcel it is made the OPEX calculation for each simulation.
3.2.3 Sensitivity Analysis to the Mass Coefficients and Superficial Area

The coefficients to be studied are the interfacial area, \( a_i \), the liquid side mass transfer coefficient \( k_L \) and the gas side mass transfer coefficient \( k_G \). The objective of this study is to vary these three parameters and see which ones are critical and which are the best values to minimize the size and the cost of the absorbers.

To run the simulation two programs PRO II and/or Program A are used. But to do the sensitivity analysis on PRO II this study would have to be done independently for each desired variation in the parameter to be studied, for example to see the effect of varying the \( k_L \) in more 20% and 50% it is needed to do two different simulations. However in this work these kind of sensitivity analysis are made in Program A, this launcher allows to perform several sensitive analysis at the same time, so the program gives a lot of values with one simulation. Using the last example it is possible to determine the values of the variation in 20 and 50% of the \( k_L \) in only one simulation.

The programs inputs are the streams conditions, simulated in PRO II for all the process, and one matrix where it is added a range of values for which both the sensitivity analysis are performed. Using the factor “CCC” it is feasible to vary the values of the desired parameters, because as already explained in the description of the launcher, this factor makes it possible to vary each variable in percentage regarding to the standard value defined for the programs used. The next table is an example of a Matrix used for the simulations, in this case the introduced example represents one system where the influence of the \( k_L \) in the absorber results is studied, in this case the superficial area and the \( k_G \) are constant.

Table 4. An example of the matrix the input in the Program A.

<table>
<thead>
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<th>CCC( k_G )a</th>
<th>CCC( a_i )</th>
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</thead>
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</tr>
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<td>1,00</td>
<td>1,30</td>
<td>1,00</td>
</tr>
<tr>
<td>1,00</td>
<td>1,35</td>
<td>1,00</td>
</tr>
<tr>
<td>1,00</td>
<td>1,40</td>
<td>1,00</td>
</tr>
<tr>
<td>1,00</td>
<td>1,45</td>
<td>1,00</td>
</tr>
<tr>
<td>1,00</td>
<td>1,50</td>
<td>1,00</td>
</tr>
<tr>
<td>1,00</td>
<td>1,55</td>
<td>1,00</td>
</tr>
<tr>
<td>1,00</td>
<td>1,60</td>
<td>1,00</td>
</tr>
</tbody>
</table>

For each selected process with packing columns multiple sensitive analysis and singular sensitivity analysis will be done. The beginning of every study is based on an independent analysis for each mass transfer parameter. The second part is the multiple analysis that consists in varying more than one parameter at the same time. The range of variations applied in the launcher is between 80% to 200% of the base value of the parameter to be studied. Still, to study only the influence of the interfacial area the values of CCC\( k_G \)a and CCC\( k_L \)a need to be equal to the CCC\( a_i \) for each variation. Summarizing this chapter, the work was split in two phases:

- Independent study of each variable:
- $k_G a \rightarrow$ variation between -20% until +100%;
- $k_L a \rightarrow$ variation between -20% until +100%;
- $a_i \rightarrow$ variation between -20% until +100%.

- Study of $k_G$ impact in the $k_L$ and $a_i$:
  - $k_G a \rightarrow$ variation between -20% until +20%;
  - Sensitivity analysis on $a_i$ and $k_L a$, variations between -20% until +100%.

Analyzing the data acquired for the two steps it can be concluded which are the best parameters to improve the column design, so now the next objective is to try to select a commercial packing that can fit within these parameters.

### 3.2.4 Selection of the best type of Packing

The main goal in this section is to estimate the cost and the dimensions of the absorber column when it is used a commercial packing.

To perform the column height computation it is necessary to obtain some correlations to compute the column diameter for each packing and the adjustment factors “CCC’s” for the mass transfer parameters.

For this work, a first list of classic different commercial packings have been used. The list is limited since literature data and/or in-house data are needed. By terms of confidentiality these packing’s are going to be used in the simulations, and mentioned as PACKING 1, PACKING 2, PACKING 3, PACKING 4, PACKING 5, PACKING 6, and PACKING 7[MANDAL1].

Theoretical correlations have been implemented for PACKING 1. For other packings, it was more convenient to adapt CCC coefficients than to implement specific theoretical correlations. Using the previous data the main goal is to identify which packing(s) allow the smallest and hence, the cheapest column in which the treated gas meets the wanted specifications. This will illustrate the impact of the packing on the process.

To compute commercial packing in the simulation, the absorber column needs to be in a rating mode, this means that is the user that imposes the diameter of the column. Then the “CCC’s” values are added to the program, factor that adjust the PACKING 1 parameters to fit with other packing parameters. Having all the inputs, starts up the estimation of the height of the column, basically all the process conditions are defined excepted the height, and it made sensitive studies to see for which packing height it is possible to reach the wanted specification.

Finally, after having the new designs it is calculated and analyzed the erected cost for the absorber column, using the economic tools it can be estimated the cost associated to each column for all the packing’s assuming that every packing has the same cost than PACKING 1. However that last assumption isn’t really truth because it is already known that there are packing’s more expensive than other’s (depending on the generation of packing and the production geographic area). But it’s really difficult to get a price for each commercial packing because those prices depends on the type of packing and on the desired volume of packing.
4 Results and Discussion

The methodology explained previously will be applied to four different cases, the first two cases with only CO₂ in the acid gas, the third case where the acid gas has the same quantities of CO₂ and H₂S and at last, the fourth case where in the gas treat will be biogas with high quantities of CO₂.

The following topics are related with the results obtained and it is important to refer that for all the cases several values will be hidden or replaced by letters and/or relative values, %, in order to protect confidential data. The values replaced by percentages are the amine flowrates and the packing height’s, for each parameters it is necessary to consider one value for the 100%, so the criteria used was:

- Amine flowrate → The 100% is the lower flowrate simulated in the absorber;
- Packing Height → The 100% is the height that let us obtain the best design for proposal.

4.1 Natural Gas with 7% of CO₂ – LNG Specification (deep CO₂ removal)

4.1.1 Cases Selection

The first study case is where the feed gas has only CO₂ and hydrocarbons, so in this case there isn’t any H₂S. The objective is to get 50 ppm of CO₂ in the treated gas so it will be used three types of lean amine solvent, one with 1 g/L of CO₂, CASE A1, other with 5 g/L of CO₂, CASE A5, and at last other with 10 g/L of CO₂, CASE A10.

Each case is conducted by the above procedure explained (methodology explained in the sub-chapter 3.2.1) and to run the simulation there are some necessary inputs like the feed stream, which is equal for every case in this subchapter and it is represented in Table 5 and Table 6. The initial composition of the lean amine stream for the three cases with a flow base of 150% Sm³/h, is shown in the Table 7.

Table 5. Operational conditions input for the feed gas with 7% of CO₂.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Feed Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absolute Pressure (bar)</td>
<td>92.6</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>40</td>
</tr>
<tr>
<td>Flowrate (kmol/h)</td>
<td>9000</td>
</tr>
</tbody>
</table>

Table 6. Composition input for the feed gas with 7% of CO₂.

<table>
<thead>
<tr>
<th>Composition (%mol)</th>
<th>CO₂</th>
<th>H₂O</th>
<th>N₂</th>
<th>CH₄</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>7</td>
<td>0.30</td>
<td>1.9</td>
<td>82</td>
<td>8.8</td>
</tr>
</tbody>
</table>
Table 7. Initial input for the lean amine streams.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>CASE A1</th>
<th>CASE A5</th>
<th>CASE A10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure (bar abs)</td>
<td>92.4</td>
<td>92.4</td>
<td>92.4</td>
</tr>
<tr>
<td>Temperature (° C)</td>
<td>45</td>
<td>45</td>
<td>45</td>
</tr>
<tr>
<td>Composition (g/l)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO2</td>
<td>1</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>ACTIVATOR + MDEA</td>
<td>C1</td>
<td>C1</td>
<td>C1</td>
</tr>
</tbody>
</table>

Using the procedure explained, the following results associated to the case selection for a tray column are represented in the following figures:

**Figure 17.** Results of trays analysis for the lean amine with 1 g/L of CO₂, for the feed gas with 7% of CO₂. The Y axe represents the logarithm of the CO₂ concentration and the x axe represents the amine flowrate and where the wanted specification is represented for a straight line.

