Amines as gas sweetening agents

Master thesis

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Title Page

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Abstract

CO_2 and H_2S are acid components present in natural gas recovered from wells in the underground. If not removed from the gas they are a cause of corrosion in equipment. H_2S is poisonous and if leakage occurs, people in the surroundings can be harmed and die. Legislation is regulating the content of H_2S in natural gas, where the limit of H_2S is 4 ppm.

There are different methods for gas sweetening. Some of the most used is adsorption and absorption.
For gas sweetening off shore absorption columns, where the gas is reacting with a liquid stream containing a sweetening agent, are the most used. Liquid solutions of an amine mixed with water are the commonly used sweetening agent.
The amine is capable of reacting with both CO_2 and H_2S to form compounds that is more soluble in the liquid phase than in the gas. In this way undesired acid components is removed from the gas stream.

Gas sweetening agent for gas absorption has been investigated and several simulations in HYSYS have been performed to investigate the important parameters in the process. The focus has been on the three amines MEA, DEA and MDEA. The simulations have been supported with manually performed calculations.

The investigation documents that DEA is the most efficient amine for gas sweetening, while MEA is the cheapest one. MDEA is inefficient and expensive and is only relevant to consider from an environmental perspective.

In general results provided by HYSYS are considered the most reliable ones, since the thermodynamic model is taking temperature, pressure and composition into consideration when evaluating the equilibrium of the reaction. This is not the case for manually performed calculations, where the equilibrium constant is considered independent of those factors.

It is recommended to perform gas sweetening with either MEA or DEA, where MEA is the recommended if there are no limitations for the flow and the capacity of the equipment is big enough. DEA is recommended for a more efficient cleaning where the equipment is limiting the flow rate.

Synopsis

CO_2 og H_2S er syrlige komponenter der forefindes i naturgas der indvindes fra boringer i undergrunden. Hvis disse ikke fjernes kan de forårsage korrosion i rør og udstyr. Desuden er H_2S giftigt og ved lækager kan både omgivelser og mennesker skades og dø. Lovgivning regulerer derfor det tilladte indhold af H_2S i natur gas, hvor grænsen er 4 ppm.

Der er forskellige metoder til ”gas sweetening”, hvor nogle af de mest anvendte er adsorption og absorption.
For gas sweetening off shore er absorptionskolonner, hvor gassen reagerer med en væskestrøm der indeholder en sweetening agent, det mest brugte. Vandige opløsninger af aminer er det mest brugte til dette formål.
Aminer kan reagere med både CO_2 og H_2S og danne produkter der er mere opløselige i vandfasen end i gasfasen. På denne måde fjernes de uønskede komponenter i gassen og over i vandfasen.

Gas sweetening agenter er i projektet blevet undersøgt, og simuleringer i HYSYS er blevet udført for at undersøge de vigtige parametere i gas sweeteing processen med aminer.
Fokus har været på de tre aminer, MEA, DEA og MDEA. Simuleringerne er blevet bakket op af manuelle beregninger.

Undersøgelsen dokumeterer at DEA er den mest effektive af aminerne når det kommer til gas sweetening. MEA er den billigste og MDEA er ueffektiv og dyr. Det er kun relevant at overveje MDEA når miljømæssige overvejelser foretages.

Generelt er resultater fra HYSYS vurderet til at være de mest troværdige. HYSYS bruger termodynamiske modeller der tager faktorer som temperatur, tryk og kompositionen af de forskellige faser med i beregningerne når ligevægten for processen evalueres. Dette sker ikke i de manuelle beregninger, hvorfor det må forventes at der er en vis fejlprocent på de opnåede resultater.

Det anbefales at bruge enten MEA eller DEA til gas sweetening. MEA er billigt og kan anbefales hvis der ikke er restriktioner på flowet og kolonnens kapacitet kan håndtere det store flow. Hvis der er restriktioner på flowets størrelse anbefales DEA, der er mere effektiv og kræver et væsentligt mindre flow.

Preface

This report is a part of the documentation for a tenth semester project in the Master program for Oil and Gas Technology on Aalborg University Esbjerg in the period February 2014 to June 2014.
The title of the project is “Amines as sweetening agents” and deals with the process where H_2S is removed from a natural gas stream with absorption processes. As sweetening agents different kinds of amines are used.
The project is defined by supervisor Rudi P. Nielsen as requested by the student, to gain knowledge about gas sweetening.

The motivation for writing this project was personal interest in the area, and a desire to investigate the topic further.
The report is meant for anyone with a back ground in oil and gas technology and interest in absorption processes and gas sweetening. This can be students, teachers or employees with work or interest in the development in the industry.

The project consists of a file containing the main simulation made in Aspen HYSYS and this report that documents the performed work. The file can be found on the attached cd and can be opened by anyone with the correct versions of the relevant software installed.

References are listed as numbers in square brackets in the text. Further clarification of the sources can be found in the reference list where the full description of each reference can be found.

I would like to thank my supervisor Rudi P. Nielsen for his assistance on the project and for his constructive criticism when needed. Furthermore I want to thank fellow student Helle Svenningsen Møller for assistance on the Matlab part of the project.

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1.0 Introduction

H_2S is a poisonous and highly corrosive compound present in natural gas when it arrives to the process plant when recovering oil and natural gas. H_2S is corrosive and is damaging the pipe systems and equipment when present. In worst case a leakage of H_2S can cost human lives, and there are several incidents in history where this has happened off shore. For these reasons H_2S has to be removed and legislations define the allowed limit to be 4 ppm.

Over time, many methods for removing H_2S have been tried out, and the industry is aiming to perform better and more efficient sweetening all the time and to minimize the expenses for the process.

A lot of different processes have been investigated, but the focus in modern time has been to develop a sweeting process using different kinds of adsorption and absorption methods. There are two focus areas when developing gas sweetening methods, dry adsorption and wet absorption.

The dry adsorption is usually non regenerative methods and consists of a filter where H_2S is adsorbed. These filters have to be changed regularly to obtain the necessary cleaning. The wet absorption is usually a regenerative process where a liquid stream is lead to react with H_2S in an absorption column to move it from the gas stream to the liquid stream catalyzed by a chemical reaction. The liquid stream is usually recovered and reused for the process.

When dealing with gas sweetening, there is a mass transfer process where H_2S is moved from one phase to another, it is important to support the theory with relevant calculations to be able to evaluate the progress of the sweetening process and establish a mass balance using equilibrium theory.

To investigate the area of gas sweetening the different methods used should be documented. Research about relevant equipment for the most used methods should be made, to be able to make a detailed model for the process.

One process is chosen and evaluated thoroughly to evaluate the efficiency of that specific cleaning method.

The aim of this project is to research the area of gas sweetening and perform a model in HYSYS that is supported by manually performed calculations to evaluate the model and identify the most efficient sweetening process.

When the most efficient process is identified, an economic perspective should be performed, to secure that the chosen model is realistic to use off shore.

2.0 Natural gas

When cleaning natural gas, the content of water, CO_2 and H_2S has to be removed to secure a high quality product for the end user. H_2S is corrosive and is damaging the equipment when the content is too high. Gas containing H_2S can be divided into two categories: Acid gas and Sour gas. The acid gas is having a high content of carbon dioxide (CO_2) and hydrogen sulphide (H_2S), and the sour gas contains moderate amounts of H_2S and CO_2. Both contain small amounts of other sulphur compounds, e.g. thiol (CSH) and carbonyl sulphide (COS). [1]
To avoid high concentrations of H_2S in pipelines, tanks and separators, which can damage equipment and in some cases can cause hazards that can damage personnel, the gas is cleaned.

To understand the presence of H_2S in natural gas, it is necessary to examine the natural gas as H_2S appear in.

Natural gas is formed in the underground and can usually be found in areas where both coal and oil are situated. Its main component is methane, but in addition it contains small amounts of butane, propane and other carbohydrates.

Natural gas is defined as a composition of light hydrocarbons with a low content of heavy hydrocarbons. When the natural gas only contains these compounds it will be defined as a dry gas.
In additional to the mentioned compounds, natural gas often contain non-hydrocarbon compounds such as hydrogen sulfide (H_2S) and other sulfur compounds, carbon dioxide (CO_2) and water (H_2O). Other compounds as nitrogen (N_2) and helium (He) can be present as well. Impurities as CO_2 and H_2S have to be removed completely or partial to match the specification for transport on shore. If the requirements are not matched, the pipelines onshore are exposed to unnecessary risks for corrosion..

H_2S forms sulfuric acid with water, while CO_2 and water forms carbonic acid. These acid gases are corrosive compounds and should be removed from the gas.
A composition of a typical petroleum gas can be seen in table 1on the next page.

Table 1: The composition of natural gas. [2]

Natural Gas	
Hydrocarbon	
Methane	70-98%
Ethane	1-10%
Propane	trace-5%
Butanes	trace-2%
Pentanes	trace-1%
Hexanes	trace-1/2%
Heptanes*	trace-1/2%
Non-Hydrocarbon	
Nitrogen	trace-15%
Carbon dioxide*	trace-5%
Hydrogen sulfide*	trace-3%
Helium	up to 5%, usually trace or none

*Occasionally gases are found, which primarily consist of carbon dioxide or hydrogen sulfide.

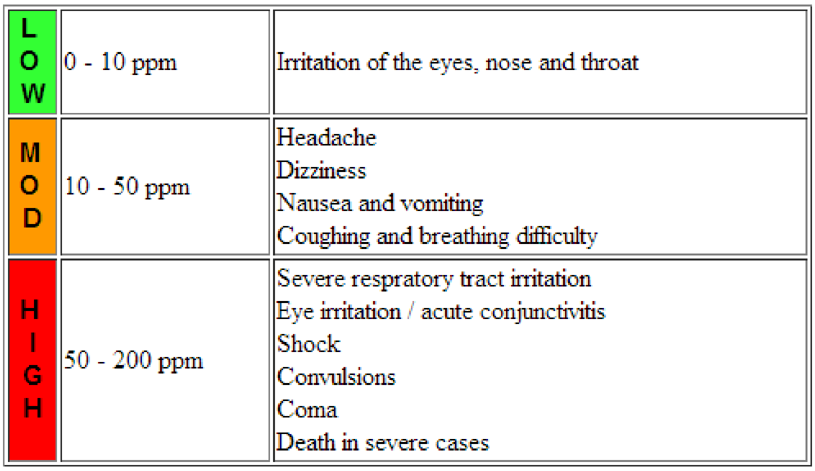
2.1 Hydrogen sulfide (H_2S)

H_2S is an extremely hazardous and toxic compound. It is a colorless, flammable gas, which can be dangerous in relative low concentrations. H_2S can be characterized by the smell of rotten eggs and can be found in e.g. sewage, fertilizers, wastewater treatment plants and gas wells.

The gas is often produced under conditions where rotten organic matter containing sulfur is decomposed in a low oxygen atmosphere. The smell of H_2S can be detected by the human nose in concentrations below 1 part per million (ppm). The smell will increase as the concentration increases. In concentration up to 30 ppm the rotten smell will be present. Above this concentration the smell will change into a more sickening sweet smell. This is dangerous because H_2S can be present without anyone observing any particularly smell. When H_2S reaches this level, it starts to be a threat to the life of humans.

In table 2 typical symptoms from exposure to H_2S is described. [4]

Table 2: Symptoms from exposure to H_2S. [4]



LOW	0 - 10 ppm	Irritation of the eyes, nose and throat
MOD	10 - 50 ppm	Headache Dizziness Nausea and vomiting Coughing and breathing difficulty
HIGH	50 - 200 ppm	Severe respratory tract irritation Eye irritation / acute conjunctivitis Shock Convulsions Coma Death in severe cases

2.2.1 Legislations for removal of H_2S

Recommended actions and precautions should be considered to provide relevant protection for personnel and to avoid exposure to potentially hazardous concentrations of H_2S.

There may be different recommendations and responsibilities for owners, operators, contractors and their employees. Some of the recommendations are mandatory by local, state or federal laws or determined by other offshore rules and regulations. For that reasons recommendations are different depending on the location and the position of the equipment and the employee.

Some general rules should be followed no matter position and location.

Personnel protection should be provided if the concentration in the work area exceeds 10 ppm in an 8-hour time weighted average (TWA) or 15 ppm as a short term exposure level (STEL) as an average over 15 minutes. These recommendations are the same as the recommendations from the American Conference of Governmental Industrial Hygienists (ACGIH). [5]

Equipment and materials should be selected to ensure high resistance to sulfide stress cracking and corrosion. In the International Standard NACE MR0175 recommendations for material and equipment selection can be found.

3.0 Gas sweetening

Many types of cleaning processes have been developed and tested for gas sweetening based on both chemical and/or physical principles. Some of the more common processes are presented in figure 1. A number of less common methods are existing, but these will not be elaborated.

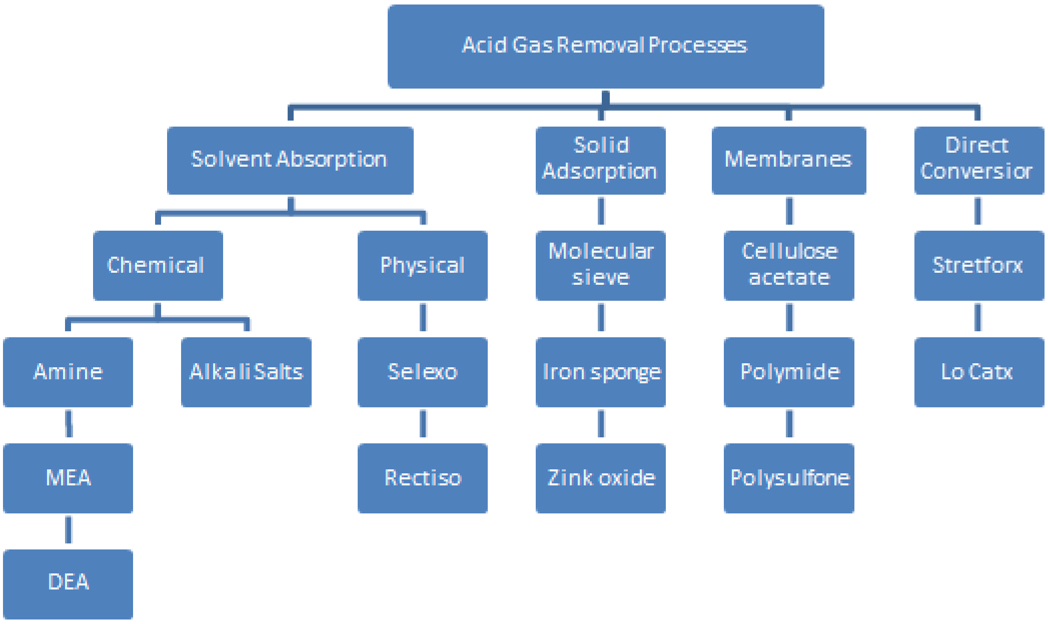


Figure 1: Methods for gas sweetening.

Methods for gas sweetening can be divided into two categories: adsorption and absorption processes.

Adsorption is a physical/chemical method where the gas is concentrated on the surface of a solid or liquid to remove impurities of H_2S. The absorption process is performed by either dissolution, which is a physical process or by reactions with other compounds, which are chemical processes. [6]

3.1 Adsorption processes

Adsorption processes have been widely used since the 1950s. They are still popular due to their high efficiency in removal of a wide variety of organic vapors and several types of inorganic gases. [25]

Adsorbers are used to decrease the concentration of undesired components in the gas and/or vapor phase, before it can be used as desired. The use of the adsorption process has been enhanced and new adsorbents have been developed in recent years.

Adsorption systems are often designed for controlling odor and other containments with an already low concentration (<10ppm). [7]

Adsorptions beds can be categorized as regenerative or non-regenerative. Non-regenerative adsorption beds are disposed when saturation conditions occurs.

3.1.1 How adsorption systems work

In the adsorption process, the vapor or gas stream passes through a stationary phase consisting of a highly porous material termed as an adsorption bed or just the adsorbent. The vapor phase compounds that are removed from the stream in the adsorbent are termed the adsorbate [25]. It will diffuse to the surface of the adsorbent and will be adsorbed since the attractive forces between the adsorbent and the adsorbate are stronger than the attractive forces between the adsorbate and the gas stream. Adsorption will occur on the surface of the material, which is illustrated in figure 2.

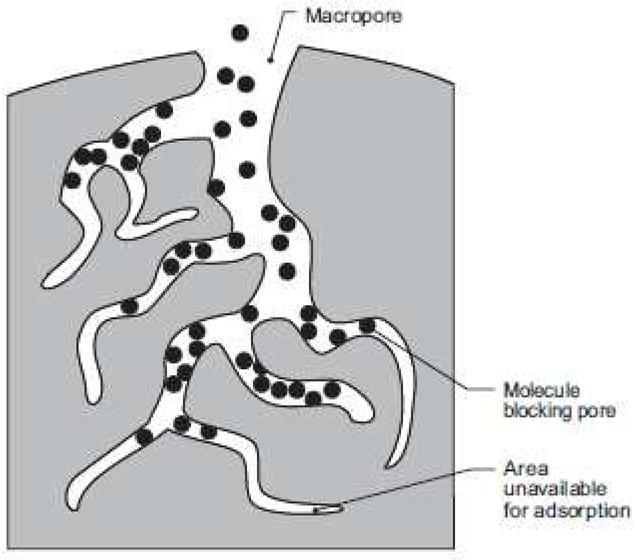


Figure 2: The undesired compounds in the vapor or liquid are adsorbed into on the surface of the adsorbent [25]

3.1.2 Types of adsorbents

Several types of adsorbents have been used during time. The most common types are:

- Activated carbon
- Molecular sieves/ zeolites
- Synthetic polymers
- Silica gel
- Activated alumina

The raw material for activated carbon is coal, wood or other carbon based products. The activation of the carbon occurs in two steps. In first step the raw material is carbonized

by heating the material without air present, until a temperature around 590°C is reached [25].
This removes volatile material, which leaves carbon and a small amount of ash from the volatile components. The surface area is then increased by activating the carbon with steam air at relatively low temperatures and carbon dioxide (CO_2) at higher temperatures. The gas will extend the surface of the carbon material and therefore increase the number and size of the pores. Activated carbon has a nonpolar surface, which is used for removing toxic gases and organic solvents. Carbon used for adsorption consists of granular particles or fibers.

