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Optimization of Operating Parameters in CO_2 Removal Unit (Rhourd Ennous field)

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Dedication

I present this work to myself foremost, to the fatigue of the years, my diligence,
and my tries to overcome obstacles that were not easy.

I also give it to the people who believed in me and loved me unconditionally.

At last, I was not making any move without God's blessing and satisfaction.

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list of abbreviations

CPF	Central process Facilities
LNG	liquified natural gas
GPM:	gallons per minute
CNG:	compressed natural gas
MMBTU:	one million British thermal units
N_{ox}:	nitrogen oxides
PSI:	pound per square inch
PFD:	Process Flow Diagrams
H_2CO_3 :	carbonic acid
H_2O :	water
MEA:	Monoethanolamine
DEA:	Diethanolamine
MDEA:	Methyldiethanolamine
TEG:	Triethylene glycol
HHV:	high heat value
P:	Pressure (bar)
T:	Temperature (°C)
MMSm³/d:	Millions standard cubed meter per day
HP;	high pressure

General Introduction

Natural gas has numerous environmental, energy security, and economic advantages. It emits fewer greenhouse gases and has lower tailpipe emissions than diesel or gasoline. Many environmentalists see natural gas as a natural bridge fuel between today's dominant fossil fuels and tomorrow's renewable fuels. However, natural gas contains impurities such as (CO_2 , H_2S , N_2 , H_2O , R-SH...), which necessitated gas treatment.

Acid gas (CO_2 , H_2S) presented in the natural gas cause a major problem during processing or transporting via pipelines and ships causing corrosion of equipment, hydrate formation, it's also reduced the high heat value.

The concentration of acid gas in the sour gas is an important consideration when choosing the type sweetening process. Some processes remove large amounts of acid gas, while others remove acid gas constituents to ppm levels. The sweetening process, on the other hand, must meet pipeline specifications. There are two focus areas when developing gas sweetening methods, dry adsorption and wet absorption.

In this study, we conduct research in the Rhourde nous CPF, which was designed to treat 10 $MMSM^3/D$ of raw gas. The goal of the CPF's decarbonization unit is to reduce the amount of carbon dioxide (CO_2) in the feed gas by 8.6 percent molar to less than 2 percent molar in the final export gas specification.

In recent years, the unconventional field has been depleted to 06 $MMSM^3/D$, prompting us to seek a new operating parameter. And because large-scale testing is frequently difficult, modeling and simulation are critical tools in this field. As a result, the HYSYS simulator is used to investigate the absorption and the regenerator columns.

The dissertation plan has been divided into four chapters.

First Chapter I, a general overview of natural gas, its physicochemical properties, and classification.

A bibliographic review of the main methods used for sour gas sweetening will be described in Chapter II.

The third chapter will present detailed descriptions of a unit for natural gas decarbonization in Rhourde nous field.

Finally, a fourth chapter discusses the HYSYS simulation results and absorption and regenerator columns. Of course, the thesis concludes with a general conclusion that highlights the key findings.

Chapter I

General Overview of Natural Gas

I.1. Natural gas compositions:

Natural gas is a mixture of hydrocarbon and non-hydrocarbon constituents, is formed primarily of methane (CH_4), it can also include significant quantities of ethane (C_2H_6), propane (C_3H_8), butane (C_4H_{10}), and pentane (C_5H_{12}) as well as traces of hexane (C_6H_{14}) and non-hydrocarbons as nitrogen (N_2), carbon dioxide (CO_2), hydrogen sulfide (H_2S), and other sulfur components such as mercaptans (R-SH), Trace quantities of argon, hydrogen, mercury and helium may also be presented.[13].

Table I.1: general compositions of natural gas [1]

<i>t</i>	Compositions	Quantities
<i>hydrocarbons</i>	Methane	70-98%
	Ethane	1-10%
	Propane	Trace-5%
	Butanes	Trace-2%
	Pentanes	Trace-1%
	Hexanes	Trace-1/2%
	Heptane	Trace-1/2%
	Nitrogen	Trace-15%
<i>Non-HC</i>	Carbone dioxide	Trace-5%
	Hydrogen sulfide	Trace-3%
	Helium	Up to 5% usually trace or none

I.2. Natural gas classification:

Natural gases are commonly classified according to their liquid contents as either lean or rich and according to the sulfur content as either sweet or sour.

- The terms "lean" and "rich" relate to the quantity of liquids that could be recovered. The term usually applies to ethane and heavier components. The industry uses GPM, or (Mscft) to measure the liquid content of a natural gas mixture. We said Lean natural gas when the liquid content less than 2 GPM. rich natural gas has between 2 and 5 GPM, and very rich natural gas has greater than 5 GPM.
- strictly speaking, "sweet" and "sour" refer to both acid gases (H_2S and CO_2) but are usually applied to H_2S alone. Sweet gas means the gas contains less than 4 ppmv of H_2S . Carbon dioxide can be tolerated to much higher levels, say 3-4 mol%, as long as the heating value of the sales gas is satisfactory, whereas a sour gas has unacceptable quantities of H_2S .[2]

I.3. Natural gas uses:

Natural gas is not used in its pure form; it is processed and converted into cleaner fuel for consumption. It is mainly used as fuel for generating electricity and heat. Natural gas in its compressed form is used as fuel for vehicles "CNG", as fuel for boilers and air conditioners worldwide, and used for making fertilizers also mainly "ammonia". A greenfield project is going on in Russia to produce LNG to run aircraft. Natural gas prices are measured in million British thermal units (MMBtus), but in some countries, it is traded in Gigajoule also.

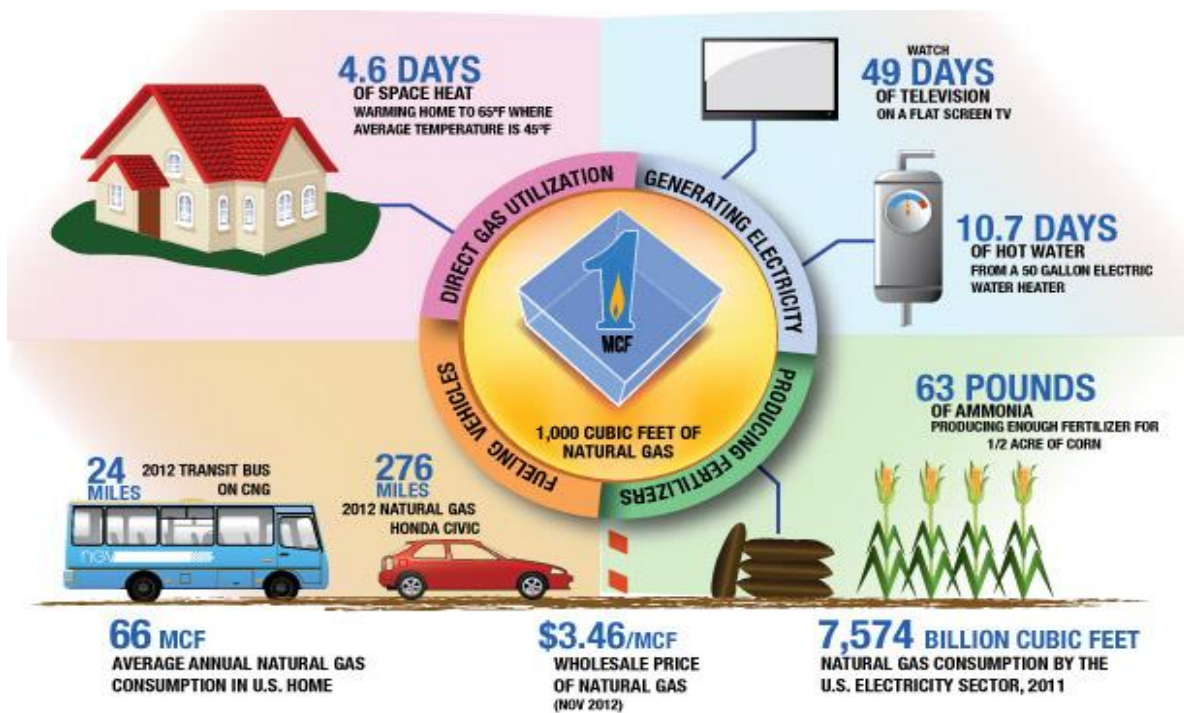


Figure I.1: what one cubic feet of natural gas can do [12].

I.4. Hydrogen sulfide H_2S :

H_2S is a toxic, corrosive, and combustible contaminant in the environment. It is a colorless gas that affects numerous regions of the body. It can prevent cellular respiration by blocking oxygen in mitochondria. Because the body can detoxify it by oxidizing it to sulfate, tiny amounts of H_2S can be tolerated.

H_2S has a rotten egg odor and is extremely harmful at low amounts. It can be scented at 5 ppm, starts to irritate the eyes at 10 ppm, and can no longer be smelled at 200 ppm because it paralyzes the olfactory nerve. The lack of smell can lead to a false sense of security. A single breath of 800 ppm H_2S is enough to cause rapid collapse and kill 50% of humans in five min.

H₂S deactivates industrial catalysts, is corrosive to metal piping, and damages gas engines. It must be eliminated from industrial processes, or removed from gas before it is used, transported, or sold. Figure below shows the result of H₂S corrosion on pipes.[11]



Figure I.2: examples of H_2S corrosion on pipes [16].

I.5. Carbene dioxide CO₂:

Decarbonization is a process that aims to reduce the carbon dioxide content, more specifically carbon dioxide «CO₂»; also called carbon dioxide, it is a colorless, inert, and toxic gas. CO₂ is one of the major greenhouse gases. It has a lifetime in the atmosphere of about 100 years. Natural gas decarbonization is performed to:

- Reduce the risk of pipe corrosion, especially in the presence of free water molecules.
- eliminate the risk of solidification in cryogenic processes
- Keep a better calorific value [22].