**Figure 18.** Results of trays analysis for the lean amine with 5 g/L of CO₂, for the feed gas with 7% of CO₂. The Y axe represents the logarithm of the CO₂ concentration and the x axe represents the amine flowrate and where the wanted specification is represented for a straight line.
Figure 19. Results of trays analysis for the lean amine with 10 g/L of CO₂ for the feed gas with 7% of CO₂. The Y axe represents the logarithm of the CO₂ concentration and the x axe represents the amine flowrate and where the wanted specification is represented for a straight line.

In the last three figures it can be seen the variation of CO₂ concentration in the treated stream between the plates 20 until 30 for the two first images and between 20 and 32 plates for the third image and for different amine flowrates.

As first analyze of this results it is possible to affirm that for all the cases that the quantity of acid gas in the out stream decrease when we increase the number of trays, however for low amine flowrate it is not feasible to obtain the wanted specification. This fact was expected because increasing the number of trays it will increase the number of equilibrium stage so the separation will have higher efficiency. Additionally when the lean amine has higher CO₂ quantities in its composition, it is observe that the mass transfer is more difficult because if we have more CO₂ in the lean amine, it will have less capacity to remove the acid compound from the natural gas.

In more details, what it is possible to observe for these cases is that in CASE A1, Figure 17, and CASE A5, Figure 18, it is possible to get the specification, but for the CASE A10, Figure 19, it isn’t possible to get the specification within the maximum of 30 plates and an amine flowrate of 200% S/3 h⁻¹, and with this quantity of CO₂ it is only possible to reach the specification if used, in the minimum, 32 plates with an amine flowrate of 200% S/3 h⁻¹, but more than 30 plate is too much because the absorber will be bigger than it is accepted, so more expensive.

Therefore between the CASE A1 and the CASE A5 the ratio \( Y_{CO_2}/Y_{CO_2} \) in each case was analyzed, summarizing the CASE A1 presents a ratio of \( Y_{CO_2}/Y_{CO_2} = 0.45 \) and the CASE A5 has a ratio of \( Y_{CO_2}/Y_{CO_2} = 0.3 \), so the best solvent is the one that lets a CO₂ transfer more close to the equilibrium, so the ratio closer to 60-80%, thus the best option is the CASE A1.

The data obtained for that solvent will be important for the following steps. Looking at Figure 17 it is observable in the sensitive analysis that it is possible to reach the specifications for various combinations of number of stages and the amine flowrate. The results show that if there is an increase of amine flowrate the number of stages needed will decrease, and the reverse phenomena occurs too. To select the best case there is the need to understand that when the flowrate increases a lot the absorber diameter will increase and that makes the column price increase too, so the criteria used for the selection of the design for plates absorber is as following:

- Proximity to the equilibrium conditions, so the case with bigger ratio of \( Y_{CO_2}/Y_{CO_2} \) (optimal between 60-80%);
- Lowest Column price in stable operating conditions, that means that allows reach the specification decreasing 10% of the flowrate. This represents the best cases for proposal.
Observing the Figure 20 and considering the previous topics, it can be consider two operational conditions:

- **CASE A1.1** - $Q = 175\% \text{ Sm}^3/\text{h}$ and an absorber with 24 plates, in this situation it is expected the lowest column price.
- **CASE A1.2** - $Q = 115\% \text{ Sm}^3/\text{h}$ and an absorber with 28 plates, this case exhibit a bigger value of $Y_{CO_2}^e/Y_{CO_2}$.

Selected the tray cases, shall be done the same kind of study for packing absorbers. The packing assumed in the simulations was PACKING 1. Applying the same methodology, in other words use the simulator to do a sensitivity analysis to the packing height for several amine flowrate and see for which combinations of height and amine flowrate can be achieved the specifications. Therefore the synthesis of that study was represent in the Figure 21.
Analyzing the Figure 21, it is possible to select two designs:

- **CASE B1.1** - $Q = 100\% \text{Sm}^3/\text{h}$, $H_{\text{packing}} = 100\% \text{ m}$, in this situation the lowest column price is expected, but in this case it is obtained an absorption height superior to the height obtained than using an absorber with trays.
- **CASE B1.2** - $Q = 115\% \text{Sm}^3/\text{h}$, $H_{\text{packing}} = 72\% \text{ m}$, this situation was select because with a 5% increase on flowrate an height decreased of ~38% is obtained. And contrary to the CASE B.1 the absorption height is lower than the packing case when compared with the trays case.

### 4.1.2 Economic Analysis

Applying the methodology related in the chapter 3.2.2 and using the data obtained in the last simulations, it is feasible to get the OPEX and CAPEX costs associated to each process. With this values and the operational conditions it may be chosen the best process conditions that achieves the most competitive and lucrative process. The Figure 22 and Figure 23 represents the determinate values for the CAPEX and OPEX using all the steps explained in the methodology chapter.

![Figure 22. The CAPEX cost for each case, for the feed gas with 7% of CO₂.](image)

![Figure 23. The OPEX cost for each case, for the feed gas with 7% of CO₂.](image)

Additionally, the CAPEX calculation is based on the cost of the equipment's. The Figure 24 shows the relative weight of each equipment for the CAPEX calculation. In that, it can be observed that the parcel that has more
weight in the CAPEX determination is the price of the columns, mainly the absorber price. In order to decrease the value of the CAPEX the best chance is to find more economic designs for the absorber.

Looking at the results obtained in the Figure 22 and Figure 23, it is safe to affirm that the cases with PACKING 1 designs are better than the trays designs, so the first ones are more competitive than the trays designs.

Performing two distinct analyzes, it is possible to decide what case is the most profitable and the one that is more adaptable to the industry reality. One of the analysis is based in the comparison of two situations with the same or equivalent flow so the CASE A1.2 and the CASE B1.2 and other comparing is between the situations with the same absorption height, so the CASE A1.1 with the CASE B1.2, with these two can be assumed that they have approximately the same column height.

Using the first approach it is observable that using the same flowrate and only changing the type of internals can be achieved a gain of 23\% in absorber height, so with packing the height needed to reach the specification is lower. However for the same situation the gain in the CAPEX represents only 2\%, when it is used a column with PACKING 1 and the gain in OPEX is 11\%.

For the second approach, the study is based in the comparison between the cases with identical absorption height, so it is observable that changing the trays for packing occurs a 16\% gain in amine flow, what means that for PACKING 1 design, it is needed less amine flowrate for sure that the specification in the treated gas. So using less amine flowrate was obtained a gain on OPEX equal to 20\% and a gain on CAPEX equal to 8\%.

So in conclusion the processes with PACKING 1 are better because they need less absorption height, less flowrate and they are cheaper. But now the decision between the two conditions with packing is more complex because the CASE B1.1 have a bigger CAPEX and OPEX, basically the CASE B1.1 as a gain in 10\% and 4\% respectively, although in the CASE B1.2 when compared with the CASE B1.1 it is possible to observe a gain of 29\% in the height of the column. So the case selected was the CASE B1.2, this case is chosen despite being the packing case with worst economic value because between the CASE B1.1 and the CASE B1.2, the first one is the most instable and because of that it is safer to choose a stable case even if it is more expensive.

Furthermore, it is interesting to analyze the weight of each parcel in OPEX, observing the previous Figure 23, the parcel that has a greater relative weight in OPEX cost is the steam used in the reboiler and the parcel with less weight in this cost is the solvent losses during the years.