Molecular sieves/ zeolites have a crystalline structure. They are able to remove compounds with a small molecular size. Some types of zeolites are shown in figure 3.

Figure 3: Some Types of zeolites [25]

Molecular sieves are e.g. used to remove humidity from exhaust streams and to remove nitrogen oxide compounds (NOx) from a gas stream.

Synthetic polymers are formed by crosslinking long chained polymers that can have a variety of functional groups. Some polymeric materials have a micro porous structure, which provides a high adsorption capacity. Most polymeric adsorption beds can be regenerated by using hot nitrogen or a hot air stream. An example of a synthetic polymer is shown in figure 4.

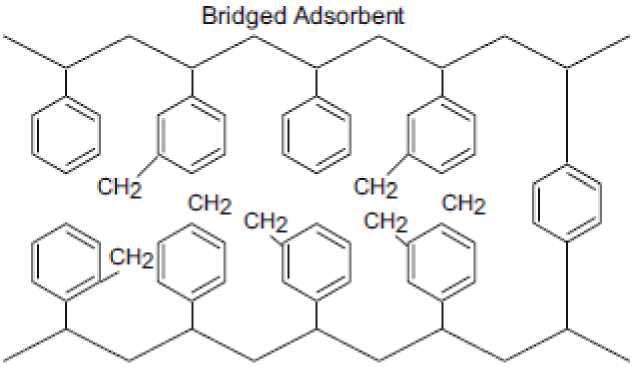


Figure 4: An example of a synthetic polymer [25]

Polymeric adsorbents is suitable for gas streams, which contains a high water vapor concentration, i.e. (>50% relative humidity) [25]

Silica gel is made by sodium silicate (Na_2SiO_3). When sodium silicate is mixed with sulfuric acid it will form a gel-like precipitant. Silica gel is used for removing humidity from different kind of gas streams.

Activated alumina or aluminum oxides are manufactured by heating alumina in a stagnant atmosphere to produce a porous aluminum oxide pellet. Aluminum oxides are primary used for drying gas, particularly at high pressures and are not comely used for removing poisonous compounds.

3.1.3 Characteristics for adsorbents

The physical properties for the adsorbent affects the capacity of the adsorption, the adsorption rate and pressure drop across the adsorbent bed. In table 3 the properties for some adsorbents can be seen. A large surface area provides a greater adsorption capacity.

Table 3: Physical properties for some adsorbents [25]

Adsorbent**	Internal Porosity (%)	Surface Area (m^3/g)	Pore Volume (cm3/g)	Bulk Dry Density (g/cm^3)	Mean Pore Diameter (A)
Activated Carbon	55-75	600-1600	0.80-1.20	0.35-0.50	1500-2000
Activated Alumina	30-40	200-300	0.29-0.37	0.90-1.00	1800-2000
Zeolites (Molecular Sieves)	40-55	600-700	0.27-0.38	0.80	300-900
Synthetic Polymers*	-	1080-1100	0.94-1.16	0.34-0.40	-

* Data provided applied to Dow XUS-43493.02 and XUS-43502.01 adsorbents.
** Data on silica gels nor available.

3.1.4 Non-regenerative adsorption systems

Non-regenerative adsorption systems are manufactured in a variety of physical configurations. They consist of a thin adsorbent bed, and have a thickness in-between 1 and 10 cm.
The life time of the adsorbent units are between six months and up to two years, depending on how many molecules will be adsorbed by the filter.
Non-regenerative adsorption systems are common used for air purification devices for small air flow streams.

3.1.5 Regenerative adsorption systems

There are three types of regenerative adsorption system: Fixed, moving, or fluidized beds. The names refer to how the vapor stream and the adsorbent get in contact.

A fixed carbon bed is a stationary adsorptions system, where the vapor is passing through the adsorption bed. It is optimal for removing poisonous compounds, and is able to purify a variety of organic vapors. It is especially suitable for low pressure streams. This type of adsorption will be optimal for solvents which are immiscible with water.

The principle in moving beds is that the vapor only passes through the unsaturated part of the carbon bed. This will reduce the distance the vapor passes through the bed, which reduces the pressure drop during the adsorption. Moving beds are in general more efficient than fixed beds.

In the fluidized bed, the adsorption material is present in a liquid phase, where the ability of the adsorbent is fluid-like. The vapor stream passes through the fluidized bed that due to the fluid-like abilities ensures a good contact surface. The vapor enters in the bottom of the fluidized bed and passes through sometimes several beds upstream. The adsorbent material can either be stationary or have a flow downstream in the adsorber.

3.1.6 Physical and chemical adsorption

Adsorption processes can be divided into two categories: Physical or chemical adsorption. The difference between the two types is the way the adsorption occurs. In physical adsorption the gas molecule is adsorbed to the absorbent due to intermolecular forces, where chemical adsorption covers the fact that a chemical bond is created between the adsorbed molecule and the adsorbent. Some data for the two types can be seen in table 4

Table 4: Some characteristics for chemisorption and physical adsorption [25]

Chemisorption	Physical Adsorption
Releases high heat, 10 Kcal/g mole	Releases low heat, 0.1 Kcal/g mole
Forms a chemical compound	Gas retained by dipolar interaction
Desorption difficult	Desorption easy
Adsorbate recovery impossible	Adsorbate recovery easy

3.1.7 Regeneration methods for adsorption

Regeneration is accomplished by reversing the adsorption process. It can be done by several methods. Most used is the following:

- Thermal changes
- Pressure changes
- Inert purge gas stripping
- Displacement cycle

All the above methods are changing the physical properties of the adsorption bed, which makes it release the adsorbed molecules.

3.2 Absorption processes

The use of absorbers to remove undesired components in vapor and gas streams has increased since 1990. The increased concerns about toxic air or volatile organic compounds (VOC) in the surroundings have demanded better and more efficient methods for removing these compounds. [8]

Absorbers are frequently used to remove acid gases which have sulfur compounds present and in similar system, where a chemical reaction or simple solubility abilities can remove unwanted compounds in a vapor stream and transferring it to the absorption material.
Absorption can e.g. occur in a liquid droplet, which is dispersed in the gas stream. The given compounds will then react with the liquid droplet and form a product soluble in the liquid. Important factors in the absorptions process are: The surface area of the liquid, where the contact with the vapor phase will happen and the flow rate, which determines the contact time between the absorption material and the given compound. An absorption process is illustrated in figure 5, where a vapor is led through a liquid absorption material.

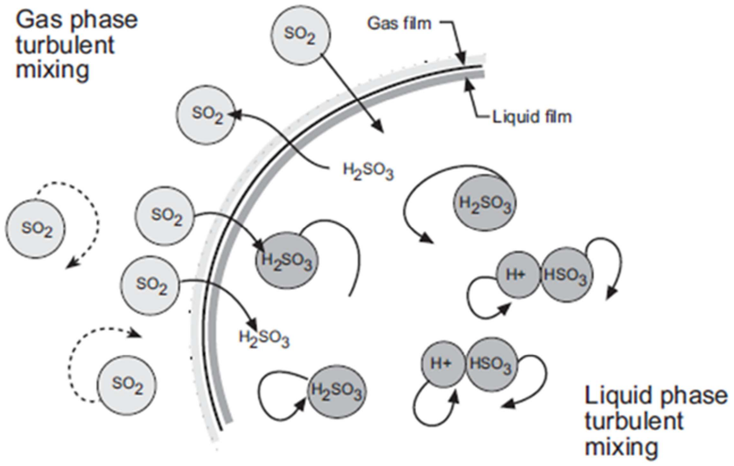


Figure 5: Illustration of an absorption process, where a gas is led through a liquid phase. [25]

Undesired compounds in the gas stream must be slightly soluble in the liquid, which is categorized as an absorbent. The mass transfer of unwanted compounds will continue until the liquid is saturated or the flow rate is limiting the contact time. When saturation is reached equilibrium conditions occurs, and the mass transfer between the gas and the liquid will be equal to each other, and no further removal will happen.

3.2.1 How absorption systems works

Absorption processes can be split into three groups:

- Absorption without chemical reactions
- Absorption with regenerative chemical reactions
- Absorption with non-regenerative chemical reaction

Absorption without chemical reactions is also called physical absorption and is when the undesired component is more soluble in the absorbent material than in the vapor phase. Equilibrium condition for the reaction depends on the partial pressure for the component in the gas phase and the temperature.

Absorption with regenerative chemical reaction is a process where the given compound reacts with the absorption material. The product of the reaction will be present in the absorption material. Equilibrium conditions for the reaction depend on the reactants, the partial pressure of the components in the gas phase and the temperature.
The absorption material can be recovered by an inverse reaction, which regenerates the material and makes it reusable.

Absorption with non-regenerative chemical reaction is almost identical to the regenerative process. The difference is that the absorption material cannot be recovered.

3.2.2 Absorption processes using a regenerative chemical reaction

The gas stream containing the undesired compound is entering the absorption column at the bottom. Here it gets in contact with the absorption material that enters in the top. This means that the flow of the absorption material is a countercurrent flow to the gas stream. The undesired component is gradually absorbed by chemical reaction.
The absorption material leaves the column in the bottom, enriched with the absorbed component. The cleaned gas will leave the absorber in the top.
The rich solvent can be recovered by undergoing one or more processes e.g. distillation, where regeneration with steam is normal. Absorption with non-regenerative chemical reactions happens the same way, with the difference that the absorption material will not be recovered.

3.2.3 Equipment for absorption

There are several setups of equipment for absorption towers:

- Spray towers
- Tray towers
- Packed-bed absorption
- Venturi absorption

The spray tower is one of the simplest devices, which are used for gas absorption. It has an open vessel with one or more sets of spray nozzles to distribute the liquid in the top. The gas stream enters in the bottom of the absorber and passes through countercurrent the liquid. Spray towers is especially used for systems where fouling can be a problem, since this specific absorber is less sensitive to plugging compared to other absorption towers. In figure 6, a spray tower is illustrated.

Figure 6: A spray tower [9]

The tray tower is consisting of vertical columns and has one or more horizontal trays provided to enhance the contact between the gas and the liquid. Tray towers can have several types of trays depending on the usage of the tower. A tray tower can be seen on figure 7 below. Underneath the figure is the different kind of trays elaborated. [10].

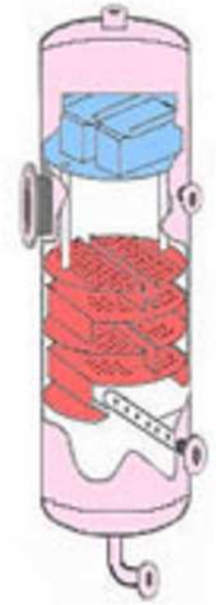
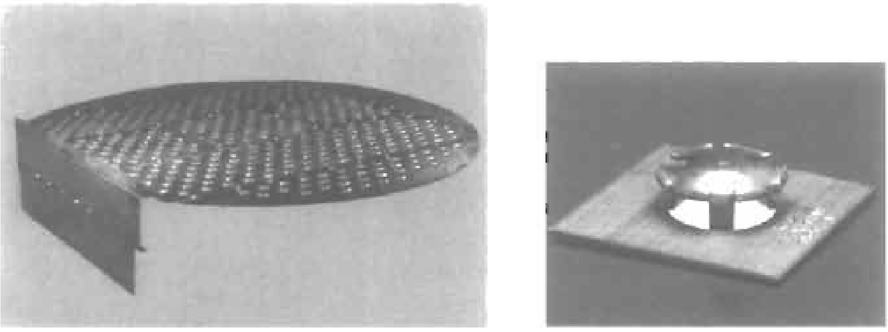


Figure 7: A tray tower [9]

The different type of trays is:

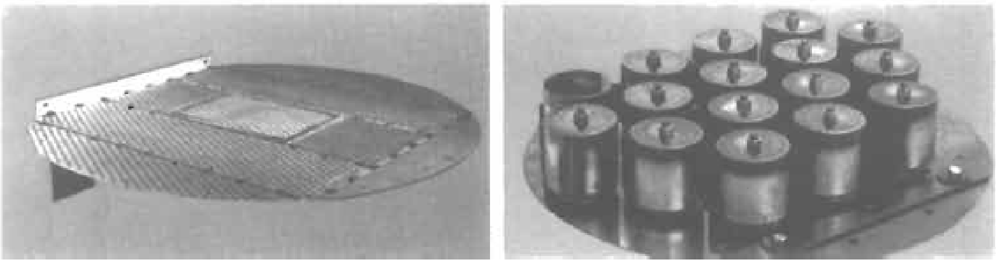
- The sieve tray is consisting of perforated plates and is the simplest type of tray.
- The impingement tray has small impingement targets above each perforation to enhance the contact of the gas and the scrubbing liquid.
- The bubble cap tray consists of risers covered with caps that both the gas and the liquid have to pass through. This enhances a good contact surface.
- The valve trays consist of lift-able valves or caps, which ensures a good contact between the gas and the liquid.

In figure 8 some of the commercial used types of trays shown.



Flexitray valve tray

Standard Flexitray valve



Sieve tray

Bubble-cap tray

Figure 8: Some typical commercial trays used for spray towers. [17]

A packed bed absorption column is a vertical column, which contains the packing material. The packing material is designed to provide a large surface area for contact between the gas and the liquid. The liquid enters in the top of the column and has a downstream flow. The gas stream enters in the bottom and haves an upstream flow. Packed beds can be categories with either structured packing or random packing. Structure packing is consisting of prefabricated sections which are fitted into the column. It has a labyrinth like passage for the flow that can be shaped like a chevron. In figure 9 a structure packing is illustrated.

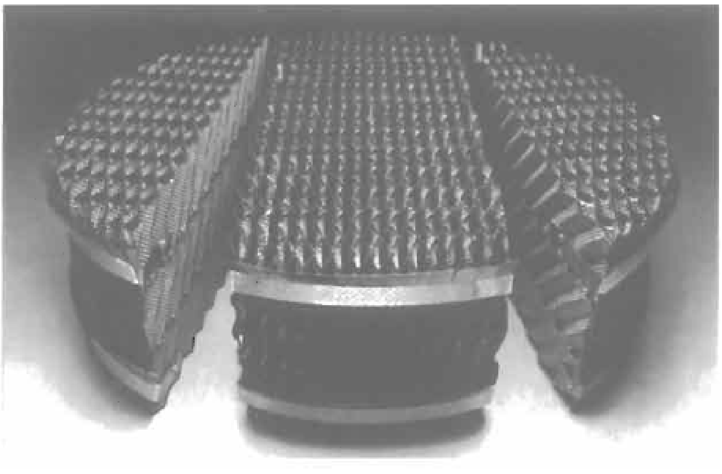


Figure 9: An example of a tray with structure packing [17]

Random packing is small elements in different shapes specially designed for the purpose. They are typically made of plastic, ceramics or metal. They can be found in many types, and they provide a large surface area for contact between the gas and the liquid. In figure 10 some elements for random packing is illustrated.

Figure 10: Example of elements for random packing. [17]

The principle of the venturi absorber, is to lead the scrubbing liquid into a venture nozzle with high velocity, which will cause a large contact area between the liquid and the gas. The venturi absorber requires a pump to achieve the high velocity and is using a lot of energy. Venturi absorbers can be used in combination with a packed bed. In figure 11 a venturi absorber is illustrated.

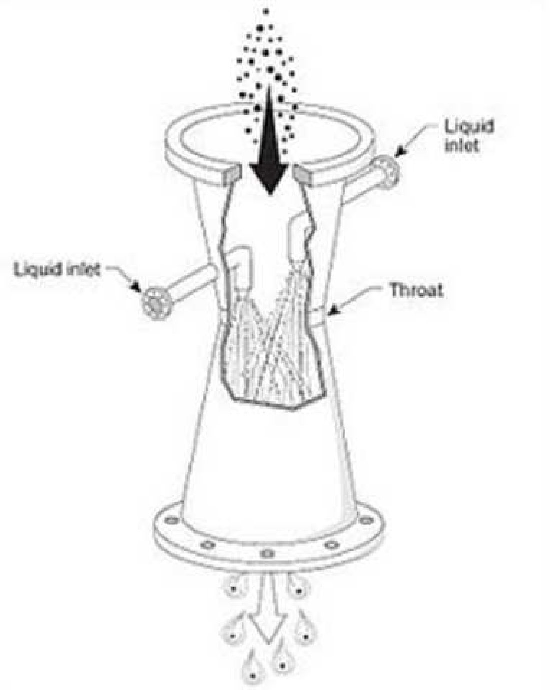


Figure 11: A venturi absorber [9]

The above mentioned methods are the most common used for absorption. There are other methods e.g liquid distribution and bio filtration beds. These will not be elaborated. There are advantages and disadvantages by all absorption methods. Some of them are illustrated in table 5.