I.5.1 Carbene dioxide characteristics:

CO₂ dissolves in water, forming carbonic acid (H_2CO_3). CO₂ from a specific concentration in the air is a potentially lethal pathway. After water vapor, is the second most significant greenhouse gas in the atmosphere. [22] The properties of this gas are shown in Table I.2

Table I.2: literature review on the solubility of CO₂ in amines-based aqueous solvents [5]

<i>Authors</i>	<i>Amines</i>	<i>temperature</i>	<i>Pressure</i>
<i>Austgen & Rochelle 1991</i>	MDEA/MEA	313°K- 353°K	0.26MPa
	MDEA/DEA		
<i>Jou & Al 1994</i>	MDEA/DEA	298°K- 393°K	0.1-20MPa
<i>Jou & Al 1995</i>	MEA	273°K- 423°K	20 MPa
<i>Xu & Al 1998</i>	MDEA/PZ	313°K- 373°K	0.876- 1013KPa

1.6. Natural gas processing objectives:

- To meet with the sale and pollution requirements, and the pipeline gas criteria.
- The produced gas must meet heating values, or woobe index standards, in order for gas turbines and combustion equipment to operate at peak efficiency and reduce NO_x, CO, and soot emissions.
- to ensure gas qualities and provide a clean and safe fuel gas to the consumers.
- Producing transportable gas to a remote location requires the gas to be delivered without allowing condensation of hydrocarbon (HC) liquids.

Chapter II:
Natural gas sweetening
processes

Introduction

The gas sweetening process refers to group processes that are used to remove CO₂ and H₂S. It refers to an important purification process that is employed to remove the acidic contaminants from the natural gas prior to sale. This sweetening can be employed using different methods to remove the H₂S and CO₂ present in the natural gas.

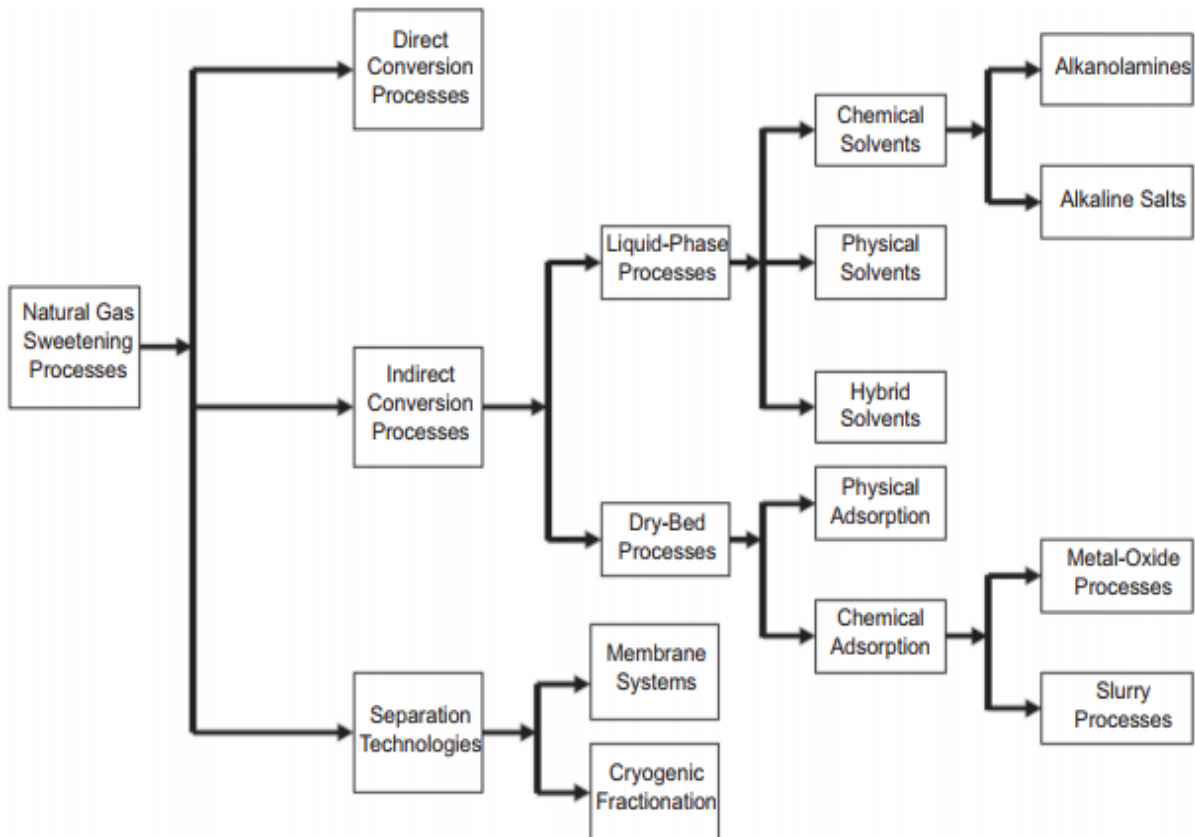


Figure II.1: the different sweetening process

II.1. Specifications for selection of process:

- H₂S and mercaptan concentration in the sour gas and sale gas CO₂ and total sulfur limits
- Maximum design flow rate
- Raw gas inlet pressure
- Requirement of sulfur recovery
- Acceptable methods of waste products disposal
- Simulation of Gas Sweetening Process
- Cost considerations

II.2. Indirect conversion processes (Acid gas removal):

Which are the processes where the acid is disposed, incinerated, and emission through the atmosphere.

II.2.1. Dry bed processes or (Adsorption processes):

adsorbents are used to decrease the concentration of undesired components in the gas and/or vapor phase before they can be used as desired. The use of the adsorption process has been enhanced and new adsorbents have been developed in recent years. Adsorptions beds can be categorized as regenerative or nonregenerative.

Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid, forming a film of molecules or atoms. It is different from absorption, in which a substance diffuses into a liquid or solid to form a solution. The term sorption encompasses both processes, while desorption is the reverse process. [25] .

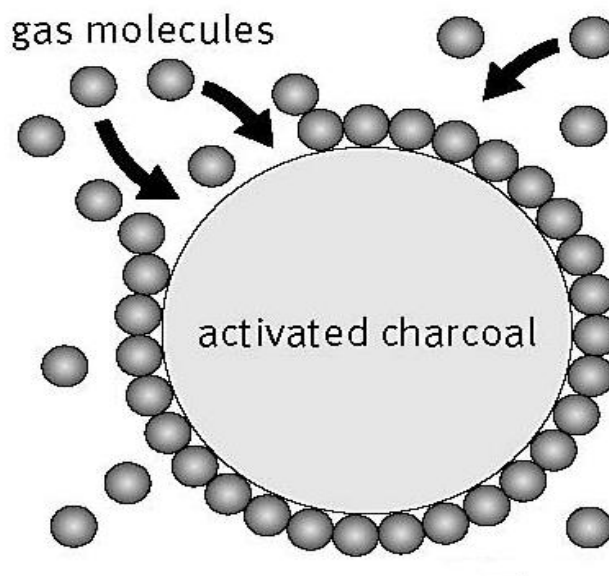


Figure II.2: adsorption process illustration

II.2.1.1. physical adsorption:

A physical adsorption is a regenerative simple approach, which attaches the target substance on a chip as a result of hydrogen bonding, van der Waals forces, electrostatic forces, and hydrophobic interactions.

- Molecular sieves/ zeolites have a crystalline structure. They are able to remove compounds with a small molecular size. they used to remove humidity from exhaust streams and to remove nitrogen oxide compounds (NO_x) from a gas stream

- **Activated Carbon:** 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. Refiners of natural gas and manufacturers and users of other high-purity gases depend on activated carbons to remove contaminants and to capture mercury compounds that can harm process equipment. Activated Carbon pellets can be used for the removal of H₂S in biogas streams, it can also be used to purify amine solutions when their regeneration. [23].



Figure II.3: Activated charcoal carbon [18]



Figure II.4: molecular sieve [19]

Regeneration methods for physical adsorption:

Reversing the adsorption process allows for regeneration. It can be done in a variety of ways, its change the physical propriety of the adsorption bed. The following is the most commonly used.

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

II.2.1.2 chemical adsorption:

Chemical adsorption occurs when the absorbate molecule is held on the adsorbent surface by chemical forces as short covalent chemical bonding occurs by the sharing of electrons. And are not regenerated.

- The iron sponge process is economically applied to gases containing small amounts of H₂S (< 300 ppm) operating at low to moderate pressures in the range of 50-500 psi. This process does not remove CO₂.
- 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.

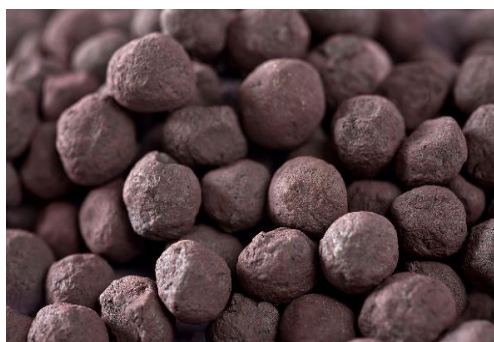


Figure II.5: iron sponge pellets [20]

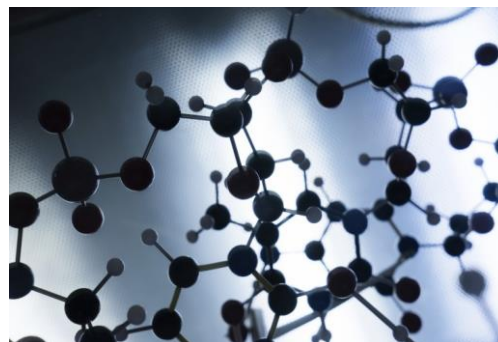


Figure II.6: synthetic polymer [21]

Table II.1: Some characteristics for chemisorption and physical adsorption [21].

Chemical adsorption	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

II.2.2. Liquide phase processes (absorption processes) :

Absorption, also known as gas absorption, is a chemical unit action that separates gases by washing or scrubbing a gas mixture with a suitable solvent. One or more of the gas combination's constituent's dissolves or absorbs in the liquid, allowing it to be eliminated from the mixture. This gaseous ingredient creates a physical solution with the liquid or solvent in some systems, while it reacts chemically with the liquid in others. The goal of such scrubbing activities could be to purify the gas. In most cases, gas absorption takes place in vertical countercurrent columns. The solvent enters the absorber from the top, while the gas mixture enters from the bottom. The solvent is used to wash away the absorbed material. which is often recovered in a subsequent stripping or desorption operation. The absorber may be a packed column, plate tower, or simply spray column, or a bubble column.