![Figure 24](image-url)
4.1.3  **Sensitivity Analysis to the Mass Coefficients and Superficial Area**

After the choice of the CASE B1.2, several sensitivity analysis to the mass coefficients and interfacial area related with the absorption phenomenon will be performed. In this section a change of each parameter between $-20\%$ until $100\%$ was made. As has already been explained in the methodology first it is made an independent study of each variable and next a study of the influence of multiple parameters at the same time, the following topic represents the sensitivity analysis done:

- Variation of interfacial area ($a_i$);
- Variation of $k_L$;
- Variation of $k_G$;
- Variation of interfacial area ($a_i$) with $k_L$ equal to the value of $a_i$ and to the value of $k$ is equal to 0.8;
- Variation of $k_G$ with $k_L$ and $a_i$ equal to one.
- Variation of interfacial area ($a_i$) with $k_G$ equal to 1.2 and $k_L$ equal to the value of $a_i$.
- Variation of $k_L$ with $k_G$ equal to 1.2.

The data acquired was compiled in three different type of graphics, the first type connects the information related with each parameter apart, so in this it is possible to notice what is the most sensitive factor in this case. The second type, shows the superficial area variation for three values of $k_G$. The last one is very similar to the second type of graphic, however in this it is made the study of the influence of several values of $k_L$ for three different $k_G$, the two last graphics let us analyze the impact of $k_G$ in the system.

![Figure 25. Sensitivity analysis to each parameter apart for the CASE B1.2.](image)
Looking at the Figure 25, it is obvious that $a_i$ is the most sensitive transfer parameter for this case, analyzing careful it is possible to affirm that increasing $a_i$ by 20% allows to reach more severe specifications. However for situations where the factor applied to the interfacial area is superior to 1.25, the results obtained are very close to the thermodynamic equilibrium, so working with these values are incorrect. For a 20% gain in $a_i$, the percentage of CO$_2$ obtained for the treat gas is lower than 1 ppm so it is obtained a CO$_2$ decrease of 97%.

Analyzing the Figure 26, it is observable that changing $k_G$ by $\pm$ 20% doesn’t have a big impact in the results obtained, so increasing the $k_G$ could add a little gain but not really significant. Furthermore when occurs an increasing in the $k_G$ doesn’t occur a decrease in the absorption efficiency.

Observing the Figure 27, it is important to refer that like in the last graphic, changing between $\pm$ 20% the value of $k_L$ doesn’t have a big impact in the results associated to the $k_L$ variation. However the gain on $k_L$ could be
interesting but when compare with the results for the $a_i$ these aren’t so attractive. Considering a 40% gain in $k_L$, the specification obtained can decrease about 87%.

Summarizing the $a_i$ is the most sensitive parameter, so with more interfacial area the packing height can be smaller and then the column price is lower. Between the $k_L$ and the $k_G$, the last one doesn’t have a significant impact in the absorption, so the gain in $k_L$ can be useful but not so useful comparing with the gain in $a_i$.

Additionally, for complete the sensitive analysis was study what is the influence of changing the CCCAi value in the absorption height. This analysis is important because it is already known that the interfacial area is the most sensitive factor however the project goal is decrease the column price, so the influence of the interfacial area in the column height can give us a better idea of the total gain obtainable for using packing with more interfacial area when compare with PACKING 1. The Figure 28 let us observe that increasing 20% of the $a_i$, the column height decrease about 21% and for an $a_i$ increase of 40% can be reach a height 31% lower than for the CCCAi=1.

![Figure 28. CCCAi influence in the packing height, for the CASE B1.2.](image)

4.1.4 Selection of the best type of Packing

Using literature and in-house data the diameter and column height associated with different commercial packing have been calculated.

Computing the new designs with commercial packing allows to acquire results comparable to the values already applicable to the case of PACKING 1 which is the reference for the present study. Thus the new designs obtained are represented in the following figures, Figure 29 and Figure 30.
Figure 29. Bed height comparison for different packing using PACKING 1 as reference, for the feed gas with 7% of CO₂.

Figure 30. Diameter comparison for different packing using PACKING 1 as reference, for the feed gas with 7% of CO₂.

On this situation, the PACKING 1 design is better than the conventional trays design but what is required is to analyze what commercial packing does a better performance than the PACKING 1. So as seen in the sensitivity analysis, this case showed the need to increase the contact area or interfacial area. It is to refer that all surveyed fillings are better than the PACKING 1 on this case, excepted for the internal PACKING 7.

The PACKING 2 is globally a good packing that gives a 17% gain in the column height and a diameter decrease lower than 1% when compared with PACKING 1. However this result has to be discussed: the gain in terms of diameter is linked to the margin of the internal design tool for PACKING 1, while no margin is taken in the software used for PACKING 2. A direct comparison between these two packing lead to a loss of capacity around 20% with the PACKING 2 that will change present conclusions. This isn’t the case for all others packings for which a direct comparison show that the capacity is keep constant or increase compared with PACKING 1 one. The PACKING 3 looks very attractive because the new design exhibits lower values of height and diameter, having a gain of 10% and 3%, respectively. Additionally it has the advantage of being more capacitive than the other packing’s, except PACKING 6.

Furthermore with the PACKING 4 the gain in height is 12% and the gain in the diameter is of 8%. The PACKING 5 is very interesting for this case because the gain obtained for the height is 18% and for the diameter occurs a loss of 1%, but if this packing is forced by heat it will have a bad performance, therefore isn’t an interesting case. The PACKING 6 is more capacitive and is more effective than the PACKING 1 but seems less interesting than PACKING 3 or a PACKING 4, because the height gain is only 8% but the diameter gain is of 15%.

The PACKING 7 is the only one that shows an increase in height, in this the height loss is of 3% but for this design the diameter shows a gain of 9%.
To complement this study it was made an economic study to see the absorber price where all packings have the same price than PACKING 1, using the Program B and Program C to make the design of each column. So the results obtained are in the following figure:

![Erected Cost Comparison](image)

*Figure 31 Absorber erected cost comparison for each packing using PACKING 1 like reference, for the feed gas with 3% of CO$_2$."

All the results and data for each packing are resumed in the Table 8, where the first column in the table represents the best packing’s for each parameter and the last column shows the worst cases.

<table>
<thead>
<tr>
<th></th>
<th>Better</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Capacity</td>
<td>PACKING 6</td>
<td>PACKING 7</td>
<td>PACKING 4</td>
<td>PACKING 3</td>
<td>PACKING 1</td>
<td>PACKING 2</td>
<td>PACKING 5</td>
</tr>
<tr>
<td>Efficiency</td>
<td>PACKING 5</td>
<td>PACKING 2</td>
<td>PACKING 4</td>
<td>PACKING 3</td>
<td>PACKING 6</td>
<td>PACKING 1</td>
<td>PACKING 7</td>
</tr>
<tr>
<td>Column cost</td>
<td>PACKING 6</td>
<td>PACKING 7</td>
<td>PACKING 4</td>
<td>PACKING 3</td>
<td>PACKING 2</td>
<td>PACKING 5</td>
<td>PACKING 1</td>
</tr>
</tbody>
</table>

Concluding when compared with the PACKING 1 the best packing’s are the PACKING 6, PACKING 3 and the PACKING 4. Therefore the PACKING 2 has a good efficiency but it is very expensive and it has a lower capacity when compared with the others. The PACKING 5 I has the best efficiency but it is the second more expensive design, and the first is the absorber with PACKING 1. The PACKING 2 and the PACKING 5 also lead to an increase of the column diameter. The PACKING 7 has a good capacity and column cost however is the worst in terms of efficiency and leads to an increase in the column height.

### 4.2 Natural Gas with 3% of CO$_2$

#### 4.2.1 Cases Selection

This study is similar to last situation, a feed gas with 7% of CO$_2$. The difference between this and the other situation is the gas composition, because in this the natural gas has less CO$_2$. The composition and the operational conditions of the feed gas stream are express in Table 9 and in Table 10.