Table 5: Some advantages and disadvantages for the mentioned absorption methods. [10]

System	Advantages	Disadvantages
Spray Towers	Simplest type of absorber Little or no plug gage problems	Absorption or removal efficiency is limited
Tray Towers	High absorption/ removal efficiency	High initial cost and complexity Higher pressure drop vs. spray or packed towers
Packed-Bed Scrubbers	Most commonly used with range of designs available Can usually operate over wide flow range	Requires scrubber liquid pumped circulation, spray and makeup system with instrumentation and alarms Packed-bed can plug or become restricted and cause a back-pressure on the vent header system
Venturi Scrubbers	Relatively simple system May provide a low suction pressure at its inlet sufficient to draw vapor from a low pressure vent header system Provides improved capture of solid particles vs. spray or packed towers	Adequate scrubbing efficiency usually requires multiple stages Requires continuous circulation pumped system with sump and liquid makeup that can be energy intensive

Both regenerative and non-regenerative absorption systems can be used to remove undesired compounds in natural gas. In table 6 an overview for removal of CO_2 is presented. The same evaluation can be made for removal of H_2S.

Table 6: An overview of methods for CO_2 absorption. [11]

CO_2 removal mechanism	Process type	Technology	Commercial name
Chemical absorption	Regenerative, continous	Amines	MEA, DEA, MDEA, DIPA, DGA, formulated solvents
		Potassium carbonate	Benfield, Catacarb, Giammarco-Vetrocoke, etc.
	Non regenerative, continuous (usual arrangement: lead/lag)	Sodium hydroxide	-
Physical absorption	Regenerative, continuous	Physical solvents	Selexol,Rectisol,Purisol,Fluor Solvent,IFPexol,etc.
Physical-chemical absorption	Regenerative, continuous	Physical-chemical solvents	Sulfinol,Ucarsol LE701,702 & 703,Flexsorb PS,etc.
Physical adsorption	Regenerative, continuous (adsorption/desorption sequence)	Molecular sieves	Z5A (Zeochem),LNG-3 (UOP),etc.
Permeation	Continuous	Membranes	Separex,Cynara,Z-top,Medal,etc.

3.2.4 Removing H_2S with physical and chemical absorption

H_2S and other compounds containing sulfur can be removed from mixtures containing hydrocarbons as natural gas. There are two commonly used methods to achieve this: Physical absorption or chemical absorption.
Various solutions of amines can be used to remove sulfur compounds in a chemical reaction. For this purpose, it is obvious that the process is a chemical absorption. Sweetening of acid gas, which is a common name for natural gas containing H_2S, can be performed by physical absorption as well.
When removing sulfur compound from acid as with a chemical absorption process, an aqueous solution of amines, which are weak alkalines, are reacting with the compounds. This reaction is reversible, and the absorption material can be recovered by changing the temperature and/or pressure of the liquid solution containing sulfur. In this way, the amine can be reused. Amines are the most commonly used in chemical absorbers.
The process where physical absorbers are used, are also called solvent processes. They are based on the solubility of the H_2S within a liquid instead of on chemical reaction between the acid gas and the liquid. Solubility is a function of the interaction between the given molecule, the partial pressure and the temperature. The absorbent can be regenerated by changing the temperature to manipulate the solubility or by using a

stripping process. Physical absorbents have a high affinity to heavy hydrocarbons. If the gas has a high concentration of C_{3+}hydrocarbons, the use of a physical absorbent may result in a significant loss of the heavier hydrocarbons.
When recovering the absorbent, the organic compounds will be removed, but not mixed with the natural gas again. Physical absorption processes should be considered if the following conditions are present:

- The partial pressure for H_2S is high,
- The concentration of heavy hydrocarbons is low
- Selective removal of H_2S is required

Many physical absorption processes are protected by a patent and is only available when buying a license. In table 7 some of the processes are listed with the eventual owner of the license.

Table 7: Overview of the different physical processes and their licensor. [12]

Process	Licensor
Solid bed absorption:	
Iron sponge	
Sulfa Treat	The sulfa treat company
Zine Oxide	
Molecular sieves	Union Carbide Corporation
Chemical solvents:	
Monoethanol amine (MEA)	
Diethanol amine (DEA)	
Methyldiethanol amine (MDEA)	
Diglycol amine (DGA)	
Diisopropanol amine (DIPA)	
Hot potassium carbonate	
Proprietary carbonate system	
Physical solvents:	
Fluor Flexsorb	Fluor Daniel Corporation
Shell Sulfinol	
Selexol	Norton Co., Chemical Process Products
Rectisol	Lurg, Kohle & Mineraloltechnik GmbH & Linde A.G.
Direct conversion of H_2S to sulfur:	
Claus	
LOCAT	ARI Technologies
Stretford	Ralph M. Parsons Co.
IFP	Institute Francais du Petrole
Sulfa-check	Exxon Chemical Co.
Distillation:	
Amine-aldehyde condensates	

3.2.5 Columns for distillation, absorption and stripping

Columns for absorption are often evaluated in amount of absorbed material per meter of column height. In this way different solutions for the same case can be compared.
To evaluate the design the flow ratio and its behavior in the column has to be analyzed. The columns can be designed with several types of separations sections, different diameter and different types of inlets. Before choosing column specifications, several limits on the basis of purchase price and operating costs are evaluated.
Afterwards the dimension for the column with attention payed to the flow specification and the packing material is determined. The height of the column can afterwards be determined to achieve the desired efficiency of the absorber. Trays, structure packing or packing material have to be a part of the evaluation to be able to design a useable column.

The packing material has to be evaluated on the following parameters to ensure high efficiency is:

- Surface area, which can be covered by the liquid and thus create a good interface between the liquid and the gas or vapor phase.
- Empty space in the packing material to ensure both streams can flow without large pressure drop.
- Mechanical and chemical resistance to the operating conditions.
- Acceptable cost for purchase and operation

Instead of using a packing material, structure packing can be used. Structure packing consists of plates made of ceramic, plastic or metal bent into a zig zag pattern and assembled in blocks, which fits into the column. The plates are perforated. Especially the metal plates are very thin and exposed to corrosion. Therefor they have to be manufactured in stainless steel, which will affect purchase price.
The plates are ensuring that the liquid flows as a steady thin film, down the plates with a countercurrent direction to the gas flow. A prerequisite for a good mass transfer between the phases is:

- Good liquid distribution on the plates.
- Low surface tension between the packing materials.

When using a packing material, the liquid is flowing downstream the column and gets mixed with the gas on the surface of the packing material. When using structure packing the solid surface of the plate are covered with the liquid and the gas is bubbling through the small channels.

When tray columns are used, the channels are covered with liquid which ensures a good contact between the liquid and the gas phase.

Some reason for a poor contact interface can be either a too high level of water on the trays. This will not let vapor or gas through the holes, and instead liquid will run through. This is known as “weeping”. Another reason for a poor interface is “blow-off”, where the velocity of the gas flow is too high, which will blow the liquid away from the

holes, which will cause a smaller contact area and liquid droplets can be torn up to the overlying tray.
The maximum velocity can be determined as seen in equation 1: [23]

$$V_{D,max} = K \cdot \sqrt{\frac{\rho_l - \rho_\delta}{\rho_\delta}}\ m/s \qquad (1)$$

Where ρ_l and ρ_δ are the density of respectively the liquid and the gas phase measured in kg/m^3 and K is a constant for the system that depends on the distance between the tray and the liquid layer on the tray, as measured from the gas discharge height to the liquid surface.
In table 8 below some characteristics for the different types of columns is shown. [23]

Table 8: An overview of parameters relevant for the choice of column. X is suitable and XX very suitable.

	Packed column				Structure packing	Tray column		
Criteria	**Plastic rings**	**Metal rings / saddles**	**Ceramic rings / saddles**	**Grate wood / plastic**		**Bells**	**Valves**	**Sieve**
Vacuum / low pressure drop	X	X	X	XX				
Low flow rate	X	X	X	X	XX	XX	X	X
High liquid flow	X	X	X			X	X	X
Low hold-up	X	X	X	X	X			
High hold-up						XX	X	X
Foaming	X	X	X	X	X			
Coating						X	X	
Solid impurities					X	X	X	X
Large boundary surface tension against plastic		X	X		X	X	X	X
Corrosion	X		X		X	X	X	X

3.2.6 Stages processes (Plate/ Packed)

There are three basic flow patterns in absorption columns. [22]

- Parallel
- Countercurrent
- Cross

Parallel flow is that the flow of both phases moves in the same direction e.g. entering in the top and exiting at the bottom. Countercurrent flow is when the two phases flows in opposite directions. For cross flow the two phases flows orthogonal to each other.

For gas sweetening, as in this project, countercurrent flow will be used in the column.

For the design of absorbers with countercurrent flow the following estimations are made: [17]

- Selection of the type of contactor (trays and packing material)
- Determining the heat and mass balance
- Estimations of the required column height (number of stages or packing height), based on the mass transfer calculations.
- Determination of the required column diameter (tray/ packing), based on the gas and the liquid flow rates.
- Mechanical design for the column.

3.3 Chemical absorption

3.3.1 Amines

Amine is the term for a functional group in organic compounds. They are alkaline substances and have a pH greater than 7.

An alkaline will accept a proton (H^+) from another species e.g. water and produce hydroxide ions (OH^-). Therefore water is essential for gas sweetening with amines. The reaction with water is illustrated below. [27]

$$B + H_2O \rightarrow BH^+ + OH^- \qquad (2)$$

The reaction between water and a proton acceptor, which can be an amine, causes formation of hydroxide and an alkaline pH, which will reduce corrosion in the pipelines.

3.3.2 Types of amines

Amines are organic compounds with ammonia (NH_3) as the fundamental compound. By replacing one or more of the hydrogen atoms with an organic hydrocarbon group, different kind of amines are formed. Replacement of a single hydrogen atom produces a primary amine, replacement of two produces a secondary amine and replacement of all three produces a tertiary amine.
In figure 12 the different types of amines are illustrated.

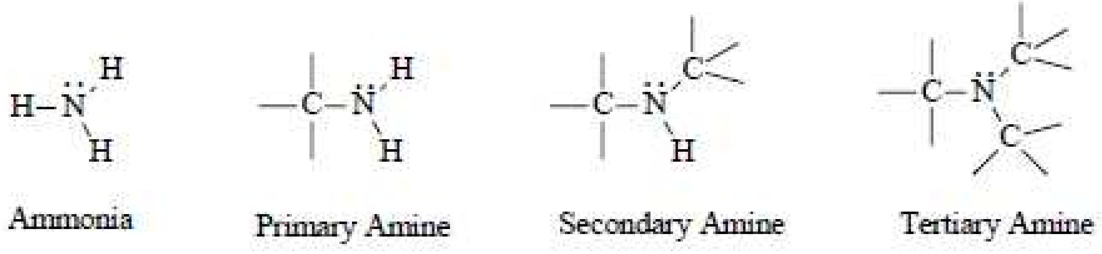


Figure 12: The different kind of amines [26]

All commonly used amines are alkanolamines, which are amines with an alcohol group (OH) attached to one or more of the hydrocarbons. This reduces their volatility compared to amines with no alcohol groups attached.

The content of H_2S in natural gas can be reduced by reactions with amines. The amine accepts a proton from H_2S, which is the first step in the decomposition of it. The reaction between the amine and H_2S is highly exothermic. Regardless of the structure of the amine, H_2S reacts with both the primary, secondary and tertiary amine.
Amines remove H_2S in a two-step process.

1) The gas dissolves in the liquid (physical absorption)
2) The dissolved gas which is a weak acid reacts with the alkaline amines.

The simplified reaction can be seen below.

$$H_2S + Amine \Leftrightarrow [Amine]H^+ + HS^- \qquad (3)$$

The reaction is more complicated than illustrated, due to bigger molecules formed by the amine solution and H_2S. To form those, water is an essential component in the process.

The primary reaction between alkanolamines and H_2S is shown below, where R_1, R_2 and R_3 denotes an organic compound, that can be either the same or different from each other. [28]

$$R_1NH_2 + H_2S \leftrightarrow R_1NH_3^+HS^- \qquad (4)$$

$$R_1R_2NH + H_2S \leftrightarrow R_1R_2NH_2^+HS^- \qquad (5)$$

$$R_1R_2R_3N + H_2S \leftrightarrow R_1R_2R_3NH^+HS^- \qquad (6)$$

There are five different types of amines for sweetening processes:

- Aqueous monoethanolamine process (MEA)
- Aqueous diethanolamine process (DEA)
- Glycol-amine processes
- Aqueous triethanolamine processes (TEA)
- Methyldiethanolamine processes (MDEA)

MEA, DEA and MDEA are the most commonly used amines for gas sweetening in the oil and gas industry.

Monoethanolamine (MEA)

MEA is the strongest alkaline between the amines. [16] For that reason MEA will be the one reacting most rapidly with the acid gas. MEA is able to remove both hydrogen sulfide and carbon dioxide from gas streams. MEA has a low molecular weight compared to the other amines, and has a greater carrying capacity for acid gases on a unit per weight or volume basis.

Diethanolamine (DEA)

DEA is in many ways similar to MEA, where DEA is a secondary amine and MEA a primary. All side groups are ethanol. DEA's reaction with carbonyl sulfide and carbon disulfide is very slow, and it is not always possible to detect reaction between those species. DEA is non-selective and removes H_2S and CO_2. It is more volatile than MEA, which will result in a more efficient recovering process, where the loss by evaporation will be small.

Methyldiethanolamine (MDEA)

Triethanolamine (TEA) was the first amine applied for gas sweetening. In modern gas treatment, it has been replaced by MDEA, since they are similar in their efficiency, but MDEA is less toxic.
MDEA is a tertiary amine like TEA, and they react the same way in gas sweetening processes. MDEA is less reactive with H_2S and CO_2, and sometimes the content of these will not be reduced enough to meet the demands for sweet gas. The flow and the temperature have to be raised to compensate for less efficiency compared to the other amines.
Due to the tertiary structure, MDEA is a more compact molecule, and therefore it is reacting slower because it is harder for the volatile component to get close to the center of the molecule.
Nevertheless the use of MDEA will still be realistic in some processes as a sweetening agent, due to its low toxicity.

The structure of the most commonly used amines can be seen below in figure 13.

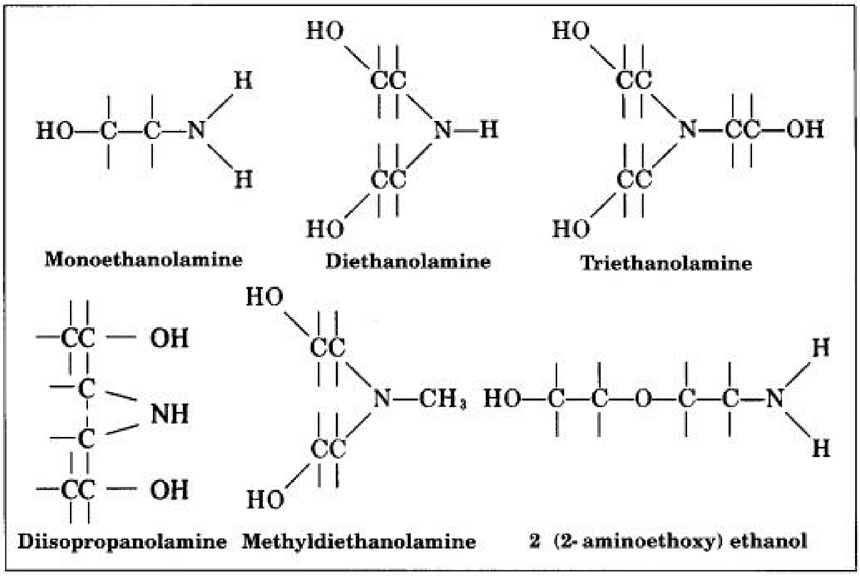


Figure 13: Structures of the most commonly used alkanolamines [17]

3.4 Stage processes and mass transfer

Separation processes are used for a lot of operations in the chemical industry. Some mixtures are easier to separate by mechanical techniques, where others need more advanced techniques applied to ensure a sufficient separation. Many types of mixtures are separated, some of them are: Gas-liquid, liquid-liquid, solid-liquid and gas-solid. Equipment and devices to perform separation processed can be divided into following categories: [18]

- Gas-liquid contacting (gas absorption and stripping, distillation, humidification or dehumidification and water cooling)
- Liquid-liquid contacting (solvent extraction)
- Gas-solid contacting (drying and adsorption)
- Liquid-solid contacting (leaching, crystallization and ion exchange)

Not all mixtures can be separated by these techniques, without supplementing with either other compounds or energy transfer. An example is removal of H_2S in a gas sweetening process, where amines are added to the absorption column to react with H_2S. The amine is also called the separation agent in this case.
Separation processes are in general based on the principle of mass transfer and referred to as mass transfer operations. The definition of mass transfer is the transportation of species from one location to another in either one phase or in two phases, where a difference in concentration occurs. The driving forces are an indication used to define how close the system is to equilibrium and they are identical to the rate of transportation. In chemical engineering there are three major types of transportation processes. [18]

- Mass transfer
- Momentum transfer
- Heat transfer

In table 9 a list of separation agents that are commonly used is shown. A separation agent can either be energy transfer, filtration units or chemical compounds.