Absorption can 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.[17]

II.2.2.1. Equipment for absorption:

Absorption towers come in a variety of configurations:

- Spray towers
 - Tray towers
 - Packed-bed absorption
 - Venturi absorption
- The spray tower is one of the most basic gas absorption devices available. It has an open vessel with one or more spray nozzles on the top to distribute the liquid. The gas stream enters the absorber's bottom and passes through the liquid's countercurrent. Spray towers are employed in systems where fouling is a concern since this type of absorber is less susceptible to plugging than other absorption towers.
- 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. There is different type of trays:
- 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 ensure good contact between the gas and the liquid.[4]

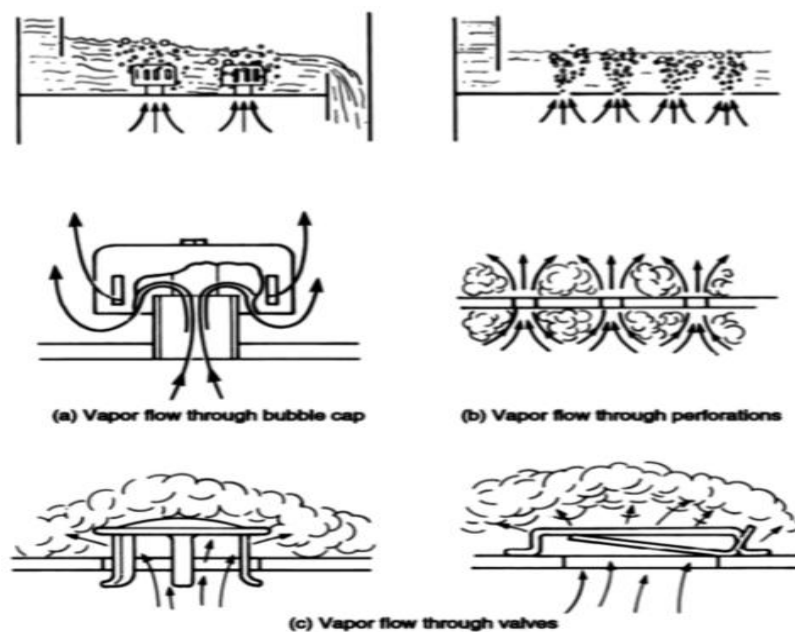


Figure II.7: types of trays [9]

- The packing material is contained in a packed bed absorption column, which is a vertical column. The packing material is designed to give a large surface area for gas and liquid contact. The liquid enters the column at the top and flows downhill. The gas stream flows upward when it enters the bottom. Packed beds are divided into two types: organized and random packing. Structure packing is made up of prefabricated components that are assembled and placed into the column.[9]

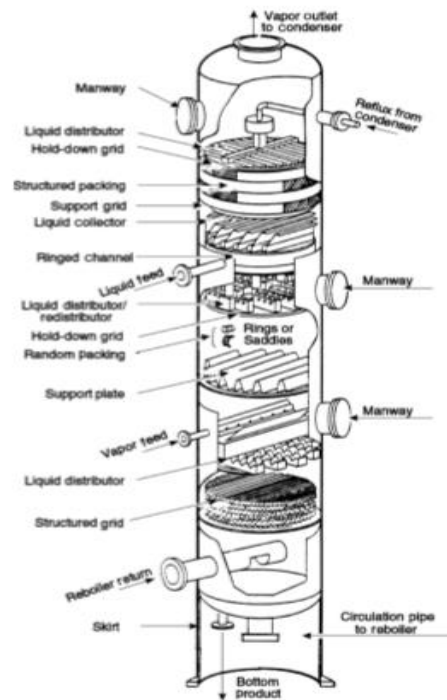


Figure II.8: Sample packed column internals [9]

- The venturi absorber's principle is to accelerate the cleaning liquid into a venture nozzle, resulting in a huge contact area between the liquid and the gas. The venturi absorber uses a lot of energy and requires a pump to produce high velocity. In addition to a packed bed, venturi absorbers can be employed.

Table II.2: advantages and disadvantages for the mentioned absorption methods [4]

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 drops 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 backpressure 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

II.2.2.2. physical absorption:

The process where physical absorbers are called the solvent process. They are based on the solubility of the H₂S within a liquid instead of on the 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. 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 H₂S is high
- The concentration of heavy hydrocarbons is low
- Selective removal of H₂S is required

In the table some of the processes are listed with the eventual owner of the license.

Table II.3: physical processes and their licensor [5].

Physical solvents	licensor
Fluor Flexsorb	Fluor Daniel Corporation
Shell sulfinol	
selexol	Norton Co. Chemical process products
Rectisol	Lurg, Kohle & Mineral Technik GmbH & Linde A.G

II.2.2.3. chemical absorption:

Chemical reaction processes remove H₂S and CO₂ from the gas stream through chemical reaction with a material in the solvent solution. Reversible or irreversible reactions can occur. The reactive material in reversible reactions removes the gases in the contactor at high partial pressure, low temperature, or both. In the stripper, high temperature or low pressure reverse the reaction. The chemical reaction is not reversed in irreversible processes, and removal of the H₂S and/or CO₂ requires continuous makeup of the reacting material.

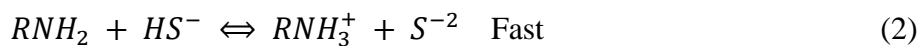
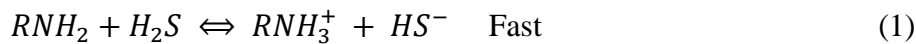
The processes remove the acid gases by the action of exothermic reaction of the solvent with the gases. The solvent used are, either an alkanolamines or an alkali-salt (hot potassium carbonate processes) in an aqueous solution.

II.2.2.4. Aqueous alkanolamine processes:

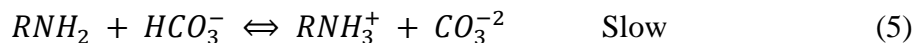
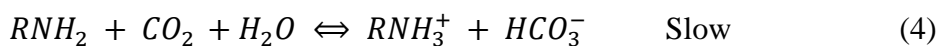
- The common amine-based solvents used for the absorption process are mono-ethanolamine (MEA), diethanolamine (DEA), and methyl-diethanolamine (MDEA) that react with the acid gas to form a complex or bond. H₂S, CO₂, and SO₂ have been termed acid gases since they dissociate to form a weak acidic solution when they come into contact with water or an aqueous medium. These amines are known as weak organic bases.

- Amines remove the acid gas in a two-step process:
 - The gas dissolves in the liquid (physical absorption)
 - the dissolved gas which is a weak acid reacts with the alkaline amines

The overall equilibrium reactions for H₂S and CO₂ as well as primary and secondary amines are represented below with a primary amine. A qualitative estimate of the reaction's velocity is provided. For the removal of hydrogen sulfide:



- The overall reactions between H₂S and amines are simple since H₂S reacts directly and rapidly with all amines to form the bisulfide by Equation (1) and the sulfide by Equation (2). For carbon dioxide removal:



[9].

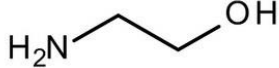
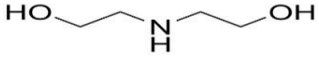
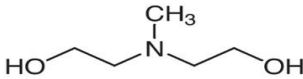
II.2.2.5. Amines:

An amine is generally a functional group with a nitrogen atom having a lone pair. Amines resemble ammonia structurally where nitrogen can bond up to 3 hydrogen atoms. It is also characterized by various properties that are based on carbon connectivity.

Types of amines:

Alkanolamines, which are amines having an alcohol group (OH) connected to one or more of the hydrocarbons, are the most often utilized amines. When compared to amines without alcohol groups, this reduces their volatility. Reactions with amines can reduce the amount of H₂S in natural gas. The initial stage in the breakdown of H₂S is for the amine to accept a proton.

Table II.4: types of amines and their characteristic

MEA		MW=61g/mol Teb=170 ^o c Vol.Mass=1020kg/m ³	-Concentration 15-18% -Very corrosive -Requires high flowrate
DEA		MW=105g/mol Teb=270 ^o c Vol.mass=1100kg/m ³	-Concentration 20-35% -Less corrosive than MEA -Widely used
MDEA		MW=119g/mol Teb=240 ^o c Vol.mass=1040kg/m ³	-Concentration up to 50% weight -Low corrosivity -Selective amine CO ₂ vs H ₂ S

Monoethanolamine (MEA):

Gas sweetening with MEA is used where contactor pressures are low and/or acid gas specifications are strict. Both H₂S and CO₂ are removed from gas streams by MEA. H₂S concentrations of less than 4.0 ppmv are achievable. At low to moderate pressures, CO₂ concentrations of 100 ppmv can be obtained. The technical points that follow need to be taken into account for MEA:

- The acid gas loading should usually be limited to 0.3–0.4 mol acid gas per mole of amine for carbon steel equipment.
- MEA is not thought to be particularly corrosive. Its degradation products, on the other hand, are extremely corrosive. MEA can be partially deactivated by COS, CS₂, SO₂, and SO₃, which may require recovery with a reclaimer.[9]

Diethanolamine (DEA):

This process is used for high-pressure, high acid gas content streams having a relatively high ratio of H₂S/CO₂. The process flow scheme for conventional DEA plants resembles the MEA process. The advantages and disadvantages of DEA as compared to MEA are as follows:

- The mole/mole loadings used with DEA (0.35–0.82 mol/mole) are much higher than those used with MEA (0.3–0.4).