The objective is to get 50 ppm of CO$_2$ in the treated gas so in this it will be used the same three types of lean amine, the CASE A1, CASE A5 and CASE A10. The composition for the three different lean amines is shown in the Table 7. For this simulation the gap of values used like input in the absorber simulation, using a lean amine with 1g/L of CO$_2$, CASE A1, is different, because the concentration of CO$_2$ in the feed gas is lower so in order to reach...
the specification, it is needed to decrease the flow used and the number of plates. So the amine flowrate variation was between 100% − 270% $\text{Sm}^3/\text{h}$ and the number of trays variation was between 19 − 30 plates.

Table 9. Operational conditions input for the feed gas with 3% of CO$_2$.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Feed Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absolute Pressure (bar)</td>
<td>92.6</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>40</td>
</tr>
<tr>
<td>Flowrate (kmol/h)</td>
<td>9000</td>
</tr>
</tbody>
</table>

Table 10. Composition input of the feed stream, for the feed gas with 3% of CO$_2$.

<table>
<thead>
<tr>
<th>Composition (%mol)</th>
<th>CO$_2$</th>
<th>H$_2$O</th>
<th>N$_2$</th>
<th>CH$_4$</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3</td>
<td>0.3</td>
<td>2</td>
<td>85.7</td>
<td>9</td>
</tr>
</tbody>
</table>

Figure 32. Results of trays analysis for the lean amine with 1 g/L of CO$_2$, for the feed gas with 3% of CO$_2$. The Y axe represents the logarithm of the CO$_2$ concentration and the x axe represents the amine flowrate and where the wanted specification is represented for a straight line.
Figure 33. Results of trays analysis for the lean amine with 5 g/L of CO₂ for the feed gas with 3% of CO₂. The Y axe represents the logarithm of the CO₂ concentration and the x axe represents the amine flowrate and where the wanted specification is represented for a straight line.

Figure 34. Results of trays analysis for the lean amine with 10 g/L of CO₂ for the feed gas with 3% of CO₂. The Y axe represents the logarithm of the CO₂ concentration and the x axe represents the amine flowrate and where the wanted specification is represented for a straight line.

Looking at the results for three cases, it is observable that they can ensure the desired specification in the treated gas using different combination of flow and number of trays. Analyzing the Figure 32, Figure 33 and at last the Figure 34, the first thing that it is possible to notice is when occurs the increasing of CO₂ in the lean amine the design obtained need more flowrate and more trays when compare with the combinations associated to the CASE A1, with lower quantity of CO₂ in the lean amine. Therefore, more flowrate and higher column height can make the process more expensive, so higher CAPEX.

Therefore, to choose the best amine solvent the criteria used were the $Y_{CO2}*/Y_{CO2}$ ratio, which represents the proximity to the equilibrium. Resuming the CASE A1 show a ratio of $Y_{CO2}*/Y_{CO2} = 0,30$, the CASE A5 has a ratio of $Y_{CO2}*/Y_{CO2} = 0,177$ and at last the CASE A10 has a ratio of $Y_{CO2}*/Y_{CO2} = 0,15$. Concluding the best solvent is the one that let to have CO₂ transfer more close to the equilibrium, thus the best option is the CASE A1.

Analyzing more closely the CASE A1, Figure 35, it’s observable in the sensitive analysis that it is possible to reach the specifications for several designs, each design has different number of stages and the amine flowrate. Observing the graphic if there is an increase of amine flowrate the number of stages required will decrease, and
the reverse phenomena occurs too. To select the best designs was used the same criteria than used for the natural gas with 7% of CO2.

Figure 35. Design to achieve specification for the CASE A1 for the feed gas with 3% of CO2, where it is represented the possible designs (amine flowrate and number of trays) that reach the specification. The orange and green points represent the two selected designs for study proposes.

So observing the Figure 35 and considering the selection criteria, it can be selected two best designs:

- **CASE A2.1** - $Q = 150\% \text{Sm}^3/h$ and an absorber with 24 plates, in this situation it is expected the lowest column price.
- **CASE A2.2** - $Q = 112\% \text{Sm}^3/h$ and an absorber with 28 plates, this case exhibit a bigger value of $Y_{CO2}^* / Y_{CO2}$

Selected the tray cases, the same study was done for a PACKING 1 absorber. So applying the same methodology, the results obtained are express in the Figure 36.

Figure 36. Possible designs for packing absorbers, for the feed gas with 3% of CO2, where it is represented the possible designs (amine flowrate and column height) that reach the specification. The orange represents the selected design for study proposes.

Analyzing the Figure 36, one case can be selected:
- **CASE B2.1** - $Q = 112\% \; Sm^3/h, \; H_{\text{packing}} = 100\% \; m$, this situation was select because this case has a absorption height lower than the absorption height in the CASE A2.2 and better ratio $Y_{CO_2}^*/Y_{CO_2}$ than trays designs.

Furthermore, the CASE B2.1 selection had other criteria as the use of the same flowrate than in the CASE A2.2, this fact allows a deeper analysis about the effect of changing the column internals in the absorption height.

### 4.2.2 Economic Analysis

Applying the methodology related with these section on the data obtained in the last simulations, it is feasible to get the OPEX and CAPEX costs associated to each process. As in the feed gas with 7% $CO_2$, the OPEX and CAPEX results are compiled in the following Figure 37 and Figure 38.

![Figure 37 The CAPEX cost for each case, for the feed gas with 3% of CO2.](image)

![Figure 38 The OPEX cost for each case, for the feed gas with 3% of CO2.](image)

The Figure 24 shows the relative weight of each equipment for the CAPEX calculation. As in the last case, the parcel that has more weight in the CAPEX determination is the price of the columns, in especial the absorber price.
Figure 39. Weight of each equipment in the process for the CAPEX calculation, for the feed gas with 3% of CO₂.

Watching the results obtained in the Figure 37 and Figure 38, it is safe to affirm that the cases with PACKING 1 designs are more competitive than the tray designs. I was performing two distinct analyzes to choose the most profitable case. One of the analysis is based in the comparison between the designs with the same flow so the CASE A2.2 and the CASE B2.1 and other comparison is between the situations with the same absorption height, so the CASE A2.1 with the CASE B2.1.

Using the first approach it is observable that using the same flowrate and only changing the type of internals achieves a 22% gain in absorber height, so with packing the height needed to reach the specification is lower. When it is changing the conventional trays to PACKING 1, it is obtained a CAPEX gain equal to 9%, however the gain in OPEX is less than 1%.

In the second approach, for designs with identical absorption height, it is obtained a 18% gain in solvent flowrate by changing the trays to PACKING 1. Considering the same approach With the gain obtained in CAPEX is 14% and the gain in OPEX is 10%.

In conclusion, as in the other case, the process with PACKING 1 is better because this needs less absorption height and less flowrate so this process is cheaper when compare with processes with tray absorber. So the case selected was the CASE B2.1.

4.2.3 Sensitivity Analysis to the Mass Coefficients and Superficial Area

Several sensitivity analysis to the mass coefficients and interfacial area related with the absorption phenomenon will be performed. In this section a change of each parameter between −20% until 100% was made, as in the last situation. Using the same methodology, first was made an independent study of each variable and the next was a study of the influence of multiple parameters at the same time, the following topic represents the sensitivity analysis done:

- Variation of interfacial area \( (a_i) \);
- Variation of \( k_L \);
- Variation of \( k_G \);
- Variation of interfacial area \( (a_i) \) with \( k_L \) equal to the value of \( a_i \) and to the value of \( k \) is equal to 0.8;
- Variation of \( k_G \) with \( k_L \) and \( a_i \) equal to one.
- Variation of interfacial area \( (a_i) \) with \( k_G \) equal to 1.2 and \( k_L \) equal to the value of \( a_i \).
- Variation of \( k_L \) with \( k_G \) equal to 1.2.

The data acquired was compiled in three different type of graphics, the first type connects the information related with each parameter apart. The second type shows the interfacial area variation for three values of \( k_G \).
and the last one is very similar to the second type of graphic, however in this it is made the study of the influence of several values of $k_L$ for three different $k_G$, the two last graphics let us analyze the impact of $k_G$ in the system.