Table 9: A list of separation agents used in the industry. [18]

Separation process	Separating agent	Typical applications
Gas absorption and stripping	Solvent	Removal of CO_2 from synthesis gas; removal of CO_2 and H_2S from natural gas; stripping volatile substances from wastewater by steam.
Distillation	Heat	Fractionation of crude oil; separation of air.
Liquid-liquid extraction	Solvent	Removal of aromatics (benzene, toluene and xylen) from gasoline reformate; recovery of penicillin from fermentation broth.
Solid-liquid extraction	Solvent	Extraction of caffeine from coffee; extraction of herbal products from barks and leaves.
Drying	Heat/drying gas	Drying of fruits; drying of polymer beads; drying of ceramic items before firing
Adsorption	Adsorbent solid	Separation of organics from a gas or an aqueous solution; drying of air.
Ion exchange	Ion exchange resin	Demineralizing of water; separation of salts
Crystallization	Heat (removal)	Production of salt, sugar etc.
Membrane separation	Membranes	Desalination of water; preparation of absolute alcohol; concentration of fruit juice; air separation.

3.4.1 Equilibrium

Equilibrium is a term used to define if there is a change in concentration of any component in a reaction system or in any phase of the system. When the system is in equilibrium, no changes will occur. If not in equilibrium, changes will happen.
In this project equilibrium theory is used stage processes, where it is assumed that a stream leaving a stage is in equilibrium according to transferring of the given compound.

When a liquid and a vapor of the same compound are in contact with each other, some of the liquid molecules will evaporate and some of the vapor molecules will condensate. This is called thermal equilibrium. The same is valid for multi component systems, where each component will be in equilibrium between the vapor and the liquid phase. When not in equilibrium, the different phases might have different temperature and/or pressure. At thermal equilibrium, evaporation and condensation will still occur, but the rate of these will be identical.
There are three types of equilibrium when working with absorption, thermal, mechanical and chemical.

At thermal equilibrium, the temperature of the two phases will be equal. The thermal equilibrium can be written as:

$$T = T_{Liquid} = T_{Vapor} \tag{7}$$

In mechanical equilibrium the forces between vapor and liquid will be equal. For stage this will mean that the pressure in the two phases is equal.

$$P = P_{Liquid} = P_{Vapor} \tag{8}$$

In chemical equilibrium there will not be produced any more of the products or the reactants in the reaction. In the reaction between an amine and H_2S, no more of each component will be produced.
Put into practice, the equilibrium is more complicated in an absorption column, since reaching equilibrium takes time, and even though it is assumed. In theory it is not sure that all types of equilibrium is reached in all stages.

3.4.2 Mass transfer

Mass transfer is the transfer of mass from one location to another or from one phase to another. Mass transfer always occurs in an interface between two phases. Mass transfer has three kinds of mechanisms: Molecular diffusion by random and spontaneous microscopic movement of molecules as a result of thermal motion and eddy diffusion (turbulent) by random, macroscopic fluid motion. [19]
The third mechanism is the bulk flow, which occur when the total rate of mass transfer is affected by the bulk flow. Diffusion occurs very slowly and eddy diffusion is the fastest. In separations processes it is important to dimension the equipment with the pace of the mass transfer in mind.
The transfer from one phase to another of a specie can be defined by using the molar flux of the component i, N_i, and is equal to the sum of the transfer due to the three mechanisms. The unit for the molar flux is moles per time unit per unit area. [19]

$$N_i = molecular\ diffusion\ flux\ of\ i + eddy\ diffusion\ flux\ of\ i + x_i \cdot N \tag{9}$$

$x_i \cdot N$ is the bulk flow flux.

3.4.3 Mass transfer principles

When one material is transferred from one phase to another across an interface, the resistance to mass transfer in each phase is created by a gradient in concentration. This is illustrated in figure 14.

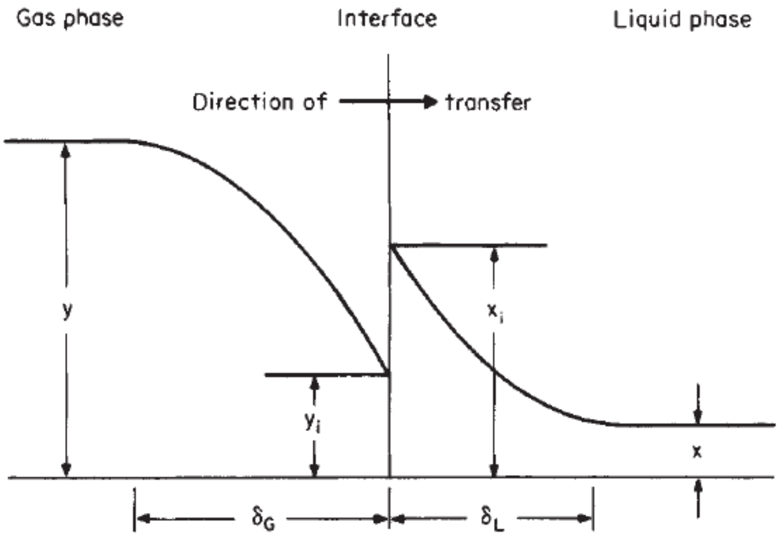


Figure 14: The concentration gradient near a gas-liquid interface. [20]

The concentration for the diffusing material in the two phases will change in the interface due to diffusion in that point. If the figure above is considered, the concentration in the gas phase is seen on the left. At the interface the concentration in the gas phase is lower than the bulk, due to molecules rapidly diffuse into the liquid phase. In the liquid phase the concentration is higher in the interphase than in the bulk phase due to the receiving of molecules from the gas phase. The difference in concentration between bulk and interface will be lowered when equilibrium gets close and the diffusion rate gets lower. In systems where the solute concentration in both phases is diluted, the rate of mass transfer will be proportional to the difference between the bulk concentration and the concentration at the interface. This is described in equation 10 below. [20]

$$N_A = k'_G \cdot (p - p_i) = k'_L \cdot (c_i - c) \tag{10}$$

Where:
N_A is the mass transfer rate
k'_G is the gas phase mass transfer coefficient
k'_L is the liquid phase mass transfer coefficient
p is the solute partial pressure in bulk gas
p_i is the solute partial pressure at interface
c is the solute concentration in bulk liquid
c_i is the solute concentration in liquid at interface

The expression can be rewritten to be a function of the molar fraction in both phases instead of concentration and partial pressure. This can be seen in equation 11 as: [20]

$$N_A = k_G \cdot (y - y_i) = k_L \cdot (x_i - x) \tag{11}$$

Where:
k_G is the gas phase mass transfer coefficient valid for using mole fractions
k_L is the liquid phase mass transfer coefficient valid for using mole fractions
y is the mole fraction solute in bulk gas phase
y_i is the mole fraction solute in gas at interface
x is the mole fraction solute in bulk liquid phase
x_i is the mole fraction solute in liquid at interface

The relation between the two mass transfer coefficients is seen in equation 12 and 13. [20]

$$k_G = k'_G \cdot p_r \tag{12}$$

$$k_L = k'_L \cdot \bar{\rho}_L \tag{13}$$

Where:
p_r is the total system pressure employed during the experimental determinations of k'_G values
$\bar{\rho}_L$ is the average molar density of the liquid phase

k_G is not depended on the total system pressure, which makes it more suitable to use as a general constant instead of k'_G, which is inversely proportional to the total system pressure.

3.4.4 Molecular diffusion

Molecular diffusion is the motion of molecules from one phase to another. All individual molecules in a liquid will move in randomly direction at different speed. The molecules will collide with each other, and the velocity and the direction of each molecule will change constantly. At high temperature the diffusion rate will be high due to more energy in the molecules and therefore greater molecular velocity. For gases, the diffusion rate is inversely proportional to the pressure, e.g. the diffusion will be more rapid.
A solution, which is not uniform in concentration, will be brought into this by diffusion. The molecule moves from an area of high concentration to an area of low concentration. The concentration gradient is depending on the rate the solute is moving. Rate diffusion is described as a molar flux termed in moles per area per time. In a solution with two or more components there will be a flux to consider for each component: [18]

3.4.5 Film theory

One of the most used theories regarding mass transfer across an interface in separation processes is the film theory. This can be either a gas/liquid interface or an interface between two liquid phases. The film model assumes that the entire resistance to diffusion will be established in the bulks themselves. This means that the molecules will pass across the interface without encountering resistance. To diffuse into the bulk of the fluid, the molecule still has to cross a thin stationary region, which is referred to as a film. In the film the resistance to mass transfer is present.

The film is considered as a kind of a membrane, where the solution is homogeneous in the phase but different on each side of the film. The difference can be described as the driving forces for mass transfer across the membrane.

The film model can be split into two types of film models: One film and two film models.

For the one film model there is only considered one film to provide resistance for mass transfer during diffusion. This film is considered to be on the surface of the liquid phase. If a model is established for the compound A in a non-volatile solvent B, there will be no resistance against diffusion in the gas phase or in the interface on that side. The component A will diffuse into the liquid film and further into the liquid bulk, where the resistance to diffusion is between the liquid phase and the liquid interphase. In figure 15, the one film model is illustrated.

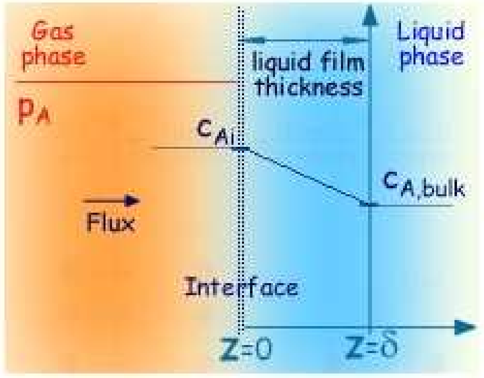


Figure 15: The one film model [21]

In the two film model, two films are present, one in the interface of the liquid and one in the gas. There for there will be resistance to diffusion on both sides on the interphase. This is illustrated in figure 16.

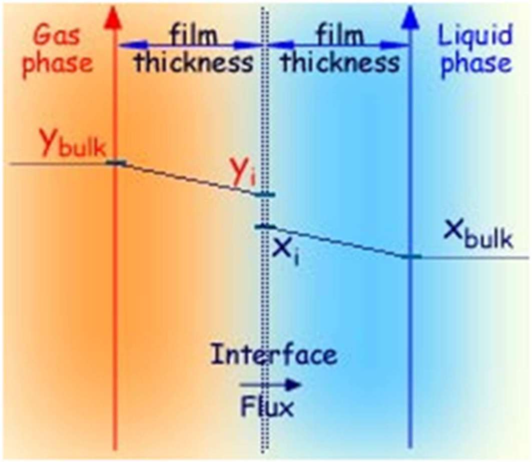


Figure 16: The two film model [21]

As described in the film model theory the entire resistance to diffusion will be generated by the films. Therefore it can be assumed that the concentration in the interphase is in equilibrium. This is be illustrated in equation 14. Where Y_i is the molar fraction of component i in the gas film, X_i the molar fraction in the liquid film and f_{eq} are the fugacity at equilibrium conditions at the interface. [21]

$$Y_i = f_{eq.}\,(X_i) \tag{14}$$

3.4.6 Handling stage processes

In stage processes, the aim is to achieve a product that meets the requirements. The average retention time in a stage for a given compound in one phase depends on the composition and amount of the second phase.

For a given stage, the retention time of the liquid will be high if the liquid height on the bottom of the stage is high. During the stay in the stage, the two phases will be in contact with each other. Their composition will therefore, at least in theory, be in equilibrium. When the two phases are in equilibrium, the maximum mass transfer in that particular stage is reached. When evaluation stage processes, equilibrium in each stage will be assumed, unless the system is specified to be faster than equilibrium can occur. To determine the number of stages required to meet the requirements of the process, the equilibrium for the given system, the flow and its parameters should be known, e.g. concentrations of the given compounds. The graphical presentation of the flow and concentration in the given phases are typically defined as shown in figure 17.

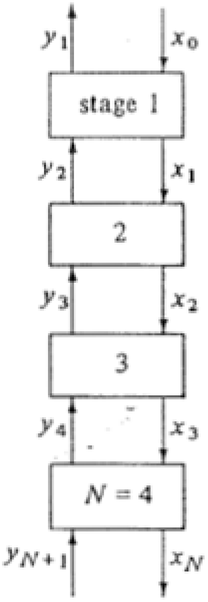


Figure 17: Outset for the stage calculations. [31]

Each box in the figure illustrates a stage where equilibrium occurs before the streams are transfered to the next stage. The numbering starts in the top and goes from 1 to N, where N is the number of stages. The liquid stream is denoted L and the gas with G. The concentration of the given compound is given by x_i and y_i that is the mole fraction in respectively the liquid and the gas phase. To determine N, equilibrium in the given stage is assumed. When this is assumed the connection between the mole fraction of component c in the gas and in the liquid phase is as given below.

$$y_i = K \cdot x_i \tag{15}$$

Where K is the equilibrium constant, that can be found in literature or by experiments.

The mass balance for an absorber can be performed as seen below. [32]

$$L \cdot x_0 + V \cdot y_{N+1} = V \cdot y_1 + L \cdot x_N \tag{16}$$

Where x_0 is the concentration of the given compound in the liquid, x_N is the concentration in the outlet stream of the liquid, y_1 is the inlet concentration in the gas and y_{N+1} is the outlet concentration for the gas. L is the liquid flow rate and V is the gas flow.

Solving the equation for y_{N+1} gives:

$$y_{n+1} = \frac{L}{V} \cdot x_n + y_1 - \frac{L}{V} \cdot x_0 \tag{17}$$

This equation expresses y_{n+1} as a function of x_n and x_0. In this way the concentration of one component can be determined as a function of the other component, when the outlet concentration of the given compound in the gas phase is known. This equation is related to the lines in a McCabe-Thiele diagram, which gives the opportunity to evaluate the stage process graphically. Using McCabe-Thiele changes in the concentration in each stage can be tracked.
By knowing all details and then setting up the mass balance, the exactly number of stages needed can be determined.

In a McCabe-Thiele diagram, the data is plotted with the composition in the liquid phase represented on the x-axis and the composition of the gas phase on the y-axis. In the same diagram equation 17 is plotted as the “operating line”.

This graphic illustration is called the McCabe-Thieles method and is a graphically solution for stage processes. The diagram is illustrated in figure 18.

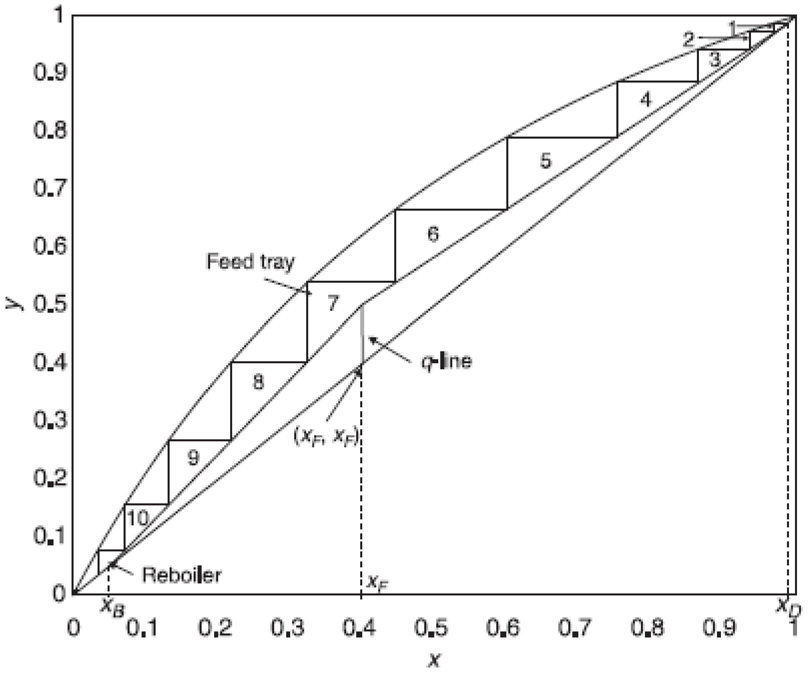


Figure 18: Graphic determination of the number of theoretical stages. [22]

When using the diagram, the starting point is in the top right corner that is representing the conditions in stage 1, $(x_{0,}\ y_1)$.The bottom left is representing the outlet concentrations for the system, $(x_N,\ y_{N+1})$.

The drawn lines numbered in the graph represent each stage in the process. A horizontal line cuts the working line and the equilibrium curve and is used to determine the fraction of the given compound in the gas and the liquid phase. Each horizontal line represents a stage in the process.

3.4.7 The Kremser Equation

Another way to find the number of stages is to use the Kremser equation. This method is used to make a quick estimate of how many stages needed for a given process. The Kremser equation is seen below.

$$N = \frac{ln\left[\frac{Y_{N+1}-K\cdot X_0}{Y_1-K\cdot X_0}\cdot\left(1-\frac{1}{A}\right)+\frac{1}{A}\right]}{ln(A)} \qquad (18)$$

Where A is the absorption factor and is defined as following:

$$A = \sqrt{A_1 \cdot A_N} \qquad (19)$$

A_1 and A_N is describing the conditions in stage one and in the last stage.

$$A_1 = \frac{L}{K\cdot V_1} \qquad \text{(Stage 1 conditions)} \qquad (20)$$

$$A_N = \frac{L_N}{K \cdot V} \qquad \text{(End stage conditions)} \tag{21}$$

Where V_1 is outlet for the gas and L_N is outlet for the liquid, assuming that the only mass transferring occurring is the desired compound.