- A reclaimer is not required because DEA does not produce a significant amount of non-renewable degradation products. Moreover, unlike MEA, DEA cannot be reclaimed at reboiler temperature.
- DEA is a secondary amine and is chemically weaker than MEA, so less heat is required to strip the amine solution.[9]

Methyldiethanolamine (MDEA):

MDEA is a tertiary amine that can be used to selectively remove H₂S to pipeline specifications at moderate to high pressure. However, because MDEA solutions only react slowly with CO₂, activators must be added to the MDEA solution to enhance CO₂ absorption. The following technical points must be considered for MDEA:

- The acid gas loadings as high as 0.7–0.8 mol/mole are practical in carbon steel equipment.
- MDEA has a number of advantages over primary and secondary amines. Lower vapor pressure, lower heats of reaction, higher resistance to degradation, fewer corrosion issues, and selectivity toward H₂S in the presence of CO₂ are some of the benefits.

Activated tertiary amines:

The addition of activators slows the reaction to bicarbonate for tertiary amines. Activators are typically primary or secondary amines that are designed to increase both carbamate hydrolysis and the rate of dissolved CO₂ hydration, making activated tertiary amines particularly suitable for efficient and cost-effective bulk CO₂ removal when selectivity is not required.

Amine solution selection:

As outlined here, many process factors should be considered when selecting an amine for a sweetening application:

- The initial choice should be based on the sour gas's pressure and acid gas content, as well as the purity specification for the product gas.
- MEA is typically not preferred under current "accepted" operating conditions due to its high heat of reaction and lower acid gas carrying capacity per unit volume of solution.
- DEA is used because it has lower heats of reaction, a higher acid gas carrying capacity, and thus requires less energy. However, its potential for selective H₂S removal from CO₂-containing streams has not been fully realized.
- MDEA, with its some outstanding capabilities, resulting from its low heat of reaction, can be used in pressure swing plants for bulk acid gas removal. MDEA is currently best known for its ability to preferentially absorb H₂S.

II.3. Separation technologies:

II.3.1. Cryogenic process:

Is a low temperature distillation. uses a very low temperature ($-73.30C^{\circ}$) for purifying gas mixtures in the separation process and purification of gases. Much of the commercial oxygen and nitrogen, and all the neon, argon, krypton, and xenon, are obtained by the distillation of liquid air. Essentially, cryogenic processing consists of lowering the temperature of the gas stream to around $-84.44C^{\circ}$. While there are several ways to perform this function the turbo expander process is most effective, Cryogenics use condensation of gases as the main principle. When CO_2 is cooled below its boiling point, it begins to condense and separate and turns into a liquid state. The main disadvantage of cryogenic separation is that it requires a lot of energy to regenerate and can reduce overall plant efficiency significantly when used on streams with low CO_2 concentrations.[8]

II.3.2. Membrane process:

A gas separation membrane are thin films that selectively transport gases through the membrane based on differences in permeabilities of the species flowing through the membrane. The permeability of gases in a membrane is related as a function of membrane properties (physical and chemical structure), The membrane properties and the nature of the permeant species determine the diffusional characteristics of a penetrant gas through a given membrane. The solubility (sportively coefficient) is a measurement of the amount of gas sorbet by the membrane when equilibrated with a given pressure of gas at a given temperature. The selectivity of the membrane to specific gas or liquid molecules is subject to the ability of the molecules to diffuse through the membrane. Gas transport through porous membranes takes place through a number of mechanisms, such as molecular sieving, Knudsen diffusion, surface diffusion, capillary condensation and micropore diffusion.[8].

Chapter III:
Natural gas treatment in
Rhourde nouss field

Introduction:

The RHOURE NOUSS region is located in the Wilaya of ILLIZI. Located 1200 km south/southeast of ALGIERS and 270 km south/south east of HASSI MESSAOUD.

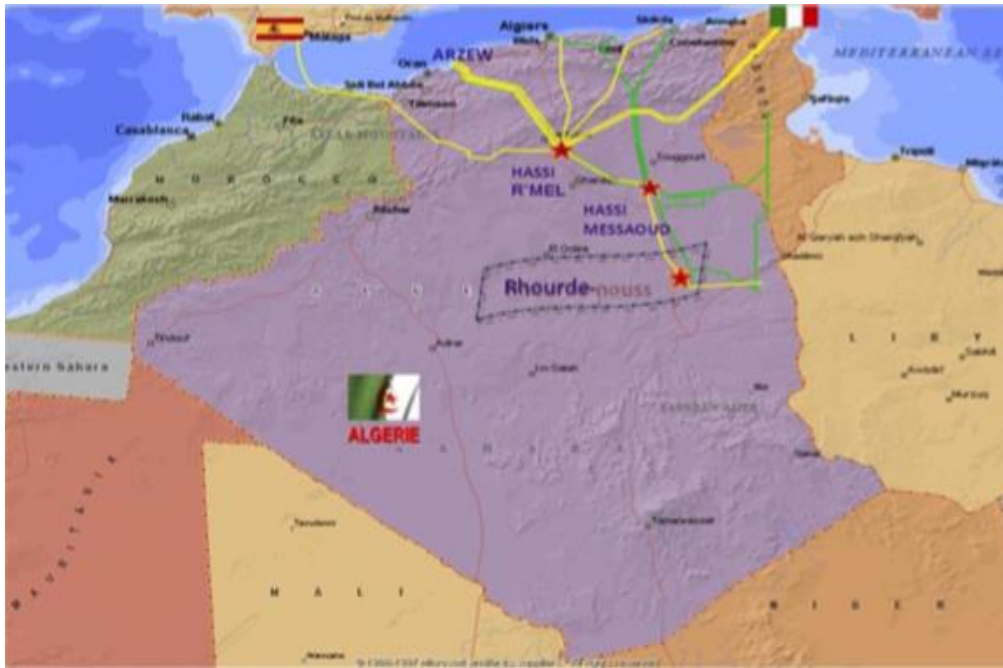


Figure III.1: The geographical situation of the Rhourde-Nouss region.

The Rhourde-Nouss region is mainly used for gas. It has:

- Phase A: Production of 50 million Sm³/d of gas.
- Phase B: Processing of 30 million Sm³/d of natural gas to recover LPG, and traces of condensate.
- CSC: A compression and separation center for oil production.
- CPF (Hamra Quartzite): 10 million Sm³/d gas treatment.

III.1. C.P.F (Central Processing Facility)

The new Hamra Quartzite (QH) treatment facility is designed to process 11 million Sm³/day of gas (dry base) from 33 production wells in four (4) fields in the Rhourde-Nouss region. The plant has a nominal production of 10 million Sm³/day and produces dry waste gas with a high heat Value (HHV) between 9,800 and 9,900 Kcal/Sm³ and CO₂ content of less than 2.0% molar.

- Export gas is sent to the GR4 transmission system pipeline
- Unstable condensate to direct to phase A.
- Heavy (associated) gas to direct to phase A.
- CO₂ carbon dioxide directed to the incinerator.[6]

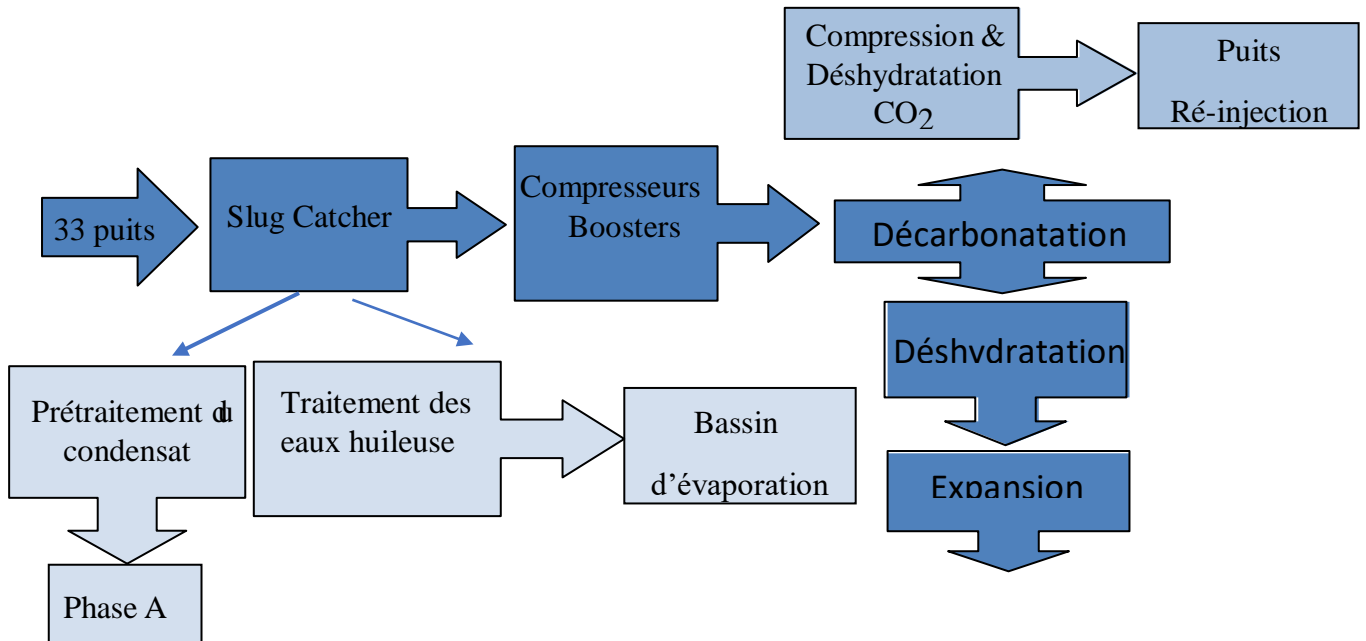


Figure III.2: CPF block diagram [7]

III.2. Specifications of sales gas products:

Table III.1: sale gas compositions [6].

Component	Mole fraction %
N ₂	0.5766
CO ₂	1.8591
Methane	88.1797
Ethane	5.4412
Propane	1.9967
i-Butane	0.6135
n-Butane	0.5939
i-Pentane	0.3101
n-pentane	0.1504
n-Hexane	0.1792
n-Heptane	0.0775
n-Octane	0.0161
n-Nonane	0.0049
n-Decan	0.0007

$n-C_{11}$	0.0000
C_{12+}	0.0001
Total	1.0000

Table III.2: sale gas conditions [7].