**Figure 40. Sensitivity analysis to each parameter apart for the CASE B2.1**

**Figure 41. Sensitivity analysis to study the $k_G$ effect in the $a_i$ for the CASE B2.1.**
Looking at the Figure 40, it is observable that the $a_i$ is the most sensitive transfer parameter for this case. Observing the data, it is possible to affirm that increasing $a_i$ by 40% allow to reach 0.6 ppm, so it is obtained a CO$_2$ decrease of 98%.

When compare with the natural gas with 7% of CO$_2$ for this situation there is a need to increase more the interfacial area to obtain almost the same specification. However for situation where the factor applied to the interfacial area is superior to 1.5, the results obtained are very close to the thermodynamic equilibrium so work with these values is incorrect.

Analyzing the Figure 41, it is observable that the changing $k_G$ by $\pm$20% doesn’t have a big impact in the results obtained, so increasing the $k_G$ could add a little gain but not really significant. Furthermore when occurs an increasing in $k_G$ doesn’t occur a decrease in the absorption efficiency.

At last, observing the Figure 42, the conclusions take are similar to the conclusions for the graphic represents in the Figure 41, this means that the changing of $k_G$ doesn’t have a big impact. However looking at the results can be attractive to do variations in $k_L$ for design improvement, so considering the data obtained it is possible to observe that when occurs an increase of 40% in $K_L$ the specification obtained decreases 61%.

Concluding the $a_i$ is the most sensitive parameter, so with more interfacial area the packing height can be smaller and then the column price is lower. Between the $k_L$ and the $k_G$, the last one doesn’t really impact the absorption and the gain in $k_L$ can be useful but not so useful comparing with the gain in $a_i$.

To complete the sensitive analysis was studied what it is the influence of changing the CCCAi value in the absorption height. This analysis is important because it is known that the interfacial area is the most sensitive factor however the project goal is decrease the column price, so the influence of the interfacial area in the column height can give us a better idea of the total gain obtainable for using packing with more interfacial area. So observing the Figure 43, it is observe that an increasing of 20% in the $a_i$ could decrease about 18% in absorption height and for an $a_i$ increase of 40% can be reach a height 29.5% lower than the height obtained for a CCCAi equal to 1.
4.2.4 Selection of the best type of Packing

As for the previous case, the study can be performed with literature and some in-house data. Enforcing the same methodology, the PACKING 1 was used like reference so computing the new designs with commercial packing allows us to acquire results comparable to the values already applicable to the case of PACKING 1.

The new designs obtained are represented in the following figures:

![Figure 43. CCAi influence in the packing height, for the CASE B2.1.](image)

![Figure 44. Bed height comparison for different packing using PACKING 1 like reference, for the feed gas with 3% of CO2.](image)

![Figure 45. Diameter comparison for different packing using PACKING 1 like reference, for the feed gas with 3% of CO2.](image)
On this case, the PACKING 1 design is better than the conventional trays designs but what is required is to analyze what commercial packing does a better performance than the PACKING 1. As seen in the sensitivity analysis the ideal case is to increase the interfacial area to gain in absorption height, so the goal is tray to find packing’s that allow to improve the mass transfer parameters and allow to obtain cheaper columns.

The PACKING 2 is globally a good packing that gives a 17.4% gain in the column height however it has almost the same diameter than PACKING 1. The PACKING 3 looks very attractive because the new design exhibits lower values of height and diameter, having a gain of 14% and 9%, respectively. Additionally it has the advantage of being more capacitive than the other packing’s, except PACKING 6, how was already said.

Moreover with the PACKING 4 the gain in height is 11% and the gain in the diameter is of 7%. For the PACKING 5 the gain obtained for the height is ~18% and for the diameter occurs a decrease of 2%, in comparison with the PACKING 1, but if this packing is forced by heat it will have a bad performance. The PACKING 6 is more capacitive than the PACKING 1 but seems less interesting than PACKING 3 or a PACKING 4, because the PACKING 6 allows to obtained a diameter decrease equal to ~13% and only allows decrease the absorption height less than 1% when compared with PACKING 1. The PACKING 7 is the only one that shows an increase in height, so the height loss is of 3% but for the diameter it shows a gain of 9%.

To complement these results, it was made an economic study to see the absorber price where all packings have the same price than PACKING 1, using the Program B and Program C to make the design of each column, the results obtained are expressed in the Figure 46.

Observing the Figure 46, all the commercial packing’s, except the PACKING 7, allow to get a column design less expensive than the design with PACKING 1, taking into account that it was considered that all the internals had the same price.

The Table 11 resume all the results and data associated to each packing where the first column in the table represents the best packing’s for each parameter and the last column shows the worst cases.

<table>
<thead>
<tr>
<th>Packing</th>
<th>Capacity</th>
<th>Efficiency</th>
<th>Column cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Better</td>
<td>PACKING 6</td>
<td>PACKING 5</td>
<td>PACKING 3</td>
</tr>
<tr>
<td></td>
<td>PACKING 7</td>
<td>PACKING 2</td>
<td>PACKING 4</td>
</tr>
<tr>
<td>Worst</td>
<td>PACKING 4</td>
<td>PACKING 3</td>
<td>PACKING 2</td>
</tr>
<tr>
<td></td>
<td>PACKING 3</td>
<td>PACKING 6</td>
<td>PACKING 5</td>
</tr>
<tr>
<td></td>
<td>PACKING 2</td>
<td>PACKING 1</td>
<td>PACKING 7</td>
</tr>
</tbody>
</table>

Concluding when compared with the PACKING 1 the most suitable packing’s are the PACKING 6, PACKING 3 and the PACKING 4. Therefore the PACKING 2 has a good efficiency and has an attractive column price. The PACKING
5 has the best efficiency but it has lower capacity and its column cost isn’t very attractive in comparison with other options. The PACKING 7 has a good capacity however is the worst in terms of efficiency and in terms of column cost. This packing also leads to an increase in the column height.

4.3 Natural gas with 3,5% of \( CO_2 \) and 3,5% of \( H_2S \)

4.3.1 Cases Selection [MANDAL2]

The natural gas that will be treated in this section has a composition a little different from the previous cases due to the fact that this has \( CO_2 \) and \( H_2S \) in its composition, unlike the previous cases in which the feed gases only contained \( CO_2 \). The feed gas composition and conditions are expressed in the Table 12 and Table 13.

\[
\text{Table 12. Operational conditions input for the feed gas with 3.5\% of \( CO_2 \) and \( H_2S \).}
\]

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Feed Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absolute Pressure at BL (bar)</td>
<td>93.1 (at BL) → 92.6 (absorber inlet)</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>40</td>
</tr>
<tr>
<td>Flowrate (kmol/h)</td>
<td>9000</td>
</tr>
</tbody>
</table>

\[
\text{Table 13. Composition input for the feed gas with 3.5\% of \( CO_2 \) and \( H_2S \).}
\]

<table>
<thead>
<tr>
<th>Composition (%mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( CO_2 )</td>
</tr>
<tr>
<td>( H_2S )</td>
</tr>
<tr>
<td>( H_2O )</td>
</tr>
<tr>
<td>( N_2 )</td>
</tr>
<tr>
<td>( CH_4 )</td>
</tr>
<tr>
<td>Others</td>
</tr>
</tbody>
</table>

The objective is to obtain the specifications shown in the Table 1, in other words the goal is to obtain a treated gas with 50 ppm of \( CO_2 \) and 4 ppm of \( H_2S \). Additionally, the initial composition of the lean amine used in process simulation is shown in the Table 14. For the initialization of the simulation was considered an initial amine flowrate of 150% \( Sm^3/h \). Unlike the cases previously performed, in here is only tested one type of lean amine, with low quantities of \( CO_2 \) and \( H_2S \). This lean amine was chosen because how was seen in the last two cases, the quantity of acid components in the lean amine affect the ratios, \( Y_{CO_2} Y_{CO_2} \) and \( Y_{H_2S} Y_{H_2S} \), so for low quantities of acid components, it is obtained bigger ratios in other words the absorption occurs closer to equilibrium conditions.