3.4.8 Specific for Packed Columns

The first parameter to determine when using a packed column is the height of the column. For this determination the method for determining the theoretical number of stages is used as described in the McCabe-Thiele method.
The method used the theory of equilibrium and the mass balance to determine at which height in the packed column will be identical to one plate in the plate column. The molar fraction of the given component in the liquid phase, x therefore has to reach the concentration as if it was passing one plate, and the same for the molar composition in the gas phase y.
This equivalent is called the Height Equivalent to a Theoretical Plate (HETP). This can be seen in equation 22 below. [30]

$$H = HETP \cdot n \tag{22}$$

Where n is the number of theoretical stages determined by the McCabe-Thiele method, HETP is the height equivalent to a theoretical plate and H is the height of the packing.

The value of HETP can be determined by the modified Granville equation. [30]

$$HETP = 28 \cdot d_p \cdot m_a \cdot \frac{V}{L} \cdot \left(\frac{H}{2{,}4}\right)^{1/3} \tag{23}$$

Where, d_p is the diameter of the packing, m_a the average slope of the equilibrium curve, V the molar vapor flow rate and L the molar liquid flow rate.

The value of m_a can be determined by the following method. [30]

$$m_a = \frac{\sum_{i=1}^{n} m_i}{n} \tag{24}$$

Where, m_i is the local slope of the equilibrium curve at theoretical plate i.

In figure 19 an example of evaluation of m can be seen.

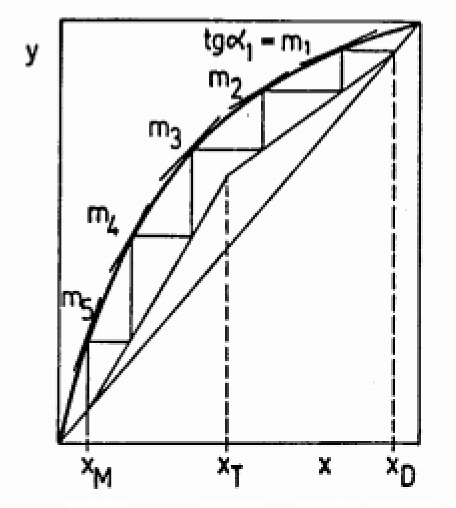


Figure 19: Determining m_i. [30]

In this way the dimensions of the column can be determined

3.5 Net present value (NPV)

Important decisions about a gas cleaning processes e.g. which type of gas cleaning, which column, which material, which demand for purity and so on, is taken on the basis of efficiency, economics and environmental considerations. It has major influence on the operation and its costs and it extends over time.
Most companies are paying attention to their income and profit. There for different solutions to project details are compared and their benefits and costs are analyzed over sometimes longer periods of time.
Some general formulas are used to create an overview. One key parameter is the present value (PV). The present value is used find the net present value (NPV).
The NPV is a key parameter compared across project, and is influencing the choice on which solution to implement. It is showing the profit for the investment at a given time.
Projects can be divided into two categories: Projects with short lifetime and projects with long lifetime. Short projects will last less than a year and longer more than a year.
Future value (FV) and present value (PV) are used to determine NPV, and is defined as what an investment can yield when including rate additions, i.e. PV is the investment including the rate. FV and PV can be determined below.

NPV for short projects

FV and PV for short projects are determined as shown below: [24]

$$FV = X \cdot (1 + i) \tag{25}$$

X is the investment and i the rate.

$$PV = \frac{FV}{1+i} \tag{26}$$

Calculating the present value is also called “discounting”. By comparing the investment with the present value it will be possible to assess whether the investment returns profit. Else other values have to be fulfilled to make the investment beneficial.
By determining the net present value (NPV), all the profits and expenses for a project, including the investments, is summed. The NPV can be found as seen in equation 27. [24]

$$NPV = PV - the\ investments \tag{27}$$

NPV for longer projects

The way to determine NPV above is only applicable for short projects. If the duration of the project is more than a year, the duration in years (n) is added to the equation, as seen in equation 28. [24]

$$PV = \frac{FV}{(1+i)^n} \tag{28}$$

If a project profits during several periods, the total PV can be determined by adding PV for each period, as shown in equation 29. [24]

$$PV(i) = \frac{FV_{(0)}}{(1+r(0))^{(n0)}} + \frac{FV_{(1)}}{(1+r(1))^{(n1)}} + \cdots + \frac{FV_{(i-1)}}{(1+r(i-1))^{(ni-1)}} + \frac{A_{(i)}}{(1+r(i))^{(ni)}} \tag{29}$$

r is the interest for the given period.
The formula for PV can be reduces as seen in equation x below. [24]

$$PV(i) = \sum_{i=0}^{n} \frac{FV_{(i)}}{(1+r(i))^{ni}} \tag{30}$$

The NPV for a longer project is then defined as seen below in equation 31. [24]

$$NPV = PV(i) - the\ investmens \tag{31}$$

NPV for different projects can be compared to see which one grants the most profit.

4.0 Problem statement

Several methods for gas sweetening exist. One of the commonly used and most tested is sweetening with a weak alkaline stream where chemical absorbents are reaction with the acid compounds.
Chemical absorbents as DEA, MEA and MDEA are commonly used in gas sweetening processes, where absorption columns are used to remove acid components in a natural gas stream.

In this project amines will be used in an absorption column for a sweetening process. To investigate the process, simulations in Aspen HYSYS can be performed, to evaluate the flow of the given amine, the flow of the water and the efficiency of each of the amines. This can be supported by manual performed calculations.

This leads to the following problem statement:

“Which of the following amines is the most efficient for gas sweetening on an off shore plant? And which one is the most attractive to use from an economic perspective”

The following topics will is interesting to evaluate:

- How efficient is MEA, DEA and MDEA in the gas sweetening process?
- What flow is needed for the given amine?
- Which one is the most attractive from an economic perspective?
- How is the concentration of the acid compounds decreased over time in the absorption column?

The investigation will be supported by manual calculations when relevant.

5.0 Background for the simulation

The aim for this project is to investigate the cleaning process for H_2S removal in natural gas. Absorption processes has been the focus, since it is recommended method in literature. [33]
Many types of compounds for gas sweetening are used. Most commonly used is the group of different amines, which has been selected for the modelling. Gas sweetening using MEA, DEA and MDEA is there for investigated in HYSYS and compared to calculations manually.
During both modelling in HYSYS and calculations, the efficiency of the three amines is investigated, and evaluated in the efficiency of the cleaning, the consumption during the process and the possibility of reusing amines for further gas treatment.
To set up the cases, some parameters have to be established. These are elaborated below.

Content of H_2S in the sweetened gas: The legislation is describing a maximum content of H_2S in natural gas at 4ppm.

Content of H_2S in the untreated gas: Literature was investigated, to get an idea of how the composition of natural gas is. The content of H_2S is usually 1-3 mole%. The purpose of this project is to model H_2S removal and for that reason the content of H_2S is chosen to be 3 %. [33]

Content of CO_2 in the untreated gas: To model a realistic gas sweetening process, which purpose is to remove CO_2 and H_2S in a natural gas stream, a certain content of CO_2 has to be present. If not, the use of the sweetening agent will be unnatural low and cannot be evaluated on its efficiency or flow.
The normal content of CO_2 in untreated natural gas is 4-5 mole%. Therefore the content of CO_2 in the gas stream is established as 4 %.

Water is added to the amine solutions. This is done to ensure a bigger surface of the liquid phase. When a gas stream is added to an absorption column with a relative high flow, the corresponding amount of amine is relatively low. If water is not added, it will not be possible to ensure a good contact between gas and liquid, which will cause the sweetening process to be less efficient.
Up to 75 mole% water is normally added when performing gas sweetening. [33] The tendency is confirmed by the amine package in HYSYS that is designed specific for modelling gas absorption, where simulations are unable to run without certain water content in the stream.

The absorption process takes place in a column which is installed with a certain amount of stages. The amount of stages is determined using a mass balance model. The mass balance model is known as McCabe-Thiele, where the concentration of one component can be determined as a function of the flows of the two streams and the concentration of the other component. By using this model the amount of accurate stages is found and literature is investigated as a reference to ensure the determined amount is realistic. [33]

An absorption system in Aspen HYSYS is built to investigate the gas sweetening process.

The two inlet streams are named acid gas and amine-water. The temperature and pressure for the system is investigated in literature, where it is described that the temperature of the amine-water stream should be at least five degrees warmer than the acid gas stream in the absorption column to avoid components of the natural gas to condensate into the liquid amine stream. The operation pressure of an absorption column is usually around 30 bars, which is chosen as the pressure for the absorption column.
The pressure in the rest of the system operates at atmospheric pressure as common on many off shore installations. [33]

5.1 Modelling

To evaluate the efficiency of gas sweetening, several cases will be modelled in HYSYS. The demand for all simulations is that the content of H_2S has to be below the 4 ppm, to match the specifications for the clean gas.

Seven cases will be modelled, to investigate the efficiency of tray and packed columns and to evaluate the thermodynamic models. The three amine types described in theory, respectively MEA, DEA and MDEA will be used.

For six of the cases, the amine packages in HYSYS will be used. This is a package where the gas phase is described with an EoS and the liquid with an activity model. The data for the packages is seen below.

- Liquid: VLE (vapor liquid equilibrium) = Mod Kent Eisenberg
- Vapor: VLE (vapor liquid equilibrium) = PR
- Enthalpy/Entropy = Curve Fit

Kent & Eisenbergs model is correlating the equilibrium solubility of acid gases in the amine solution and the solubility of light hydrocarbons is modelled using Henry constant, which adjusts for the ionic strength effect. The solubility of the heavy hydrocarbons are modelled using a thermodynamic model where the fugacity is determined.
As an EoS, the Peng Robinson model is used by the amine package.

5.2 Specifications for the models

The composition of the gas stream is shown in table 10 below:

Table 10: The composition of the gas stream.

Molar composition	
Methane	0,8433
Ethane	0,0613
Propane	0,0183
i-Butane	0,0063
n-Butane	0,0070
i-Pentane	0,0052
n-Pentane	0,0037
n-Hexane	0,0016
n-Heptane	0,0012
n-Octane	0,0005
n-Nonane	0,0001
n-Decane	0,0000
Water	0,0000
Nitrogen	0,0018
Carbon dioxide	0,0400
Hydrogen sulphide	0,0300

An overall setup for the simulations is shown below in figure 20.

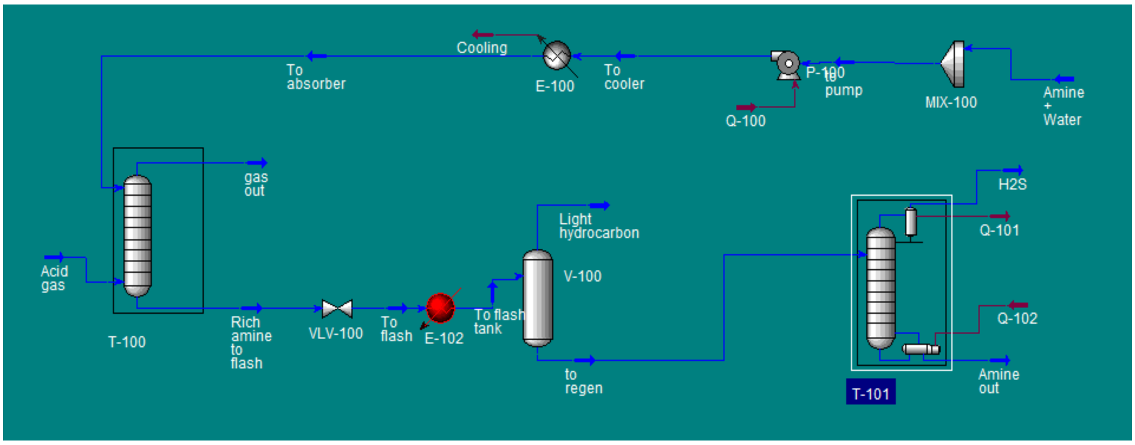


Figure 20: The general setup of the case.

The acid gas is entering the absorber in the bottom, where the amine solution in entering in the top. To illustrate the amine is reused the stream is entering a mixer. In the real world, the regenerated amine from the distillation column will be led to the mixer, where more of the amine solution will be added to ensure the optimal composition for gas sweetening. The pump is raising the pressure from 1 bar to 30 bars that is the operation pressure of the absorber. A heat exchanger is installer to cool the amine solution to the desired operation temperature.

The sweetened gas from the absorber is led to the pipe system and transported on shore and the liquid is led to a flash tank, where the stream is heated with the purpose of flashing out most of the content of hydrocarbons in the stream.
The amine solution is then led to a distillation tower, where the stream is cleaned for H_2S to the same level as the sweetened gas. The recovered amine can then be mixed with water and in theory led to the mixer, where it can be reused for the new sweetening process.

5.3 Description of the cases

Investigation A

Investigation A is consisting of case 1, 2 and 3, where the purpose is to evaluate the flow and amount of the given amine, to be able to compare the sweetening process when using different amines. In the absorber, trays will be used and the setup is given as described above.
The number of stages is determined by calculation using a step wise model and the Kremser model for each of the amines, and then averaged, to use the same number of stages for each amine, to make the only variable the flow. In this way the efficiency of the given amines are investigated. The use of amines is as following:

Case 1: MEA
Case 2: DEA
Case 3: MDEA

Investigation B

Investigation B is consisting of case 4, 5 and 6 and is identical to investigation A, with the difference that a column with a packed material will be used. The use of the amines in the cases is as following.

Case 4: MEA
Case 5: DEA
Case 6: MDEA

Investigation C

To evaluate the importance of a suitable activity model and equation of state, investigation C will be made, to compare the amine package with the PR EoS. Therefore case 1 will be performed using PR as an EoS for both phases in the system instead of using an activity model for the liquid phase. In the end the two simulations will be compared. An overview is presented below:

Case 1: Using the amine package
Case 7: Using the PR EoS

Data for the simulations

Most of the parameters for the cases are identical. These are presented in table 11 below.

Table 11: Parameters for the given cases.

Parameter	Value
Amine stream temperature	40 ºC
Gas stream temperature	35 ºC
Operating pressure	30 bar
Total gas flow	7471 kmol/h

To evaluate the flow in the simulation models, the strategy has been to minimize the use of the given amine, since it is expensive compared to water.
To avoid unrealistic results, the maximum flow of water is determined to be 30.000 kmol/hour. The flow and composition is then determined as the minimum amount of amine that gives a satisfactory cleaning of the acid gas and matches the demands for the flow.
An adjust unit for the absorption column could have been made, where the flow of the liquid amine stream is adjusted automatically in relation to the H_2S content in the sweetened gas. But when it is desired to adjust both the flow of water and the amine, this is not possible, since it will produce one equation with two unknowns.

This project does not only concern the cleaning aspect of the process, but also the economic aspects. Therefore the distillation unit is installed, to evaluate the reuse of each of the amines.
It has not possible to find the demands for removing the acid components from the amine stream in literature. Therefore it was decided to remove H_2S from the liquid stream to the same level as in the absorption column, which is 4 ppm. Then the amine solution has to be considered cleaned for H_2S.
As this simulation is performed in steady state, the regenerated stream exiting the bottom of the distillation column is not leaded back into the absorber through the mixer. This procedure makes it possible to evaluate the percentage of reuse for the amine.
After the absorption column a flash tank is installed for the purpose of flashing out the light hydrocarbons that have been transferred to the liquid phase in the absorption column. As this project do not concern environmental aspects, the loss of the light hydrocarbons exiting the top of the tank is not evaluated. It is assumed that the hydrocarbons will be collected and reused as the installations on the platforms allow it.

Equipment as pumps, valves, heating and cooling units are also installed in the simulation to establish conditions that are similar to real installations.

When the general setup is established, the investigation of the cases can be performed. Investigation A and B are similar to each other, with the difference that investigation A is performed with sieves where investigation B is performed with a packed column. In principle there is no difference between these two structures, because packed columns is evaluated with theoretical stages, where a column using sieves is defining that one sieve is equal to one stage. This means that the number of stages is equal to each other, and therefore the cleaning of the gas in the two columns will be identical if the only difference is the presence of a packing material. For that reason, the results from investigation B is excluded from the evaluation of the cleaning processes, since these are identically to the results from investigations A

For investigation C, which is an evaluation of the efficiency of the amine package, another fluid packed containing the Peng-Robinson EoS is used. It was not possible to perform the simulation, which probably is due to the PR EoS' poor ability to determine the abilities for the liquid phase, that contains polar compounds, which the PR EoS is poor for predicting abilities and phase splits.
The PR EoS predicts two liquid phases in the absorber, which makes it unable to provide any useable result for the simulation. Due to this, investigation C has been excluded from evaluation of the results.

6.0 Calculations

To support the simulations, certains calculations by hand has to be performed. This is done to establish the number of stages that should be used in Aspen HYSYS. Furthermore stage calculations have been done to compare the results of the simulation by calculations made by hand for the stage processes. In this way the flow of the liqiud amine stream and the composition can be compared by the flow determined in HYSYS.