Flow rate operation	8.6 million Sm^3/day
Pressure	96 bar g
Temperature	60° C
Molecular weigh	18.9
Water content in sale gas	< 1.0 $ppmv$
Hydrocarbon Dew point	-9.3 °C and 96 bar g

III.3. Description of the decarbonization unit:

The goal of the decarbonization unit is to reduce the amount of carbon dioxide (CO_2) in the feeder gas by 9% molar to the final export gas specification by less than 2%. This unit is based on a combined counter-absorption technology current with an amine solution, followed by a desorption (regeneration) step in which CO_2 is removed from the amine solution.

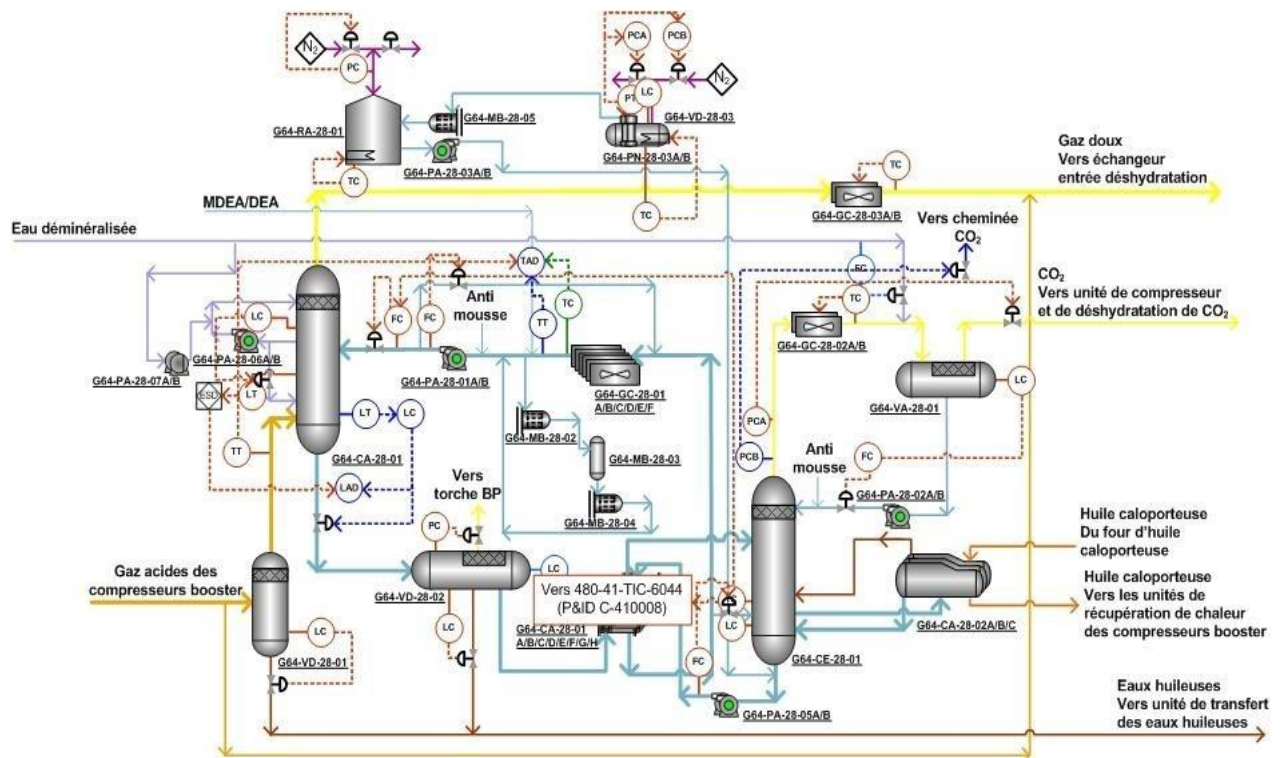


Figure III.3: process flow diagram of the AGRU [6].

III.3.1. The mains equipment of the CO₂ removal unit:

- **CO₂ Absorber G64-CA-2801:**

The CO₂ absorber is designed for the removal of CO₂ from the natural gas stream. The gas is routed to the bottom of the vertical absorption column where it is contacted with a countercurrent flow of a-MDEA solution descending through a structured 18 valve trays bed. Decarbonated gases (sweet gas) leaving the top of the absorber, having a content of less than 2% molar of CO₂ and being saturated with water, are cooled from 73°C to 60°C by a battery of decarbonated gas aero-coolers (G64 GC-28-03A/B), then routed to the gas dehydration system.

To reduce amine loss in the sweet gas leaving the column, the upper part of the absorber has a washing system with demineralized water that is continuously recirculated by washing water pumps G64-PA-28-07A/B.

- **Flash drum (G64 -VD-28-02)**

At 80°C, the rich amine from the CO₂ absorber is routed to the Rich Amine Flash drum to remove some CO₂ and light hydrocarbons by lowering the rich amine pressure from 82 barg to 4.8 barg. The flash drum has a skimmer that allows for the drainage of a layer of hydrocarbons that may form during normal operation. This drainage is directed at the oily water system.

- **Rich/Lean amine heat exchanger (G64-GA-28-01A/B/C/D/E/F/G/H):**

The rich amine, at 80°C, comes from the flash flask and passes through the tubes of the Rich/Poor Amine Heat Exchangers to preheat up to 103°C through a heat exchange with the hot poor amine from the Regenerator. The preheated rich amine is then directed to the amine regenerator. This flow is bi-phasic since a small amount of gas vaporizes as a result of warming.

The lean amine, cooled to approximately 89°C, is directed through a line to the aero-coolers of the recycled amine before being pumped and circulated to the absorber.

- **CO₂ Stripper (G64-CE-28-01):**

The amine regenerator is the CPF's highest column. It is 40 meters above ground and has 17 trays to completely desorb the amine's CO₂. It's removed from the amine through evaporation (depletion) using heat supplied by the reboilers. Reflux provides the column with the necessary cooling.

The energy for the reboilers is supplied by heat transfer oil. To prevent amine degradation, the reboiler temperature is kept below 128°C. The regenerator's head gas, essentially water-saturated CO₂, is sent to the condenser to condense the water by cooling the gas from 90 to 55°C. Then, the condensed CO₂/water mixture is sent to the amine regenerator's head. (Reflux drum) where condensed water is separated from the gas. The CO₂ is sent to the incinerator for disposal. However, the water is returned to the regenerator head as reflux to provides the necessary cooling to the column.

The "hot" lean amine solution collected at the bottom of the regenerator column is pumped to 10 barg at a flow rate of 665 m³/h by the amine booster pumps to the shell side of the lean/rich amine heat exchangers for thermal exchange with the rich amine "cold" from the Rich Amine Flash drum, reducing the temperature from 128°C to 90°C.

The lean amine from the lean/rich amine heat exchangers is routed to the amine aero-coolers, reducing the temperature from 90 to 60°C.

In order to avoid condensation of hydrocarbons, which could promote foaming in the absorption column, the temperature of the lean amine must be kept 5°C warmer than that of the acid gas that feeds the CO₂ absorber.

Downstream of the aero-amine coolers, to remove traces of hydrocarbons, a flow of about 10% of the total amine flow passes through an activated charcoal filter (G64-MB-28-03).

To be able to introduce the poor amine into the absorber, dedicated pumps are used which ensure a pressure of 90 bar g.

- **Amine storage (G64 -RA28-01):**

The decarbonization unit has an amine storage tank that can hold the entire volume of the unit.

The amine buffer tank contains an inert gas (nitrogen) to keep the amine from coming into contact with oxygen.

III.3.2. Issues that have arisen in a decarbonation unit:

The use of amine solution in the natural gas decarbonation process can cause serious problems

- Corrosion: Some of the major factors that affect corrosion are:
 - Amine concentration (higher concentrations favor corrosion)
 - Rich amine acid gas loading (higher gas loadings in the amine favor corrosion)
 - Oxygen concentration
 - Heat stable salts (higher concentrations promote corrosion and foaming)
- Solution Foaming: Foaming of the liquid amine solution is a major problem because it results in poor vapor/liquid contact, poor solution distribution, and solution holdup with resulting carryover and off spec gas. Among the causes of foaming are:
 - suspended solids, liquid hydrocarbons, surface active agents, such as those contained in inhibitors and compressor oils, and amine degradation products, including heat stable salts. One obvious cure is to remove the offending materials; the other is to add antifoaming agents.

Signs of foaming are:

 - High differential pressure of the columns
 - Difficulties in the control of low levels
 - High content of hydrocarbons in sour flue gas
 - High content of a-MDEA in the reflux condensate
 - Foam test results out of specified range
- Heat Stable Salts: As mentioned above, these amine degradation products can cause both corrosion and foaming. They are normally dealt with through the use of amine reclaimers.[9].

Chapter IV:
Modeling & Simulation of the
decarbonization unit

IV. 1. Problem statement:

The Hamra Quartzite CPF of the Rhourde-Nouss is designed to treat a nominal load of 10 million Sm³/day from “unconventional” field and produces dry waste gas with a high heat Value (HHV) between 9,800 and 9,900 Kcal/Sm³. The objective of the decarbonization unit in the CPF is to reduce the amount of carbon dioxide (CO₂) in the feed gas by 8.6 % molar to less than 2 % molar in the final export gas specification.

In this CPF, activated MDEA is used in an absorption column for a sweetening process using (48% MDEA, 2% DEA, 50% H₂O) with well-defined parameters such as flow rate, temperature, and amine composition.

In our case, the field has been significantly depleted. As a result, the flow of processed crude gas has decreased. Knowing that at the start of the CPF complex's operation (January 2014), 10MSM³/J were processed, and that currently, 6M SM³/J are processed.

This necessitates the redefinition of new parameters that are appropriate for the new operating conditions, which is the main objective of our work.

To optimize this unit, we use a «HYSYS» process simulator, and we choose the following strategy:

- Description of the decarbonization unit.
- Carry out the CPF simulation
- Validate the model you've chosen.
- Optimization of the current case unit.
- Results and Interpretations.
- Conclusion.