\[
\text{Table 14. Initial input for the lean amine stream.}
\]

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Lean Amine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure (bar abs)</td>
<td>92.4</td>
</tr>
<tr>
<td>Temperature (° C)</td>
<td>45</td>
</tr>
<tr>
<td>Composition (g/l)</td>
<td></td>
</tr>
<tr>
<td>( CO_2 )</td>
<td>1</td>
</tr>
<tr>
<td>MDEA+ACTIVATOR C1</td>
<td></td>
</tr>
<tr>
<td>( H_2S )</td>
<td>0.11</td>
</tr>
</tbody>
</table>

To simulate the rigorous absorber the variation range used for the amine flowrate was between 100% – 200% \( Sm^3/h \) and the variation considered for the trays was between 20-30 trays.
However, it is important to notice that in here the goal isn’t only the removal of CO$_2$ but also the removal of H$_2$S, so the data obtained using the absorber simulation will be a little different from the previous cases just because with this natural gas should be consider the specifications for CO$_2$ and H$_2$S. For the first and second cases already solved in the last chapters, the results obtained were only express in one graphic for each lean amine, in that graphic is presented the quantity of CO$_2$ for different combinations of amine flowrate and number of plates. In this case, as the feed gas has CO$_2$ and H$_2$S, it will be obtained the same type of graphic however in more quantity, one for the removal of H$_2$S and other for the removal of CO$_2$.

Using the same methodology as in the previous cases, it was achieved the following results:

![Figure 47 Results of trays analysis for a natural gas with 3.5% of CO$_2$ and H$_2$S, for the removal of CO$_2$. The Y axe represents the logarithm of the CO$_2$ concentration and the x axe represents the amine flowrate and where the wanted specification is represented for a straight line.](image1)

![Figure 48 Results of trays analysis for a natural gas with 3.5% of CO$_2$ and H$_2$S, for the removal of H$_2$S. The Y axe represents the logarithm of the H$_2$S concentration and the x axe represents the amine flowrate and where the wanted specification is represented for a straight line.](image2)
Considering the results shown in the Figure 47 and Figure 48, the first thing possible to notice is the existence of a limiting component, because considering the same columns designs, in other words the same combinations of amine flowrate and number of trays, the results obtained for the H$_2$S removal show the possibility of use more designs for ensure the specification in the treated gas when compare with the data obtained for the CO$_2$ removal. So in this case the CO$_2$ is the limiting component, which means that during the absorption process occurs a selective removal of H$_2$S. Moreover this phenomena occurs because the lean amine used is a tertiary amine, so it is less reactive and less basic what causes a selective reaction with H$_2$S in the presence of CO$_2$.

Analyzing more closely the Figure 47 and the Figure 48, it’s observable in the sensitive analysis that it is possible to reach the specifications for several designs, each design has different number of stages and the amine flowrate. For the removal of H$_2$S, almost all the combinations of solvent flow and number of trays allow to reach the specification in this component, however the removal of CO$_2$ is the limiting step in the absorption so to select what are the designs that can ensure the specifications of H$_2$S and CO$_2$ in the treated gas is necessary to make a combinations between the data from the two graphic.

Looking carefully to the results can be selected several tray designs, so the following figure represents the designs that allow to achieve the specification of H$_2$S and CO$_2$ in the treated gas.

![Figure 49 Design to achieve specification for the CASE A1, for the feed gas with 3.5% of CO$_2$ and H$_2$S, where it is represented the possible designs (amine flowrate and number of trays) that reach the specification. The orange points represents the selected design for study proposes.](image)

Observing the Figure 49 and considering the selection criteria, it can be selected one best design:

- **CASE A3.1** - $Q = 137\%\ S m^3/h$ and an absorber with 25 plates, in this situation it is expected the lowest column price. So this is the best design for proposal so it is possible to reach the 50 ppm's decreasing 10% of the flowrate.

It hasn’t been selected others trays designs, for example with lower amine flowrate, because observing the Figure 49 for designs with lower flow the absorption process is more instable, in other words for little variations in the flow it is obtained a big variation in the absorption height to ensure the right quantity of CO$_2$ and H$_2$S in the treated gas. Additionally, designs with bigger flow weren’t selected because considering the data in the graphic can be observed that for big variation in this the absorption height is almost the same, so the process will be more expensive.

Selected the tray case, shall be done the same kind of study for packing absorbers. The packing compute in the simulations was PACKING 1. In the previous cases were made several sensitivity analysis to see for which combinations of packing height and amine flowrate can be achieved the specifications in the treated gas. However in this particular case, the decision was only select one packing design with the same amine flowrate than the CASE A3.1. This decision was taken to ensure a better analysis on the influence of change the type of internal in terms of design and in terms of CAPEX and OPEX. Having the desired flowrate for the column design
the next step is simulate a packing column and so for what height the specification of the acid component can be ensured. The result obtained was:

- **CASE B3.1** - \( Q = 137\% \, S m^3/h, \, H_{packing} = 100\% \, m \) and 2 beds, this situation was select because this case has an absorption height lower than the absorption height in the **CASE A3.1**.

### 4.3.2 Economic Analysis

Performing the process simulations for the previous two designs and using the tools described in the methodology, it is possible to get the OPEX and CAPEX costs associated to each process. The economic results are compiled in the following Figure 50 and Figure 51.

![Figure 50](image.png)

*Figure 50 The CAPEX cost for each case, for a feed gas with 3.5% of CO₂ and 3.5% of H₂S.*

![Figure 51](image.png)

*Figure 51. The OPEX cost for each case, for a feed gas with 3.5% of CO₂ and 3.5% of H₂S.*

The Figure 52 shows the relative weight of each equipment for the CAPEX calculation. Seeing the figure can be concluded that the parcel that has a bigger weight in the CAPEX determination is the price of the columns, manly the absorber price.
Figure 52. Weight of each equipment in the process for the CAPEX calculation, for a feed gas with 3.5% of CO₂ and 3.5% of H₂S.

Watching the results represented in the Figure 50 and Figure 51, it is possible to affirm that the PACKING 1 design is better than trays design because making the comparison between the CASE A3.1 and the CASE B3.1 the CAPEX gain obtained for changing the type of internal is equal to 12%, although considering the OPEX can be verified that there isn’t any gain in this parameter. The OPEX cost is equal for both cases because in these are used nearly the same quantity of operational utilities, due to the fact that it is used the same amount of amine solvent, then therefore the electricity and the steam required to transport and to regenerate the solvent is similar and globally it is obtained the same OPEX cost.

To select the best case was only considered the CAPEX influence because as was already seen in both processes are used the same amine flowrate and the process conditions are very similar so the OPEX doesn’t have a great influence in the Design selection. Concluding the best design selected is the CASE B3.1 because the design with PACKING 1 is better than conventional trays, so for the same flow and operational conditions it is needed less absorption height which leads to the achievement of a cheaper process.

4.3.3 Sensitivity Analysis to the Mass Coefficients and Superficial Area

Using the CASE B3.1, several sensitivity analysis to the mass coefficients and interfacial area related with the absorption phenomenon will be performed. Initially, it is made an independent study of each variable and next a study of the influence of multiple parameters at the same time, the following topics represent the sensitivity analysis done:

- Variation of interfacial area \( a_i \);
- Variation of \( k_L \);
- Variation of \( k_G \);
- Variation of interfacial area \( a_i \) with \( k_L \) equal to the value of \( a_i \) and to the value of \( k \) is equal to 0.8;
- Variation of \( k_G \) with \( k_L \) and \( a_i \) equal to one.
- Variation of interfacial area \( a_i \) with \( k_G \) equal to 1.2 and \( k_L \) equal to the value of \( a_i \).
- Variation of \( k_L \) with \( k_G \) equal to 1.2.