6.1 Determing the composition by hand calculations.

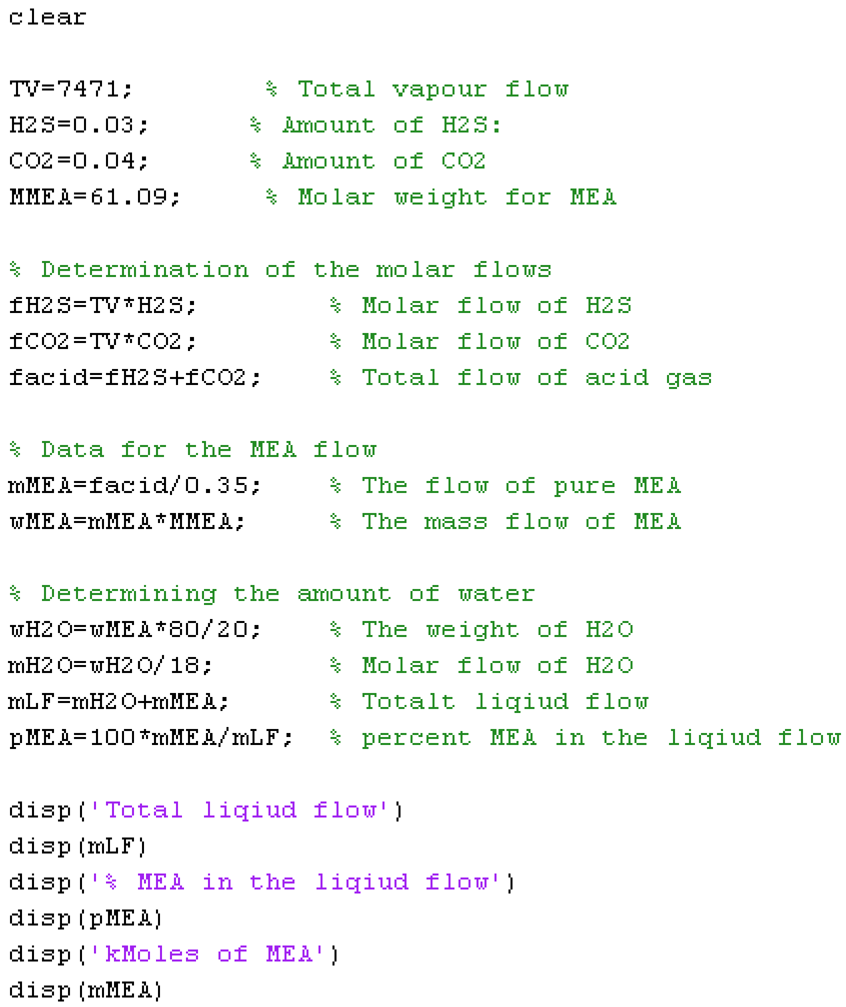
The total gas flow (V=7471), was used to determine the molar flow of respectively H_2S and CO_2 in the gas. To perform the calculations, the ratio between water and the amine has to be known, as well as the ratio between the acid gas and the amine. These values have been found in literature and can be seen below in table 12. [33]

Table 12: The ratio between the amine and water flow and between the acid gas and the amine content. [33]

Amine	Weight % Amine	Mol acid gas/mol Amine
MEA	20	0.35
DEA	30	0.50
MDEA	50	0.4

To determine the composition for the liquid stream, the ratio between the acid gas and the amine was determined. Afterwards the molar mass of the amine was used to determine the amount of water that is defined in weight percent. A script to determine the given values has been performed in Matlab, where then relations can be determined just by changing the composition of the streams.

An example of the script for MEA can be seen below. Data entered in the script is the total molar flow of the vapour phase, the molar fraction of CO_2 and H_2S and the molar weight of the amine used for the sweetening process.



```
clear

TV=7471;         % Total vapour flow
H2S=0.03;       % Amount of H2S:
CO2=0.04;       % Amount of CO2
MMEA=61.09;      % Molar weight for MEA

% Determination of the molar flows
fH2S=TV*H2S;        % Molar flow of H2S
fCO2=TV*CO2;        % Molar flow of CO2
facid=fH2S+fCO2;    % Total flow of acid gas

% Data for the MEA flow
mMEA=facid/0.35;    % The flow of pure MEA
wMEA=mMEA*MMEA;     % The mass flow of MEA

% Determining the amount of water
wH2O=wMEA*80/20;    % The weight of H2O
mH2O=wH2O/18;       % Molar flow of H2O
mLF=mH2O+mMEA;      % Totalt liqiud flow
pMEA=100*mMEA/mLF;  % percent MEA in the liqiud flow

disp('Total liqiud flow')
disp(mLF)
disp('% MEA in the liqiud flow')
disp(pMEA)
disp('kMoles of MEA')
disp(mMEA)
```

The same procedure is followed for DEA and MDEA, and the following data for the flows are obtained.

Total liquid flow (MEA):	$2.1779x10^4$ kmol/h
% in the liquid flow (MEA):	6,861 %
kmoles of (MEA):	$1.4942x10^3$ kmol/h

Total liquid flow (DEA):	$1.5301x10^4$ kmol/h
% in the liquid flow (DEA):	6,836 %
kmoles of (DEA):	$1.0459x10^3$ kmol/h

Total liquid flow (MDEA):	$9.9626x10^3$ kmol/h
% in the liquid flow (MDEA):	13,123 %
Moles of (MDEA):	$1.3074x10^3$ kmol/h

The flow of the different liquid streams was used in the stage model, to determine the number of stages needed for the process. From literature it was determined that absorption columns for sweetening processes normaly has about 20-30 stages. [33]

6.2 Stage calculations

To determine the flows by manually calculations, the stage model is used. The outset for the calculations is the cascade as seen in figure 21.

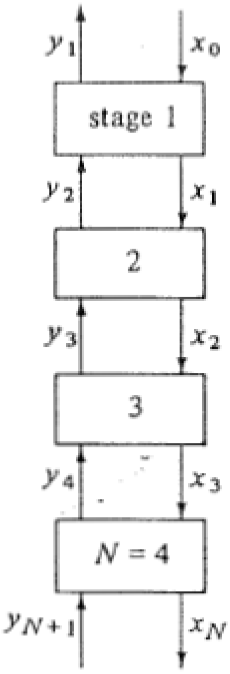


Figure 21: Outset for the stage calculations. [31]

Every step in the cascade is assumed to be in equilibrium. From that knowledge the mass balance can be written as shown below.

$$L \cdot x_0 + V \cdot y_{N+1} = V \cdot y_1 + L \cdot x_N \qquad (32)$$

V= 7471 kmol/h
L= 21779 kmol/h (MEA), 15301 kmol/h (DEA) and 12500 kmol/h (MDEA)

The mole fraction of H_2S in the gas stream entering in the bottom is identic to Y_{N+1} and is 0.03. The content of H_2S in the exit streams is 0.000004, which is identical to y_1.

In the stage model, it is assumed that the molar flows of the liquid stream entering in the top and the gas stream entering in the bottom are constant. Only H_2S is miscible in the two phases. The equilibrium between H_2S in the two phases is then as shown in equation 33.

$$y_i = K \cdot x_i \tag{33}$$

The K-value is the equilibrium constant for the transfer of H_2S from the gas to the liquid phase that is dependent on the temperature and operating conditions. Normally it is assumed constant for manual calculations and can be found in tables. The equilibrium constant for the given amines can be seen below in table 13.

Table 13: The equilibrium constant for each of the amines for the transfer of H_2S from the gas to the liquid phase.

Amine	K
MEA	2,05
DEA	1,45
MDEA	1,25

The relation between the content of H_2S in the inlet stream and the outlet stream is as following.

$$V \cdot y_1 = \left(\frac{0{,}000004}{0{,}03}\right) \cdot V \cdot y_{N+1} \tag{34}$$

By substituting this expression into the H_2S mass balance and solving for X_N the equation will be as illustrated in equation 35 below.

$$x_N = x_0 + \frac{V}{L} \cdot \left(1 - \frac{0{,}000004}{0{,}03}\right) \cdot y_{N+1} \tag{35}$$

X_0=0 and Y_{N+1}=0.03 which reduces the equation to the following.

$$x_N = \frac{V}{L} \cdot \left(1 - \frac{0{,}000004}{0{,}03}\right) \cdot (0{,}03) \tag{36}$$

With all the constants for the system given, the mass balance for each stage in the cascade can be defined as following:

$$L \cdot x_0 + V \cdot y_{n+1} = V \cdot y_1 + L \cdot x_n \tag{37}$$

Solving for Y_{n+1}:

$$y_{n+1} = \frac{L}{V} \cdot x_n + y_1 - \frac{L}{V} \cdot x_0 \tag{38}$$

To determine the number of stages needed and the concentration of H_2S in each stage, a serial of calculations is performed. The first stage where the value for y is above 0.03 is defined as the last stage in the column. The value for x in that stage is used as a reference, and it has to be close to the determined x_N.

Because of equilibrium conditions, the expression for y_1 can be reduced to the following:

$$y_1 = Kx_1 \tag{39}$$

The following values of y can be defined as a function of y_1.

$$y_2 = (A + 1)y_1 \tag{40}$$

$$y_3 = (A^2 + A + 1)y_1 \tag{41}$$

For determining $y_{4,}$ A^3 is added, and for each values of y, A in the power of the number minus one is added to the expression. A is called the absorption factor and is defined as:

$$A = \frac{L}{V \cdot K} \tag{42}$$

From the determined equilibrium relationship and the values for y, the corresponding values for x can be determined are illustrated below.

$$x_n = \frac{y_n}{K} \tag{43}$$

The calculations have been performed in excel and the results is shown below in table 14. Detailed information about the composition in each step can be seen in appendix 1. For the calculations, the flows determined in Matlab are used. The X_n – determined is the values calculated for the given step and the X_N reference is the one found by using the already known value for y_{N+1} that is 0.03. This is identic to the inlet concentration of H_2S in the gas stream.

Table 14: The determined values for the stage calculations.

Parameter	MEA	DEA	MDEA
X_n - determined	0,0151937	0,026581	0,024785
X_N - reference	0,010289734	0,014646109	0,017928009
y_n - determined	0,031147	0,038542	0,0309812
Y_n reference	0,03	0,03	0,03
Number of stages	23	24	27*

* When using the determined flow for MDEA, the number of stages provided by the stage method is 83. This is unrealistic, which lead to adjusting the liquid flow by adding water until a total liquid flow at 12.500 kmol/h is reached. This provides an acceptable number of stages for MDEA (27), where a realistic number according to literature is between 20 and 30. [33]

6.3 Using the Kremser Equation

The Kremser equation is used for a quick estimation of the number of stages in an absorption process. There is no need for evaluation of the equilibrium conditions in each step, but instead an evaluation of the flow in and out of the absorber and the desired concentrations.
The Kremser equation is shown below in equation 44.

$$N = \frac{ln\left[\frac{Y_{N+1}-K\cdot X_0}{Y_1-K\cdot X_0}\cdot\left(1-\frac{1}{A}\right)+\frac{1}{A}\right]}{ln(A)} \qquad (44)$$

All compositions in the equation are known, since it is the content of H_2S in the inlet and outlet of the gas stream and the content in the inlet of the liquid stream. A is defined like below:

$$A = \sqrt{A_1 \cdot A_N} \qquad (45)$$

A_1 and A_N is determined as shown below.

$$A_1 = \frac{L}{K\cdot V_1} \quad \text{(Stage 1 conditions)} \qquad (46)$$

$$A_N = \frac{L_N}{K\cdot V} \quad \text{(End stage conditions)} \qquad (47)$$

When using the Kremser equation, it is assumed that the only compound transferring from one phase to another is H_2S. The L_N is the liquid flow added the flow of the transferred H_2S. Opposite is V_1 the gas flow minus the transferred amount of H_2S. The needed parameters and the results of the calculations is shown below in table 15.

Table 15: The parameters and results of the Kremser equation.

Parameter	**MEA**	**DEA**	**MDEA**
L [kmol/h]	21779	15301	12500
L_N [kmol/h]	22003,13	15525,13	12724,13
V [kmol/h]	7471	7471	7471
V_1 [kmol/h]	7246,87	7246,87	7246,87
A_1	1,465999	1,456134	1,379906
A_N	1,481085	1,477463	1,404648
A	1,473523	1,46676	1,392222
N	20,08928	20,305	23,13734

As seen in the table above, the Kremser equation is providing less numbers of stages compared to the equilibrium stage model. The equilibrium stage model is usually predicting better results, where Kremser is the quick method to get a rough estimate for further calculations.

6.4 Stages in HYSYS

The equilibrium stage model and Kremser has been used to determine the number of stages. The equilibrium stage model provided between 23 and 27 stages for the absorber while the Kremser equation provide results between 20 and 23 stages. To model in HYSYS 25 stages is chosen for all of the simulations. When choosing the same number of stages, the only variable is the flow of the liquid stream and the composition of it. This makes it possible to compare the flows and evaluate the efficiency and the costs for the process.

The strategy described when introducing the simulation is used when working with HYSYS.

7.0 The results

The results from the simulation in HYSYS are shown below in table 16. The results are compared to the results from manual calculations.

Table 16: Results from HYSYS and calculations.

	MEA calc.	MEA HYSYS	DEA calc.	DEA HYSYS	MDEA calc.	MDEA HYSYS
Total liquid flow [kmol/h]	21779	29610	15301	14265	9963***	25100*
Total amine flow [kmol/h]	1494	610	1046	765	1307	3100*
Composition [% Amine]	6,86	2,06	6,84	5,36	13,12	12,35*
Price [dkkr/ton]	8704	8704	7616	7616	13600	13600
Cost [dkkr/h]	794.414	324.354	837.608	694.255	2.118.064	5.023.786
Reuse [%]	-	99,99**	-	99,99**	-	99,99**

*Absorption using MDEA is done at a temperature at 70 °C to raise the efficiency of MDEA and the need of catalyzing the process to minimize the flow.
** Using HYSYS gives a high regeneration percent for the amine. Several sources are documentation a realistic reuse percent around 80 % for most types of amine, which is evaluated more realistic.
*** This flow is adjusted to be 12500 in the calculations of number of stages for MDEA

As seen in the table, HYSYS demands a higher flow for MEA while the flow for DEA is lower compared to manual calculations. For MDEA the flow is higher as well.
It is not possible to perform a decent simulation for MDEA without raising the temperature, and the flow will have to be unrealistic high to perform the needed sweetening of the gas.
In literature, it is documentated, the MDEA not always provide the needed cleaning of the gas, but it is still used due to it being untoxic compared to the other amines.
When the prices for one hour is evaluated, MDEA is expensive compared to the other amines. According to manually calculations the price for MEA and DEA is higher compared to the prices related to the flow determined by HYSYS. For MDEA HYSYS is providing the most expensive process.

7.1 McCabe-Thiele diagrams for the absorption process

The theory of McCabe Thiele is a key to understanding stage processes. It is related to the equilibrium stage method, where the results can be used to construct McCabe Thiele diagrams for the three different amines.

In figure 22 a McCabe Thiele diagram for the absorption process with MEA is shown. The composition of the two streams in each stage can be followed with respect to H_2S.

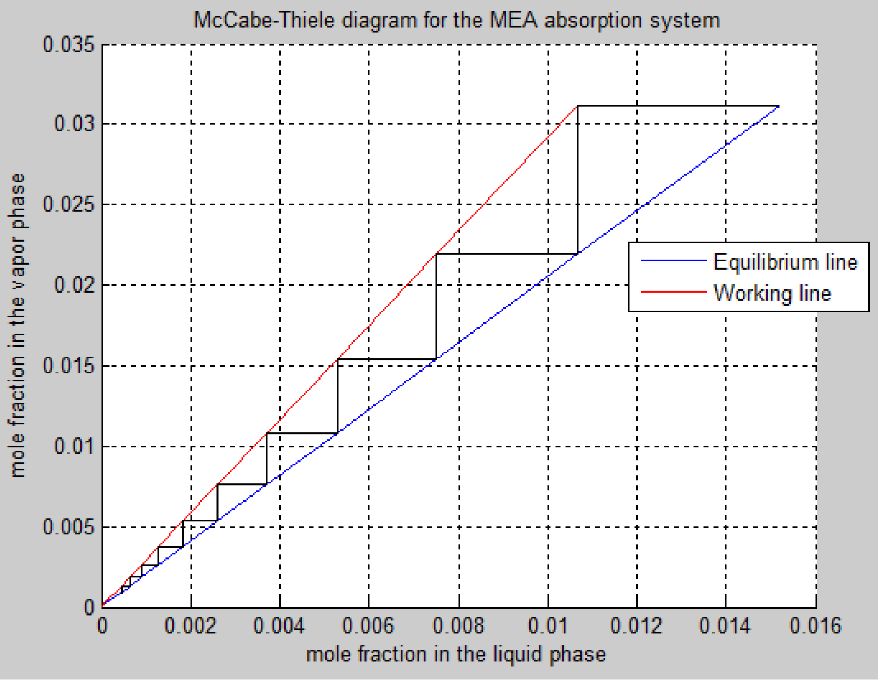


Figure 22: McCabe Thiele diagram for the absorption using MEA.

In figure 23 the McCabe Thiele diagram for absorption with DEA and the composition with respect to H_2S in the given stages can be seen.