IV.2. Decarbonization unit description:

The feed gas arrives at a pressure of approximately 81 bar and a temperature of 55°C from the inlet manifold is routed to the bottom of the absorption column, where it comes into contact with a countercurrent flow of lean a-MDEA solution, which enters the top of the column at around 55°C via a liquids distributor (diffuser). The treated gas leaves the absorption column with a CO_2 concentration around 1.89% at a pressure of 82.5 bara and a temperature of 73°C before proceeding to the export gas dehydration facilities.

The rich a-MDEA solution comes from the bottom of the absorption column at a temperature of around 82°C in the flash drum. As the amine solution is flashed from high pressure to low pressure in the flash drum, CO_2 will instantly separate from the solution. and then preheated to 103°C by heat exchange with the lean a-MDEA in the lean/rich exchanger this done to enter the top of the stripper where the solution is brought into countercurrent with water vapor produced in the reboiler at a reduced pressure.

this then allows to move the reactions in the direction of desorption of the acid gases. The recovered alkanolamine solution is cooled before being reintroduced at the head of the absorption column.

The absorber operates at high pressure and low temperature and the regenerator operates at low pressure and high temperature.

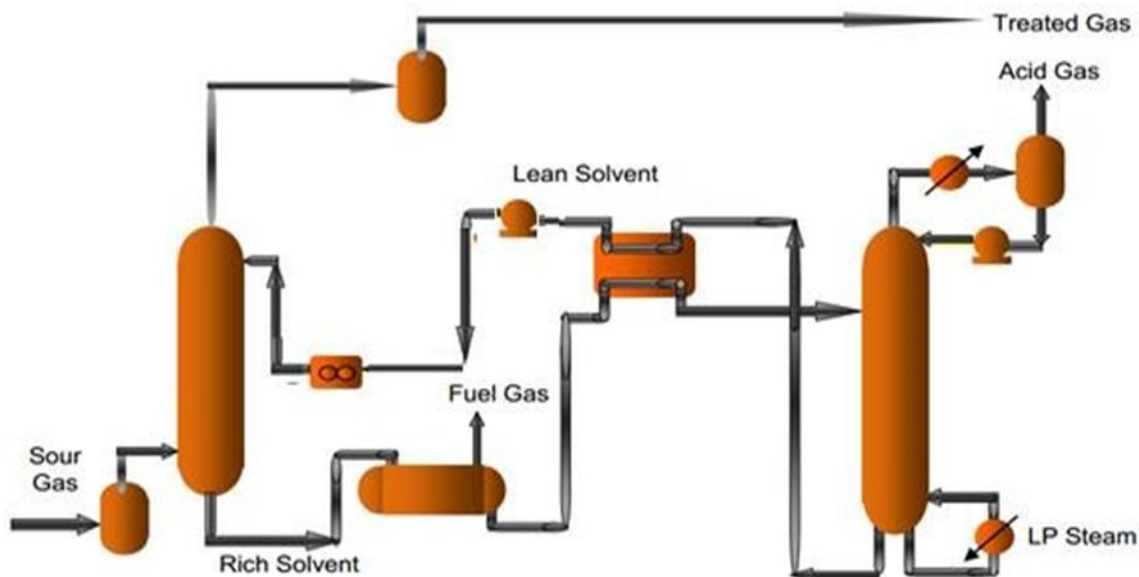


Figure IV.1: Simplified schematic of acid gas removal unit [8].

IV.3. Simulation:

At the most abstract and simple level, a process simulation model is a representation of a chemical process plant to facilitate design, analysis, or other types of studies of the behavior of that plant. Often this refers to creating a mathematical representation using computer software. All simulation models share several basic characteristics:

- Representation of the thermodynamic behavior of material
- A representation of equipment that is encountered in a chemical process plant
- Representation of chemical reaction connections between equipment to represent the flow of material [3].

IV.3.1. Benefits of Simulation in Gas Processing Plants:

- During the conceptual phase, the results of the simulation will be used to determine approximate equipment sizes, and power and utility consumption to estimate of the investment required for the plant and of the operating costs.
- During the front-end engineering design phase, the simulation model will provide sufficient information for a detailed design of each piece of equipment, the piping that will connect them, and the instrumentation.
- through the start-up of the plant, dynamic simulation models will provide information on the tuning of the process control system and on the validity of the proposed start-up scenarios and may help the training of the engineers and operators on the operation of the plant.
- Another very important aspect is the use of models to define safety equipment and to ensure that the safety system is designed to protect the plant and the people operating the plant under all incident scenarios.[3].

IV.3.2. Simulation with HYSYS:

The HYSYS Simulator is a set of mathematical models, and correlations of unit operations (distillation, separation, etc.). so is a computer program for the simulation of processes in the gas industry, refining processes, and petrochemicals, In a steady state and in a dynamic situation.

IV.3.3. Use of HYSYS software:

- Engineering
- Establishment of material and energy balances of an industrial process
- Sizing of the equipment
- Readjustment of operating parameters in case of change of composition -of the power supply.
- Determination of equipment performance
- Optimization of processing units

IV.3.4. Simulation steps to follow:

- Establish the list of components (CO₂, H₂O, Amine, C₁, C₂, etc.).
- The Choice a thermodynamic model.
- Establish the PFD procedure diagram.
- Specification of parameters and operating conditions for each stream or equipment (pressure, temperature, flow rate, etc..).
- Interpretation of results
- Conclusion

IV.3.5. Simulation of the decarbonization unit:

The following are the components:

Table IV.1: actual composition of raw gas at the absorber inlet

composition	Mole fractions %
Nitrogen	0,5255
CO_2	8.5798
Methane	81.3801
Ethane	5.0603
Propane	1.8813
i-Butane	0.5896
n-Butane	0.5804
i-Pentane	0.3212
n-Pentane	0.1557
n-hexane	0.2323
n-heptane	0.1429
n-octane	0.0493
n-nonane	0.0270
n-decan	0.1010
n- C_{11}	0.0031
H_2O	0.4360
Total	100
Total	1

IV.3.6. Model selection for thermodynamics:

Thermodynamic models are needed to calculate the physical, chemical, and energy properties of fluids. The thermodynamic model is used to calculate the mixing properties (density, compressibility factor, enthalpy, etc.); as well as to calculate the equilibrium of the phases in the currents (Stream), and in the units of the separations.

IV.4. Model validation:

We must first validate the chosen model in order to obtain reliable results in our study for the current case of the decarbonization unit. For this, we compare the results found in our design case model with the results provided by the (constructor), keeping in mind that the average absolute deviation should not be exceeded 7%. [5]

Table IV.2: absorber simulation result

Operation parameters						
	Sweet gas stream			Rich amine stream		
	constructor results	Hysys results	Error (%)	constructor results	Hysys results	Error (%)
Pressure(bar)	82.30	82.30	0.0	82.5	82.5	0.0
Temperature(°C)	73.00	64.74	11.31	80.1	84.3	5.24
Flow (kg. mole/h)	15797	15820	0.14	21825	21720	0.48
Composition						
MDEA	/	/	/	11.89	12.01	1.01
DEA	/	/	/	0.56	0.57	1.78
N_2	0.52	0.55	5.76	/	/	/
CO_2	1.81	1.87	3.31	5.55	5.45	0.06
H_2O	0.53	0.49	7.54	81.73	81.81	0.04
Methane	87.38	87.45	0.08	0.10	0.09	3.14
Ethane	5.42	5.44	0.36	/	/	/
Propane	2.01	2.02	0.49	/	/	/
i-butane	0.63	0.63	0.0	/	/	/
n-butane	0.62	0.62	0.0	/	/	/
C_{5+}	1.08	0.98	9.25	/	/	/

- As obvious in the table above the average absolute deviation is less than 7%, which we can assure the accuracy of our chosen model.

IV.5. Optimization of the decarbonation unit (current case):

As explained previously, depletion of the field reduces the raw gas flow from 10 MMSM³/D to 06 MMSM³/D. This necessitates redefining the appropriate new parameters in order to reduce CO₂ content, which is the main objective of our study. This section consists of researching the effect of operating parameters on CO₂ content and determining the optimal parameters for reducing CO₂ content to less than 2%. The following operating parameters will be evaluated:

- amine rate.
- The temperature of the lean amine stream.
- Consumption of energy.

IV.5.1. Amine rate:

In order to treat 10 MMSM³/D, the CPF uses 20554 kg. mole/h as an amine flow but if we use the same flow amine to sweet the current raw gas 6 MMSM³/D, the CO₂ content will decrease to 0.7%, while the sale gas specification is 2%.

- what led to finding a new adequate flow rate. The amine flow rate is decreased from 20554 kg mol/h to 8000 kg mol/h, and the corresponding CO₂ content is recorded, the results are shown in the plot below.