As in the previous situations the data acquired was compiled in three different type of graphics, the first type is connected with the information related with each parameter apart, in other words in this graphic is possible to notice what is the most sensitive parameter. The second type shows the superficial area variation for three values of \( k_G \). In the last type of graphic, it is made the study the of the influence of several values of \( k_G \) for three different \( k_G \), the two last graphics let us analyze the impact of \( k_G \) in the system.
Considering that now the natural gas used has two components that should be removed therefore will be done sensitivity analysis for the both components, for the $H_2S$ and $CO_2$. So for each component it is obtained three graphic to study the influence of mass transfer parameters in the absorption process.

**Figure 53.** Sensitivity analysis to each parameter apart for the CASE B3.1, for the $CO_2$.

**Figure 54.** Sensitivity analysis to each parameter apart for the CASE B3.1, for the $H_2S$. 
Figure 55: Sensitivity analysis to study the $K_G$ effect in the $a_i$ for the CASE B3.1, for the $CO_2$.

Figure 56: Sensitivity analysis to study the $K_G$ effect in the $a_i$ for the CASE B3.1, for the $H_2S$. 
Looking at the previous graphics is secure to affirm that the removal of CO\(_2\) is the limiting step in the absorption process, in fact observing the data when it is reached the wanted percentage of CO\(_2\) in the treated gas the quantity of H\(_2\)S it is already 90% lower than the required for the H\(_2\)S specification, the 90% it is an average between the results shown in the Figure 53, Figure 54, Figure 55, Figure 56, Figure 57 and the Figure 58.

Using the sensitivity analysis information the limiting compound is the CO\(_2\) because the H\(_2\)S is easily removes when compare with the CO\(_2\). This phenomenon can be explained by the use of the MDEA as a solvent. The MDEA can influence the removal of CO\(_2\) and H\(_2\)S, because how it was explained in the state of art, the MDEA is a selective solvent, which means that there are a selective elimination of the H\(_2\)S in comparison with the CO\(_2\).

Looking at the Figure 53, for the CO\(_2\) removal, the \(a_i\) is the most sensitive transfer parameter in this case, so it is important to refer that increasing the \(a_i\) by 30% allows to reach 0.9 ppm, consequently it is obtained a CO\(_2\) decrease of ~97%.

Observing the Figure 54, for the H\(_2\)S removal, the \(a_i\) and the \(k_L\) are the most sensitive factors in comparison with the \(k_G\). However between the \(a_i\) and the \(k_L\), the most sensitive parameter is the \(a_i\), because considering an increase of 20% in the interfacial area, using like reference a CCCAl=0.8, the quantity of H\(_2\)S decreases almost 93% and for an increase of 20% in the \(k_L\), using like reference a CCCkLA=0.8, the quantity of H\(_2\)S decreases 85%.
Additionally, can be seen that for the CO\(_2\) the thermodynamic pinch is reached for an increase of 45\% in the interfacial area, but for the H\(_2\)S that pinch it is reached with an increase between 5\% - 20\% in the interfacial area.

Analyzing the Figure 55, Figure 56, Figure 57 and Figure 58 it is observable that the changes in the \(k_G\) by ±20\% doesn’t have big impact in the results obtained, so increasing the \(k_G\) could add a little gain but not really significant. Thus the \(k_G\) influence is bigger for the CO\(_2\) than for the H\(_2\)S.

For the CO\(_2\), the changing of \(k\) doesn’t have a big impact. However could be interesting to consider the gain on \(k_L\) but when it is done the comparison these results with the data obtained for \(a_i\), these aren’t so attractive. Considering a 40\% gain in \(k_L\), the specification obtained decreases 81\% for the quantity obtained for the CCCkLA=1. Although for the H\(_2\)S the variation on \(k_L\) has a similar effect to the interfacial area variation.

For this case the selection of the minimum concentration of the two components in the treated gas. Overall, the interfacial area is the parameter that has a bigger influence in the absorption process. Because the \(a_i\) was considered the best parameter to change, it was studied what it is the influence of changing the CCCAi in the absorption height. The influence of the interfacial area in the column height can give us a better idea of the total gain obtainable the most sensitive parameter need to be an average between all the factors for the CO\(_2\) and H\(_2\)S, but the principal criteria is to ensure for using packing with more interfacial area. Looking at the Figure 59, it is observe that an increasing of 20\% in the \(a_i\) could decrease about 16\% in absorption height and for an \(a_i\) increase of 40\% can be reach a height 28\% lower than the height obtained for a CCCAi equal to 1.

![Figure 59 CCCAi influence in the packing height, for the CASE B3.1.](image)

### 4.3.4 Selection of the best type of Packing

As in previous cases, the packing PACKING 1 is used as reference packing. The commercial packing’s computation allow to obtain new designs for the column, so depending on the type of internal used can be obtained columns with lower diameters and heights. The new designs obtained are represented in the Figure 60 and Figure 61. In these the relative values for the height and diameter for each design are shown, using like reference the PACKING 1.
The PACKING 1 design is better than the tray design, however what is required is to analyze what commercial packing to do better performance than the PACKING 1. The goal is try to find a group of packing that allow to improve the designs parameters and to reduce the column cost.

Analyzing the results can be seen that the PACKING 2 is a good packing that gives a 15.8% gain in the column height however the gain in the diameter is equal to 1.4%. The use of PACKING 4 shows a gain in absorption height of 11.4% and a gain in the diameter of 9.2%. Moreover the PACKING 3 looks a good choice because using this design can be achieved a gain in the absorption height of 14% and a gain in the diameter equal to 7.4%.

For the PACKING 5 the gain obtained for the height is ~17% and for the diameter occurs a loss about 2%, but if this packing is forced by heat this will have a bad performance. The PACKING 6 is more capacitive than the PACKING 1, using this packing the gain obtained for height is 7% and the gain for the diameter the is ~15%.

The PACKING 7 shows an increase in height, in this the height loss is of 4% but for this design the diameter shows a gain of 9%.

To complement this study it was made an economic study to see the absorber price where all packings have the same price than PACKING 1, using the Program Band Program C to make the design of each column, the results obtained are in the Figure 62.
Figure 62. Absorber erected cost comparison for each packing using PACKING 1 like reference, for the feed gas with 3.5% of \( \text{CO}_2 \) and \( \text{H}_2\text{S} \).

Analyzing the data expressed in the Figure 62, it is possible to observe that all the designs with commercial packing are less expensive than PACKING 1 design, however it was considered that all internals have the same price than PACKING 1, this assumption is an approximation because it is already known that each packing has different cost.

The Table 15 has all the results and data associated to each packing, where the first column in the table represents the best packing’s for each parameter and the last column shows the worst cases.

<table>
<thead>
<tr>
<th></th>
<th>Better</th>
<th>Worst</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Capacity</strong></td>
<td>PACKING 6</td>
<td>PACKING 7</td>
</tr>
<tr>
<td><strong>Efficiency</strong></td>
<td>PACKING 5</td>
<td>PACKING 2</td>
</tr>
<tr>
<td><strong>Column cost</strong></td>
<td>PACKING 6</td>
<td>PACKING 4</td>
</tr>
</tbody>
</table>

Concluding when compared with the PACKING 1 the most suitable packing’s are the PACKING 6, PACKING 3 and the PACKING 4.

The PACKING 6 has the better capacity and better column cost however its efficiency isn’t the best one. The PACKING 4 looks very attractive because it has good efficiency, capacity and it is one of the cheapest designs. The PACKING 3 can be a good compromise because it has a good column price and its capacity and efficiency are in the middle of the table. The PACKING 2 presents a good efficiency but it isn’t the best in terms of capacity and column cost. Therefore the PACKING 5 and PACKING 7 are packing’s that have bigger column cost. Although the PACKING 5 is the packing with better efficiency and worst capacity and the PACKING 7 is the worst in terms of efficiency but one of the best in terms of capacity.
4.4 Biogas (with high quantity of $CO_2 \geq 40\%$)

In this chapter the feed gas that will be treated is a biogas, thus the methodology and the process used is a little different from the previous cases. The biogas typically refers to a mixture of different gases produced by the breakdown of organic matter in the absence of oxygen. Biogas can be produced from raw materials such as agricultural waste, manure, municipal waste, plant material, sewage, green waste or food waste. It is primarily methane, carbon dioxide and may have small amounts of hydrogen sulfide so for this gas it is necessary to remove the acid component for it can be sold. However, the European specification for the biogas is the obtainment of a treated gas with 97% of methane in a dry basis.