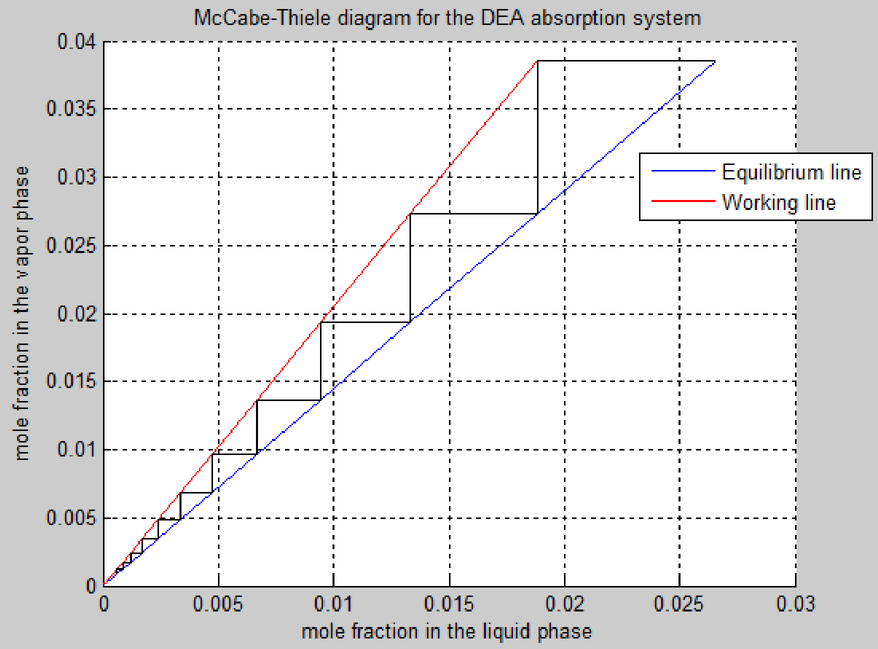


Figure 23: McCabe Thiele diagram for the absorption using DEA.

In figure 24 the McCabe Thiele diagram for absorption with MDEA and the composition of the streams with respect to H_2S can be seen.

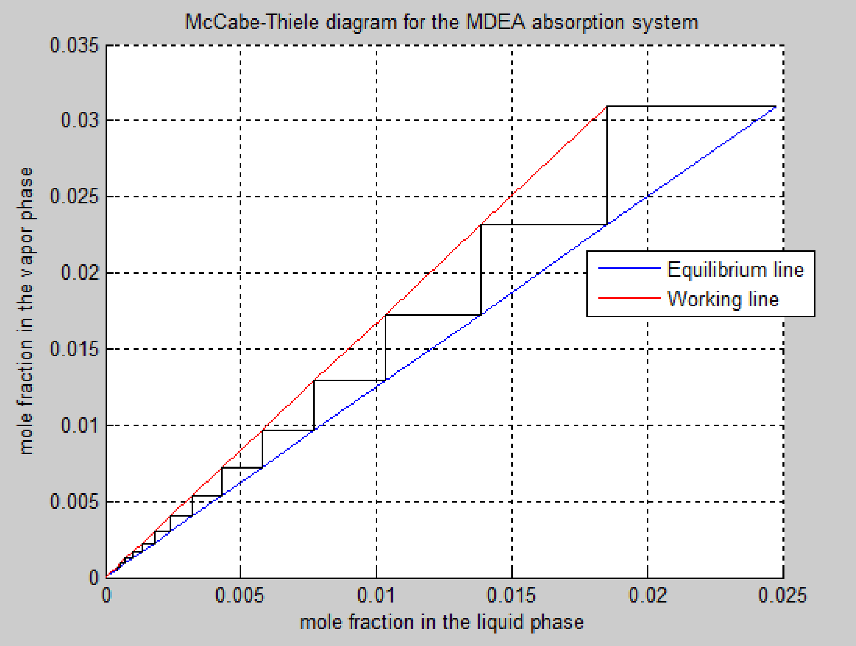


Figure 24: McCabe Thiele diagram for absorption with MDEA.

In figure 25 the McCabe Thiele diagram for the three absorption processes is compared. It has to be noticed that the equilibrium line for MEA is overlapping the working line for DEA. It can be seen that the three systems lines vary for the three types of amines. The lines for MEA have the biggest slope, which led to the conclusion that it needs the fewest steps. The lines DEA has a bigger slope than the lines for MDEA, which illustrates that DEA needs less stage than MDEA to provide a sufficient cleaning of the gas.

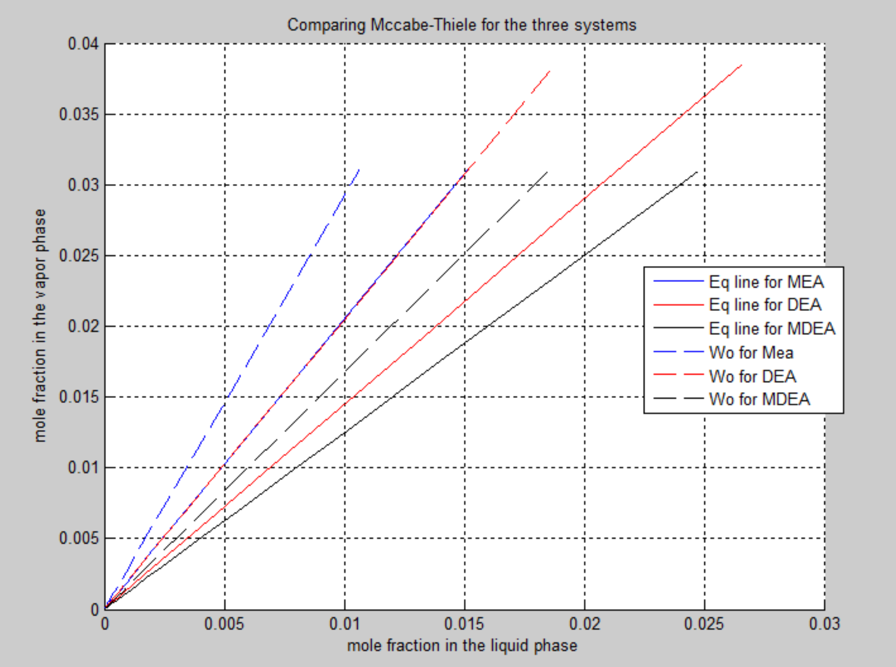


Figure 25: Comparing the McCabe Thiele diagrams for the three systems.

7.2 The development in concentration

In figure 26 the composition of the two acid components, H_2S and CO_2, is shown as a function of the stages for the absorption process with MEA in HYSYS.
In the top, where the liquid is entering, the concentrations of the two components in both phases are low. In the bottom, where the gas is entering, the concentration of the components are high, due to the high concentration in the gas, which will cause the liquid to absorb more of the acid components

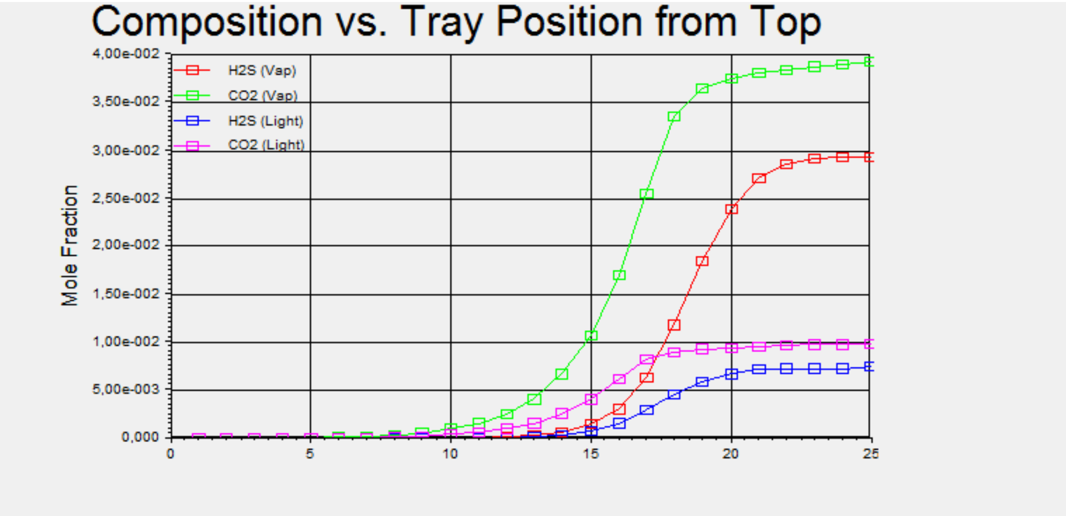


Figure 26: Composition vs. stage number when using MEA.

In figure 27 the same development can be seen for the absorption process using DEA. Compared to the absorption with MEA, the content of CO_2 and H_2S is decreasing much faster. Related to theory, where DEA is described as more efficient than MEA, this makes good sense.

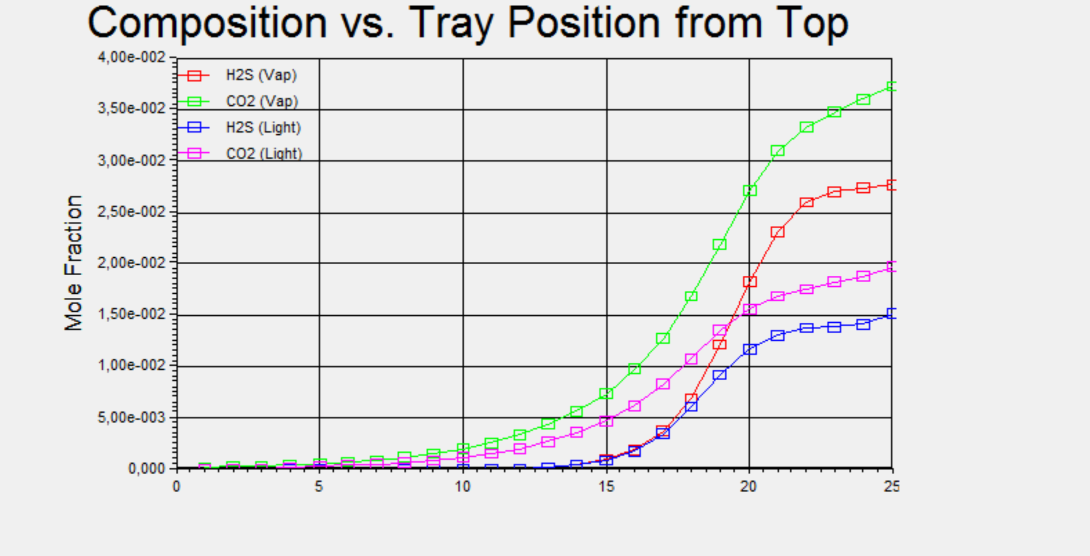


Figure 27: Composition vs. stage number when using DEA.

In figure 28 the development when using MDEA is shown. It seems that MDEA is efficient when reducing the content of H_2S in the gas stream, but not when removing CO_2. The CO_2 content is decreasing really slowly, and it is not reduced to the same level as in the other absorptions, even when the flow is relatively high.

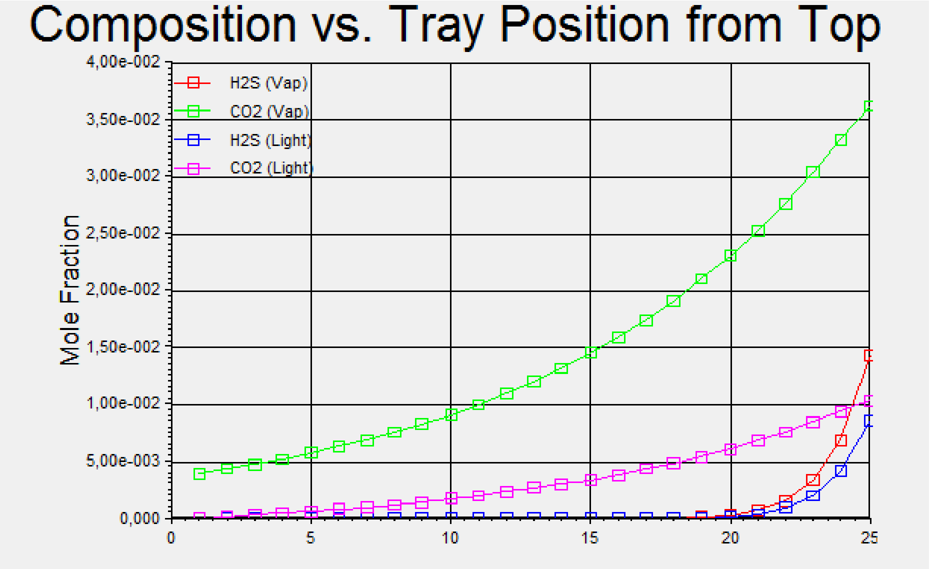


Figure 28: Composition vs. stage number when using MDEA.

7.3 Evaluation of the equilibrium constant

Related to the absorption is the equilibrium constant, K. A high constant provides a fast transfer, while a low constant provides a slow transfer.
In the manual calculations, the constant is assumed to be independent of the temperature and composition, even though theory describes it as being dependent.
HYSYS provides the option of following the development of K on each stage, which can be used to evaluate the consequences of deciding K being independent of changes in the system in the manual calculations.

In figure 29 below K is pictured as a function of the stage number for the two acid components in the absorption process using MEA. It can be seen that K is around four in the bottom where the acid gas is entering the absorption column. After stage 20 it starts to decrease, and it is around zero for the first 15 stages.
The value for K found in literature is 2.05 for acid gasses which is an estimate in the middle of the area for K in the process. It illustrates the weakness of using K as an independent constant, since it will provide more accurate results accepting it is varying. This will complicate the model a lot when manually doing the calculations, which is why it is accepted as being the same no matter the conditions of the system.

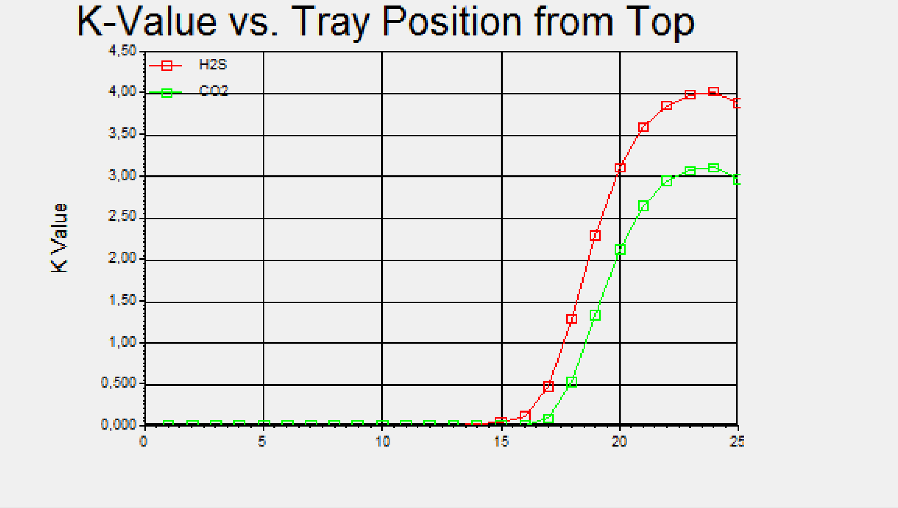


Figure 29: K-values as a function of stage number using MEA.

In figure 30 the development of K in the absorption process using DEA can be seen.
In the bottom K is around two, while it is rising at the low concentrations of the acid components in the top of the absorber. For most of the stages K is between one and two, which makes the values found in literature on 1.45 for acid gasses a good estimate for this area.
In the top of the absorber, the value for K is higher, but the impact of this is low due to the low concentrations of the acid components in the top.
Compared to the development for MEA, K is developing the opposite for DEA. When using MEA, K is decreasing in the top of the absorber, where it is increasing when using DEA.

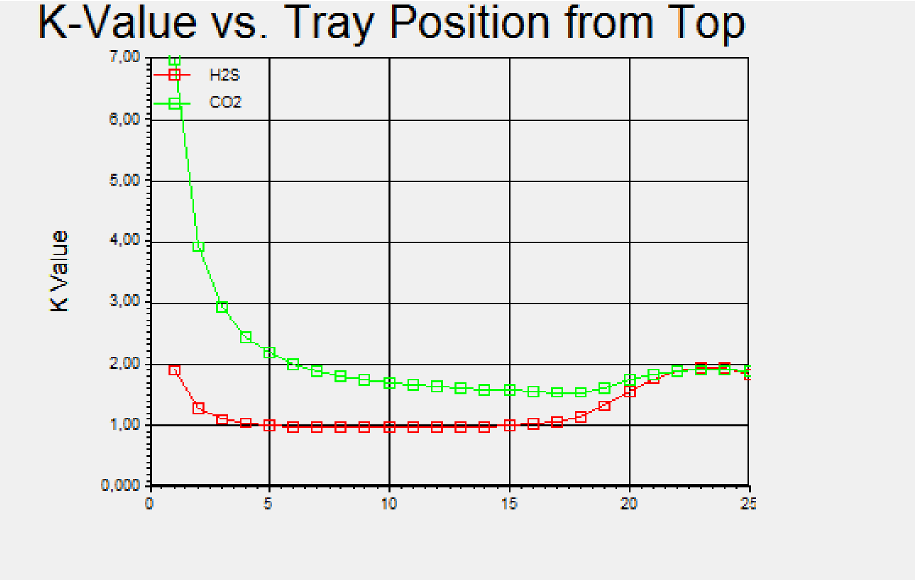


Figure 30: K-values as a function of stage number using DEA.

In figure 31 the development of K in the process using MDEA is shown. For H_2S, K is almost constant, but not for CO_2, where it is rising a lot in the top of the absorber.
In literature, the estimate for acid gasses is 1.5 which seems like a fair estimate for H_2S. For CO_2 is does not seem like a good estimate at all, since the value is higher in all the stages.