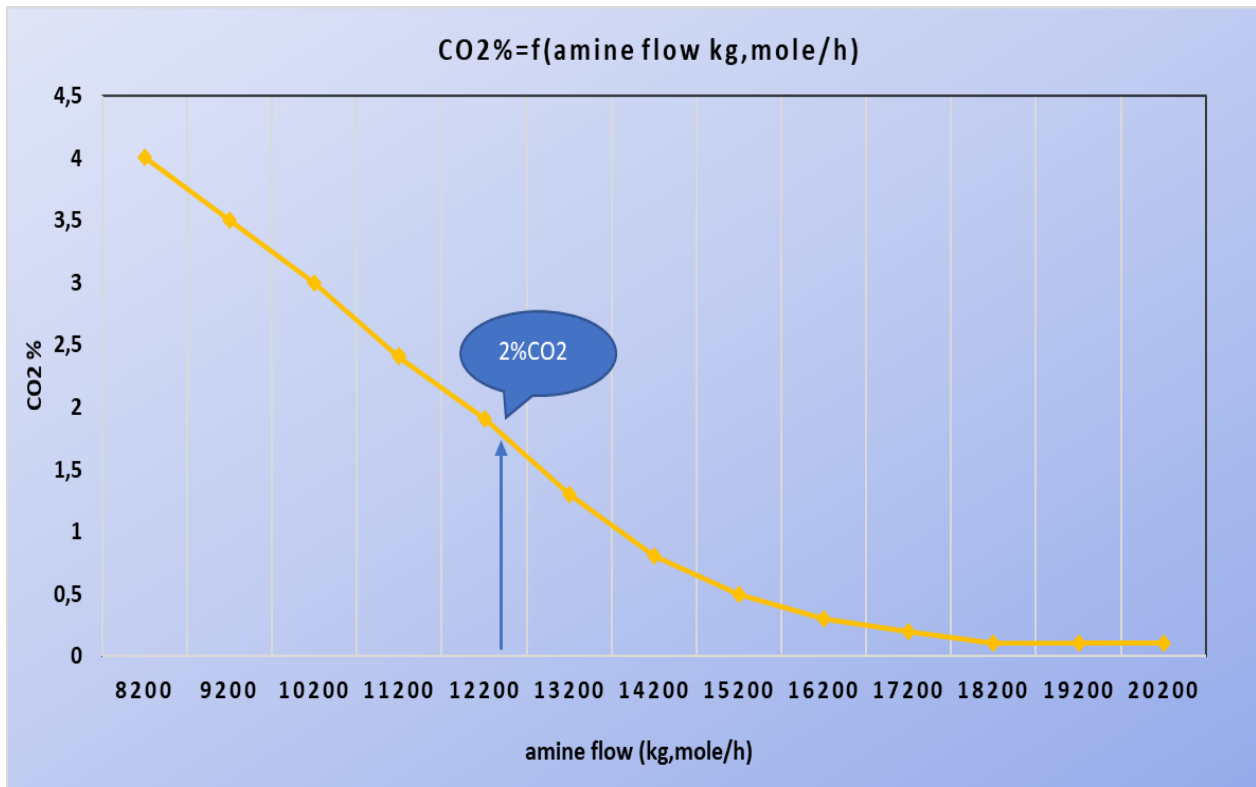


Figure IV.2: CO2 content as a function of amine flow

- the CO2 content in the treated gas is inversely proportional to the flow of amine injected into the column. As a result, a critical flow rate must be maintained to ensure that the transport requirement is always met.
- According to the plot, the optimum amine flow rate for 2 percent CO2 in the treated gas is: $\varphi_{opt} = 12250 \text{ kg.mole/h}$

IV.5.2. The temperature of the lean amine stream:

To find out the effect of temperature on CO2 content, the amine temperature was varied from 40 to 65°C, with 25°C intervals because generally the absorption process occurs in that range. while the optimum flow rate found:

$\varphi_{opt} = 12300 \text{ kg.mole/h}$ remained constant.

The temperature optimization results shown in the following figure:

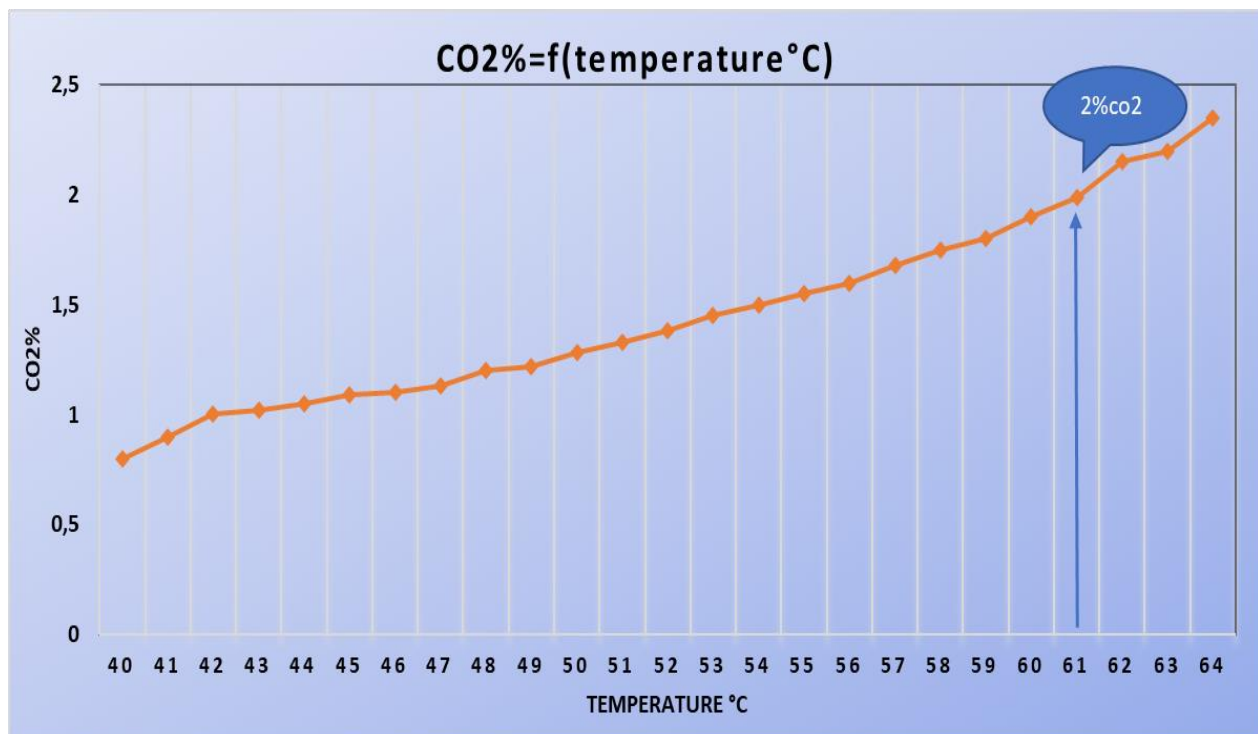


Figure IV.3: CO2 content as a function of amine temperature

- The optimum amine temperature corresponding to 2% CO2 in the treated gas, according to the plot, is: $T_{opt} = 61^{\circ}\text{C}$
- The temperature of the lean-amine 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.

IV.5.3. Consumption of energy:

- In order to get know the desorption energy needed to regenerate the amine solvent in the stripper we observe the simulated results in the reboiler.
- The figure below illustrates the evolution of energy demand as a function of the lean amine molar flow.
- And the second figure shows the simulation result and the optimum energy consumption of the condenser.

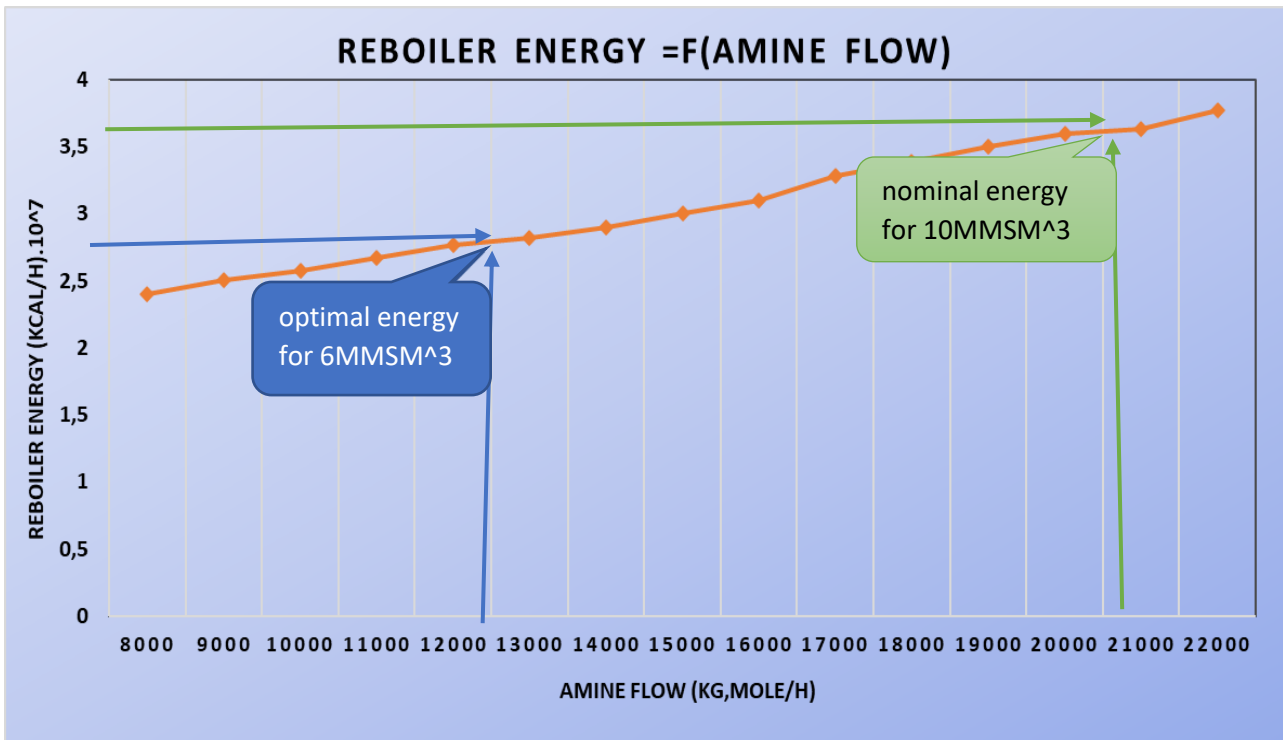


Figure IV.4: energy consumption in function of the amine flow at the regenerator level(reboiler).