In here the procedure used has some differences in relation to previous procedures. So the major difference occurs in the first and second step, in other words in the “Cases Selection” and “Economic Analysis” stages. In this study, the operational conditions were already defined, so the objective is to get the value of the absorber diameter considering a specific amine flowrate and a specific absorption height. Furthermore, the CAPEX calculation isn’t done because the process flowrates are very small and the tools used for the design and for the economic study don’t work on this range of capacity.

The most commonly used processes in Biogas upgrading, in other words biogas purification, are:

- Membrane processes (1 or more stages);
- Water wash processes;
- Pressure Swing Adsorption Processes;
- Amine sweetening processes (attractive for the biggest capacity).

Before, performing the determination of the column diameter it is important to emphasize the differences between the biogas and the natural gas sweetening. So the following topics represent these differences:

- **Process works at atmospheric pressure** → for the biogas sweetening all the process works near to the atmospheric pressure contrary to the natural gas situation. In the previous cases, the absorber works at high pressure, so now for the biogas it works at ~1 bar. Additionally, this fact will affect the process flowsheet, for example, now there isn’t any need for a medium pressure flash for the rich amine. Besides that, the number of pumps and the position where these pumps are changed for ensure the liquid circulation between equipment’s. The flowsheet used for this process is described in the Figure 63.

![Figure 63. Biogas sweetening process.](image)

- **Packing Regenerator** → unlike the previous cases the regenerator is filled with packing, due to the fact that the flows are very small. The regenerator will have a small diameter so it is impossible to use the classical valve trays. To the situation in question it was assumed that the regenerator has 5 theoretical stages.
• **Equipment’s inputs** ⇒ Due to the fact that the operational conditions in here are different, it is necessary to define new operational conditions for all the equipment’s.

• **Environment Constraints** ⇒ Biogas equipment’s shouldn’t be too high, then several columns could be erected (total number would be limited by the induced pressure drop). The biogas entering the unit is at atmospheric pressure and the increase of pressure necessary to allow the gas to flow through the unit is done with a blower which can’t give a big pressure rise (~500mbar max).

• **Main goals** ⇒ In the last cases the objectives were defined and chosen several trays and PACKING 1 designs and with these some economic analysis were performed to select the best designs. Using the best designs the objective was to study the mass transfer parameters influence in the absorption and finally the main goal was to compute several commercial packing to optimize the process. However the main goals of this study are the absorber optimization and the comprehension of the mass transfer parameters in the absorption process.

As in the other cases the main objectives/goals for this feed gas were successfully achieved. However the data associated to the absorber and regenerator design, results from the sensitivity analysis and results associated to the packing selection can’t be shown in this report because these are confidential.
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5 Conclusions

The optimization for several sweetening processes has been developed. Four process optimizations were conducted, the main difference between each process is the feed gas composition. These were mainly biogas and natural gas, with only CO$_2$ or CO$_2$+H$_2$S and the specification to achieve.

Concerning several process configurations were studied what are the best absorber designs for each feed gas. The results obtained allow to conclude that the use of PACKING 1 designs are more competitive and efficient than conventional trays designs, observing the results obtained for all the cases the PACKING 1 designs allow to obtain columns with lower diameter and lower absorptions heights, which leads to the CAPEX reduction. The improvement of the absorber column it is essential because it represents the equipment that has a bigger weight in CAPEX calculation, more specifically the absorber represents 17 – 25% of CAPEX. In terms of solvent flows, the use of smaller flowrates allow to decrease the CAPEX and OPEX, because if it is used less amine it will be necessary less energy to regenerate the amine and less energy for the pumps and aircoolers, so it is obtained a lower OPEX. Moreover, using less solvent decrease the size of the equipment’s so these will be smaller and cheaper, the result is the achievement of smaller CAPEX’s.

Several sensitivity analysis to the mass transfer parameters have been done, these are important for the project because changes in these parameters could provide some gain on absorption height, resulting in a decrease of the CAPEX. The previous results show that globally the interfacial area is the most sensitive factor, increasing this parameter allows us to decrease enough the absorption height. In some cases the $k_L$ influence could be very interesting but not so attractive as the influence of the interfacial area, except for the biogas case. For the biogas, an increase in the $k_L$ has a similar effect when compare with an $a_i$ increase. In all the cases, $k_G$ variations between ±20% doesn’t have a big impact in the absorption process. For the natural gas with H$_2$S and CO$_2$, it is observed that the CO$_2$ is the limiting component, because the removal of this component it is more difficult when compare with the H$_2$S removal.

As already seen the PACKING 1 designs are already very attractive however the objective is try to find more efficient contact technologies that can improve the absorber design and the CAPEX and the OPEX of the process. According to the sensitive analysis conclusions, it is possible to reduce costs if one can find commercial packings that can generate high interfacials while capacity is kept constant or ideally increased. Simulations have been performed for several commercial packings characterized in the open literature.

Globally for all the cases, the packings that fit better with the specification are the PACKING 3, PACKING 2, PACKING 4 and PACKING 6. The conclusions only takes into account the results associated to the process analysis, and should be discussed with the project team about chemical engineering considerations to ensure that the results obtained can be applied to project conditions.

Considering all the conclusions and results associated to this master thesis can be outlined some future perspectives for this subject, as in short term enlarge packings list to new generation packings that are not fully characterized in the open literature.
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6 Bibliography


[4] Internal document belonging to the IFPEN.


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7 Annexes

7.1 Random packing’s

<table>
<thead>
<tr>
<th>Picture</th>
<th>Packing</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="" alt="Rasching ring, ceramic (left), metal (right)" /></td>
<td>Rasching ring, ceramic (left), metal (right)</td>
</tr>
<tr>
<td><img src="image" alt="Bert saddle, ceramic" /></td>
<td>Bert saddle, ceramic</td>
</tr>
<tr>
<td><img src="image" alt="Intalox/Novalox/Torus" /></td>
<td>Intalox/Novalox/Torus</td>
</tr>
<tr>
<td><img src="" alt="Ceramic (left), plastic (right), Pall ring, ceramic (left), metal (right)" /></td>
<td>Ceramic (left), plastic (right), Pall ring, ceramic (left), metal (right)</td>
</tr>
<tr>
<td><img src="image" alt="Hy-Pal, metal. Notice doubling of tongues and the corrugation of sides compared to the Pall ring" /></td>
<td>Hy-Pal, metal. Notice doubling of tongues and the corrugation of sides compared to the Pall ring</td>
</tr>
<tr>
<td><img src="image" alt="Teflon, plastic" /></td>
<td>Teflon, plastic</td>
</tr>
<tr>
<td><img src="image" alt="Cascade mini ring, plastic left, metal right" /></td>
<td>Cascade mini ring, plastic left, metal right</td>
</tr>
<tr>
<td><img src="" alt="Intalox Metal Tower Packing (MTP)" /></td>
<td>Intalox Metal Tower Packing (MTP)</td>
</tr>
<tr>
<td><img src="image" alt="Top-Pak ring, metal" /></td>
<td>Top-Pak ring, metal</td>
</tr>
<tr>
<td><img src="image" alt="Nutter saddle, plastic left, metal right" /></td>
<td>Nutter saddle, plastic left, metal right</td>
</tr>
</tbody>
</table>

*Figure 64. Random Packing.*
7.2 Cape Open

The Cape Open is referred in the sub-chapter 3.1.1, and it is reported that the use of the Cape Open allows to apply models in every compliant of process modelling environment (PME). The Figure 65 help to understand this concept. So the cape open allows to connect the PME with kinetic and hydrodynamic models (proprietary or in house models) and thermodynamic models defined by the user, in other words it works as an interface between the several parts of the simulator.

![Figure 65. Cape Open Simulator structure.](image)