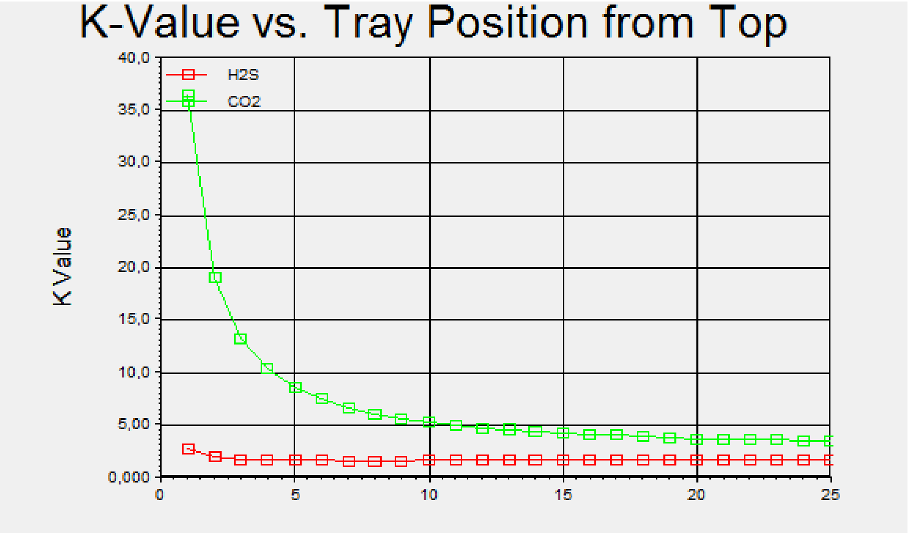


Figure 31: K-values as a function of tray number for the process using MDEA.

8.0 Reuse and cost

In the simulation in HYSYS a distillation column is installed with the purpose of evaluating the percentage of reuse for the amine, since it will be reused in reality. When installing the distillation column and defining that the content of H_2S in the regenerated amine has to be 4 ppm, it shows that 99,99 % of the amine content can be reused.

It has not been possible in literature to determine the H_2S content in the recovered amine, which is why the demand has been determined to be 4 ppm with the argument if it is good enough for the sweetened gas, it is good enough for the amine.
In literature it is described that it is possible to reuse around 80 % of the amine, depending on composition and which amine is used. [33]

It is not possible to compare the recovery process for the three performed cases regarding the use of amines, when no difference is provided in the reuse process. Therefore the most realistic economic evaluation will be the cost pr. hour as shown above.
If assumed that 80 % can be recovered, the cost per following hour can be determined. This is shown in table 17 below. The evaluation is only performed on the cases simulated in HYSYS.

Table 17: The cost for the first hour and the following ones.

Parameter	MEA	DEA	MDEA
Cost for the first hour [dkkr]	324.354	694.255	5.023.786
Cost pr. following hour assuming 80% reuse [dkkr]	64.871	138.851	1.224.757

This investigation has been performed with the same number of stages to be able to evaluate the efficiency of the given amines. Therefore an optimization for each amine has not been performed, since the purpose of the project has been to compare the different types of amines.

When designing equipment for off shore, several parameters have to be evaluated. The price for acquisition, design and installations is dependent and a variety of factors. One of the key parameters is the material for the absorber. Some off shore installations is performed in concrete and some in steel. The material also depends on the type of plant, e.g. if it is a permanent installation or a drilling rig. It is impossible to make evaluation of materials and abrasion without specific information about installation type and area. No standards for design are used on the current installations off shore, which means that no standard design can be applied. This means that a huge part of the costs for installation is design and installation. The price also depends in which part of the world the installation is meant for, since there is different legislation in different areas. Therefore no price example has been made for installation of a column off shore. [34]

9.0 Discussion

Simulations in HYSYS have been performed to investigate the gas sweetening process and determine which amine of the three investigated that is the most efficient. The results are compared to manually performed calculations to evaluate the results.

Using the stage model based on the McCabe-Thiele method, it is determined that the stages needed for the three amines MEA, DEA and MDEA is respectively 23, 24 and 27. The 27 stages for MDEA is determined with a flow adjusted compared to the factors founds in literature. If not adjusted, the number of stages would be 83, which is unrealistic high compared to the normal amount that is between 20 and 30 stages.
The equilibrium constant, K, is assumed constant for the stage calculations and not dependent on the temperature or concentrations.
The stages needed are determined by the Kremser equation as well, that is a formula used for a quick and rough estimate of the number of stages needed for an absorption process. Similar to the stage model, the equilibrium constant is assumed to be constant and not dependent on concentrations or temperature. Opposite the stage model, where the flow is considered constant throughout the absorption column, the Kremser equation is taking into consideration that a mass transfer of H_2S from the gas phase to the liquid phase is occurring.
The number of stages determined by the Kremser equation is 20, 20 and 23 for the given amines.

When the equilibrium constant found in literature is compared to the development of the equilibrium constant in HYSYS, it is obvious that it is a mistake to consider K as a constant no matter the concentrations in the system. For all three of the amines, K is developing as a function of the composition of the two streams in the given phase.
For MEA the values for K for both CO_2 and H_2S are high in the bottom and low in the top of the absorption column. The tendency is opposite for DEA.
For MDEA the equilibrium constant is almost constant for H_2S no matter the concentration, and it is the only component where it is acceptable to assume K as a constant. For CO_2 the values for K are raising a lot at low concentrations. Due to the low concentrations, the impact of this is low, but it is demonstrating the weakness of models for manually evaluation of absorption models.
From the development of K it can be assumed, that it is important to support manual performed calculations with other models, to ensure correct results that is taking into consideration that K is not a constant.
The manually performed calculations were used for a rough estimate for determining the number of stages in HYSYS, where 25 stages were chosen.

When performing the simulations in HYSYS, the flow of MDEA had to be raised a lot, to make the simulation run. The concentration of H_2S was reaching the desired level with a relatively low flow, but the concentration of CO_2 remained high. Therefore the flow of both water and the amine had to be adjusted to a higher level than expected, to ensure an efficient sweetening of the gas. A limit for the water flow was defined at 30.000 kmol/h, since a higher flow is unrealistic in off shore installations. This conclusion was confirmed when looking into literature.

If the development of the acid components from the HYSYS simulation is observed, it can be seen that MEA is reducing the containment of both CO_2 and H_2S. It was observed in the simulation that when the content of H_2S was at 4 ppm, the content of CO_2 was at an acceptable level as well, and no further amount of the amine or water has to be added. The same tendency was shown for DEA, where the content of the acid components is reduced faster than for MEA, even though the flow of DEA is lower.

When observing the development of the acid compounds when sweetening with MDEA, it is seen that the content of H_2S is reduced fast. Then content of CO_2 was not reduced to an acceptable level, and it was necessary to add further of MDEA and water to perform an acceptable sweetening of the gas.
Even at the limit decided for the flow, the content of CO_2 was not reduced to the level as in the simulation with MEA and DEA.
This shows what was described in literature, that MDEA does not always perform an efficient sweetening in the gas.

In literature MEA is described as the cheapest of the amines while DEA is described as the most efficient of the amines. This was confirmed by the manual performed calculations.
When simulating in HYSYS, it seems necessary to use more DEA than MEA, which is opposite what is described in literature.
There is no valid explanation to this, since all experiences in industry are supporting the fact that DEA is the most efficient. In general the student is evaluating the calculations in HYSYS as the most reliable ones, since the amine package has been developed for the purpose of gas sweetening, and many process engineers are trusting this package.
The water flow in the streams is lower for DEA than for MEA, which is the same tendency as shown in manually performed calculations.

In the simulations performed in HYSYS, a distillation column was installed to evaluate the opportunities of reusing the given amine. In literature the reuse percentage described is around 80 % depending on the type of amine.
A spec for the column where the acceptable concentration of H_2S is set to be 4 ppm has been made. The temperature of the column, the pressure and the number of stages are all in the range described in literature, but the reuse percent is much higher than anyone has described as obtainable. The student cannon provide any reasonable explanation for this, other than HYSYS somehow is not defined with all factors that are relevant in real systems.
It was desired to evaluate the price for using each of the amines, to be able to recommend the best one form both an efficient point of view but also from an economic point of view. Since waste cannot be evaluated, this is not possible.

10.0 Conclusion

During this project the gas sweetening process using three different amines, MEA, DEA and MDEA, have been investigated in HYSYS and by manually performed calculations.

Seven cases have been defined in HYSYS to investigate different parameters of the sweetening process.
When simulating a packed column in HYSYS, the simulation is made with theoretical stages, where one theoretical stage is identical to one stage in a tray column. Due to this, simulation with a packed column provides the same results at simulations with a tray column
Doing the simulation with the PR EoS instead of the amine package to evaluate the efficiency of the amine package provided no usefull result, since PR predicts two liquid phases in the absorber, and is unable to solve every stage due to that. The same happens in the distillation column.

The manually performed calculations predicted fewer stages in the process than the simulation in HYSYS. This is due to the manually calculations being performed without paying attention to the influence off temperature, pressure or concentration gradients when evaluating the equilibrium constant. This is a mistake that have been documented by investigating the equilibrium constant and its development in HYSYS.

The manually calculations is supporting the theory and identifies DEA as the most efficient of the amines. DEA demands the lowest flow of both the amine and the water to perform a satisfying gas sweetening.
MEA is providing a satisfying sweetening as well, when evaluating the manually performed calculations. There is a need for a higher flow, but since MEA is a lot cheaper, sweetening with MEA will be the cheapest process.
MDEA is documented inefficient and expensive by the manually performed calculations, and sweetening with this agent is only recommended from an environmental perspective.

Evaluating the sweetening process in HYSYS shows that MEA is the most efficient of the chosen amines. This is conflicting with what is documented in literature, and the student believes that this is due to the thermodynamic models in HYSYS. HYSYS is evaluated as the most trustworthy of the used methods in general, but since it have been documented in literature that DEA is the most efficient, the opinion of the student is that the manually performed calculations is the correct ones regarding DEA.

In general, the student recommends gas sweetening with MEA or DEA. It is believed that the most efficient is DEA and the cheapest is MEA.

11.0 Reference List:

Source	Type	Description
1	Book	Fundamentals of Petroleum Refining Mohamed A. Fahim, Taher A. Al-Sahhaf, Amal Elkilani, first edition (2010) Elsevier ISBN:978-0-444-52785-1
2	Book	Petroleum and natural gas Handbook Standard handbook of petroleum and natural gas engineering William C. Lyons, Ph.D., P.E., volume 2, (1996) Gulf Professional Publishing ISBN 0-88415-643-5
3	Book	Production chemicals for the oil and gas industry (kap.15) Malcolm A. Kelland (2009) CRC press ISBN 978-1-4200-9290-5
4	Webpage	http://www.safetydirectory.com/hazardous_substances/hydrogen_sulfide/fact_sheet.htm Title: H2S Safety Factsheet
5	Report/ publication	API RECOMMENDED PRACTICE 49, Recommended Practice for Drilling and Well Servicing Operations Involving Hydrogen Sulfide
6	Book	Handbook of natural gas transmission and processing Saeid Mokhatab, William A. Poe & James G. Speight (2006) Gulf Professional Publishing is an imprint of Elsevier ISBN 13: 978–0–7506–7776–9
7	Book	Conjugate Heat and Mass Transfer in Heat Mass Exchanger Ducts Li-Zhi Zhang, first edition (2014) Elsevier ISBN:978-0-12-407782-9
8	Webpage	http://www.scribd.com/doc/93197549/Designing-of-Absorbers
9	Webpage	http://www.indiamart.com/composite-tanks-vessels/frp-scrubbing-system.html
10	Book	Safe Design and Operation of Process Vents and Emission Control Systems A John Wiley & SONS (2006) ISBN: 978-0-471-79296-3
11	Publication	http://www.igu.org/html/wgc2009/papers/docs/wgcFinal00145.pdf Title: Sweetening technologies – a look at the whole picture.
12	Book	Surface Production Operations, Design of Gas-Handling Systems and Facilities Ken Arnold & Maurice Steward, Volume 2 (1999) Elsevier ISBN 0-88415-822-5

13	Webpage	http://www.scielo.br/scielo.php?script=sci_arttext&pid=S0104-66322009000100004
14	Publication	http://www.auburn.edu/~deruija/pda1_amines.pdf Title: Amines and quaternary ammonium compounds.
15	Publication	http://waset.org/publications/15675/removal-of-co2-and-h2s-using-aqueous-alkanolamine-solusions Title: Removal of CO2 and H2S using Aqueous Alkanolamine Solutions
16	Book	Gas and liquid sweetening DR. R.N. Maddox, Second edition (1997) Campbell Petroleum Series
17	Book	Gas Purification Arthur L Kohl,& Richard Nielsen, Fifth edition (1997) Gulf Publishing Company ISBN 0-88415-220-0
18	Book	Principles of mass transfer and separation processes Binay K. Dutta, third edition (2009) Asoke K. Ghosh ISBN-978-51-203-2990-4
19	Book	Separation Process Principles Chemical and Biochemical Operations, Third edition (2011) J. D. Seader, Ernest J. Henley & D. Keith Roper JohnWiley & Sons ISBN 978-0-470-48183-7
20	Book	Perry’s Chemical Engineers’ Handbook Robert H. Perry & Don W. Green, Seventh edition (1997) The McGraw-Hill Companies ISBN 0-07-049841-5
21	Webpage	http://www.hyper-tvt.ethz.ch/fundamentals-masstransfer-filmodel.php
22	Book	Mass Transfer Operations for the Practicing Engineer Louis Theodore Francesco Ricci (2010) Published by John Wiley & Sons, Inc., Hoboken, New Jersey ISBN 978-0-470-57758-5
23	Book	Kemiske enhedsoperationer Karsten H. Clement, Peder Fangel, Anker Degn Jensen og Kaj Thomsen, 5.udgave, 1.oplag. (2004) Polyteknisk Forlag ISBN 87-502-0941-8
24	Book	Cost-Benefit Analysis, Concepts and Practice Anthony E. Boardman, David H. Greenberg, Aidan R. Vining and David L. Weimer (2006) Pearson Prentice Hall ISBN 0-13-143583-3
25	Publication	Control of gaseous emissions APTI Course 415, Third edition John R. Rich Ards PH.D PE (2000)

26	Publication	Principle of drug action 1, (2005) Amines and quaternary ammonium compounds
27	Book	Organic Chemistry 9. edition Solomon and Fryhle ISBN: 9780471684961
28	Article	Reaction Mechanism and Kinetics of Aqueous Solutions of Primary and Secondary Alkanolamines and Carbon Dioxide Olgac BAVBEK, Erdogan ALPER (1999)
29	Article	Experimental and theoretical study of pool boiling heat transfer to amine solutions S. M. Peyghambarzadeh1, M. Jamialahmadi, S. A. Alavi Fazel and S. Azizi (2009)
30	Webpage	http://cuo2.kkft.bme.hu/packed.pdf
31	Book	Transport processes and unit operations third edition Christie J. Geankoplis, 1993 Prentice-Hall International, Inc. ISBN: 978-0139304392
32	Article	Absorption Design Calculation BGHiggins/UCDavis/Feb2_ 08
33	Book	Oilfield Processing of Petroleum: Natural gas, Volume 1, By Francis S. Manning, Richard E. Thompson Pennwell Books ISBN:0-87814-343-2
34	Personal Contact	MGH Consult – consulting engineering

12.0 Appendix 1

Composition for MEA

Stage	x_n	y_n
1	1,951E-06	0,000004
2	4,726E-06	9,69E-06
3	8,672E-06	1,78E-05
4	1,428E-05	2,93E-05
5	2,226E-05	4,56E-05
6	3,361E-05	6,89E-05
7	4,974E-05	0,000102
8	7,268E-05	0,000149
9	0,0001053	0,000216
10	0,0001517	0,000311
11	0,0002177	0,000446
12	0,0003115	0,000639
13	0,0004449	0,000912
14	0,0006346	0,001301
15	0,0009044	0,001854
16	0,001288	0,00264
17	0,0018335	0,003759
18	0,0026092	0,005349
19	0,0037122	0,00761
20	0,0052808	0,010826
21	0,0075114	0,015398
22	0,0106833	0,021901
23	0,0151937	0,031147

Composition for DEA

Stage	x_n	y_n
1	2,76E-06	0,000004
2	6,66E-06	9,65E-06
3	1,22E-05	1,76E-05
4	1,99E-05	2,89E-05
5	3,09E-05	4,48E-05
6	4,64E-05	6,73E-05
7	6,83E-05	9,91E-05
8	9,93E-05	0,000144
9	0,000143	0,000207
10	0,000205	0,000297
11	0,000292	0,000423
12	0,000415	0,000602
13	0,000589	0,000854
14	0,000835	0,00121

15	0,001182	0,001713
16	0,001672	0,002424
17	0,002364	0,003428
18	0,003342	0,004845
19	0,004723	0,006848
20	0,006673	0,009676
21	0,009429	0,013671
22	0,01332	0,019314
23	0,018817	0,027284
24	0,026581	0,038542

Composition for MDEA

Stage	x_n	y_n
1	3,2E-06	0,000004
2	7,48E-06	9,354E-06
3	1,32E-05	1,652E-05
4	2,09E-05	2,611E-05
5	3,12E-05	3,895E-05
6	4,49E-05	5,614E-05
7	6,33E-05	7,914E-05
8	8,79E-05	0,0001099
9	0,000121	0,0001511
10	0,000165	0,0002063
11	0,000224	0,0002801
12	0,000303	0,000379
13	0,000409	0,0005113
14	0,000551	0,0006883
15	0,00074	0,0009253
16	0,000994	0,0012426
17	0,001334	0,0016672
18	0,001788	0,0022355
19	0,002397	0,0029963
20	0,003212	0,0040146
21	0,004302	0,0053775
22	0,005762	0,0072019
23	0,007715	0,0096438
24	0,01033	0,0129123
25	0,01383	0,0172872
26	0,018514	0,0231431
27	0,024785	0,0309812