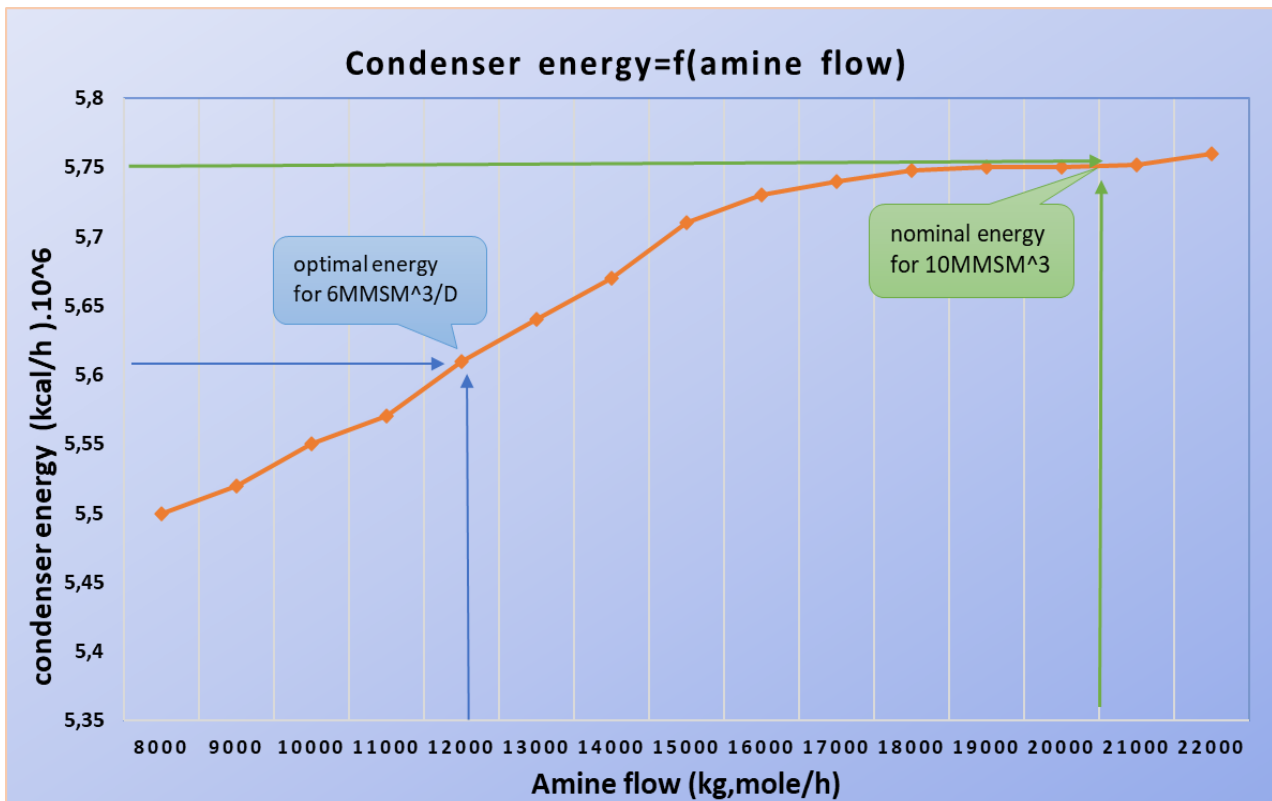


Figure IV.5: energy consumption in function of the amine flow at the regenerator level (condenser).

- The first chart shows that the reboiler consumption of energy for the new raw gas flow of 6 MMSM³/D is less by 23% than the nominal consumption of energy. so, the optimal energy is: $2.8 \times 10^7 \text{ kcal/h}$.
- We notice that the condenser consumption energy of the new raw gas flow is: $5.61 \times 10^6 \text{ kcal/h}$.
- The new parameters found previously flow and temperature (φ_{OPT} and T_{OPT}) and as the low amine temperature is constant, however the amine flow has changed considerably and it directly affects the energy consumption at the level of reboiler, and condenser of the decarbonation unit.

IV.5.4. Conclusion

We had assured the "Hysys" validity after comparing the "design case" with the results provided by the constructor. The optimization of the operating parameters of the decarbonization unit is directly related to the chemical absorption phenomenon, the latter is favored by the high pressure, the low temperature, and the amine flow.

General conclusion

The study presented in this thesis contributes to research on natural gas decarbonization and the acid gas removal unit. by using the "Hysys" software simulation we get rid of the complexity of the process and the technical difficulties of experimental studies on actual configurations, in the oil and gas processing industry.

The CPF of Rhourde nouss was made to treat 10 MMSM³/D of the raw gas and the objective of the decarbonization unit in the CPF is to reduce the amount of carbon dioxide (CO₂) in the feed gas by 8.6 % molar to less than 2 % molar in the final export gas specification.

In the recent years, the unconventional field keep depletes reaching 06 MMSM³/D, what led us to find a new operating parameter such as: the amine flow rate, the temperature of lean amine stream, and the consumption of energy of the regenerator column.

We did the optimization using the Hysys software, after we validate the chosen model, fixing the pressure parameter at 82 bar because is related to the design of the complex, found out the following result:

- For the amine flow we do the simulation in interval of [8200-20200] kg. mole/h, the optimum amine flow rate for 2 percent CO₂ in the treated gas is:

$$\varphi_{opt} = 12250 \text{ kg. mole/h}$$

- In the temperature we limited in [40-64] °C because the absorption process occurs in a temperature that's ranging in that interval. the suitable value is $T_{opt} = 61^{\circ}\text{C}$.
- Because the new amine flow rate discovered is 60% of the nominal flow rate, the unit's energy consumption is reduced.

The optimization of the decarbonization unit parameters shows that the absorption column has a high degree of operating flexibility, allowing the sweet gas specifications to be met regardless of raw gas flow rate.

The sweetening process has a large parameter can affect its performance. I think the corrosion is an interesting topic to study because Corrosion is a major issue in nearly all sweetening plants. The combination of H₂S and CO₂ with water virtually guarantees the presence of corrosive conditions in parts of the plant.

Reference List

source	type	Description
1	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
2	Book	Handbook of Natural Gas Transmission and Processing Principles And Practices (Fourth Edition/Saied Mokhatab, William A. Poe,John Y. Mak)
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عنوان المذكرة: التحسين الأمثل لإعدادات التشغيل في وحدة إزالة ثاني أكسيد الكربون منطقة "رورد النص"
اللقب: بن أحمد الاسم: أية رحيله المؤطر: عبد المعز أحمد
الملخص:

تتطلب عمليات معالجة الغاز باستخدام مذيبات الألكانولامين المائية مدخلات طاقة كبيرة إلى المتجرد لإزالة الغازات الحمضية من المحلول الغني بثاني أكسيد الكربون. في السنوات الأخيرة، جذب ميثيلديثانولامين، MDEA، الانتباه كعامل لمعالجة الغاز. يخضع الغاز الطبيعي لمنطقة رورد النص الغازية حاليًا للمعالجة بمحلول مائي من MDEA المنشط لتحسين امتصاص ثاني أكسيد الكربون مع تقليل الطاقة أثناء تجديد المذيب والوصول إلى المواصفات المعتادة. والهدف من وحدة إزالة ثاني أكسيد الكربون هو خفض محتوى ثاني أكسيد الكربون إلى أقل من 2 في المائة، أي المعيار المطلوب من حيث الجودة والمواصفات. ويتطلب الاستنفاد الكبير للحقل الغازي إعادة إعدادات جديدة لتكيف مع ظروف التشغيل الجديدة. ترتبط كفاءة الوحدة ارتباطًا مباشرًا بظاهرة الامتصاص الكيميائي، ويفضل هذا الأخير الضغط العالي ودرجة الحرارة المنخفضة وكمية الأمين مقارنة بمعدل تدفق الغاز المعالج. يثبت تحسين معايير وحدة إزالة ثاني أكسيد الكربون أن عمود الامتصاص يتمتع بمرونة واسعة في التشغيل، مما سيساعدنا على تحقيق مواصفات الغاز المعالج مهما كان معدل تدفق الغاز الخام. الكلمات المفتاحية: معالجة الغاز؛ ثاني أكسيد الكربون؛ ميثيلديثانولامين؛ تحسين؛ حقل رورد النص

Thesis title: optimization of operating parameters in CO2 removal unit (Rhourde nous)

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Abstract:

Gas treatment processes using aqueous alkanolamine solvents require substantial energy input to the stripper to remove the acid gases from the charged solution. In recent years, methyldiethanolamine, MDEA, has attracted attention as a gas treatment agent. The natural gas of the gaseous region of Rhourd Ennous is currently undergoing treatment with an aqueous solution of activated MDEA to Improve the absorption of carbon dioxide while decreasing the energy during the regeneration of the solvent and reaching the usual specifications. The objective of the CO2 removal unit is to reduce the CO2 content to less than 2%, i.e. the standard required in terms of quality and specifications. The considerable depletion of the deposit requires the redefinition of new parameters adapted to the new operating conditions. The efficiency of the unit is directly linked to the phenomenon of chemical absorption, the latter is favored by the high pressure, the low temperature, and the quantity of amine compared to the flow rate of the treated gas. The optimization of the CO2 removal unit parameters proves that the absorption column has wide flexibility of operation, which will help us to achieve the specifications of the treated gas whatever the raw gas flow rate.

Key words: gas processing; carbon dioxide; optimization; removal unit; Rhourde nous; simulation

Thème de mémoire : Optimisation des paramètres de fonctionnement de l'unité de décarbonatation (Rhourde nous)

Nome : BEN AHMED ; Prénomme : Aya Rahila ; Encadreur : ABDELMOUIZ Ahmed

Résumé :

Les procédés de traitement des gaz à l'aide de solvants alcanolamine aqueux nécessitent un apport énergétique important au régénérateur pour éliminer les gaz acides de la solution chargée. Ces dernières années, la Methyldiethanolamine, MDEA, a attiré l'attention en tant qu'agent de traitement gazeux. Le gaz naturel de la région gazeuse de Rhourd Ennous est actuellement en cours de traitement avec une solution aqueuse de MDEA activé pour améliorer l'absorption du dioxyde de carbone tout en réduisant l'énergie pendant la régénération du solvant et atteindre les spécifications habituelles. L'objectif de l'unité d'élimination du CO₂ est de réduire la teneur en CO₂ à moins de 2 %, c.-à-d. la norme requise en termes de qualité et de spécifications. L'épuisement considérable du gisement nécessite la redéfinition de nouveaux paramètres adaptés aux nouvelles conditions d'exploitation. L'efficacité de l'unité est directement liée au phénomène d'absorption chimique, ce dernier est favorisé par la haute pression, la basse température et la quantité d'amine par rapport au débit du gaz traité. L'optimisation des paramètres de l'unité d'élimination du CO₂ prouve que la colonne d'absorption a une grande flexibilité de fonctionnement, ce qui nous aidera à atteindre les spécifications du gaz traité quel que soit le débit de gaz brut.

Les mots clés : traitement de gaz ; dioxyde de carbone ; optimisation ; simulation