الجمهورية الجزائرية الديمقراطية الشعبية
People's Democratic Republic of Algeria
وزارة التعليم العالي والبحث العلمي
Ministry of Higher Education and Scientific Research
المدرسة الوطنية العليا للتكنولوجيات المتقدمة
Higher National School ofAdvanced Technologies

**Department du second cycle**

Final Year Project to Obtain the Diploma of

**MASTER 2**

Field **: Process Engineering**

Specialty: **Organic Processes**

Theme

# Extraction process of mercaptans and $H_2S$ from LPG

Caustic and amine absorption

Realized by

SAOUDI Rania

Supervised by:

Mrs. SIZIANI Dhaouya

**Defended on 24 / 06 / 2024** **In front of the jury composed of:**

| | | | |
|---|---|---|---|
| Mr. BERKACHE Kamel | ENSTA | MCA | President |
| Mrs. SOUILAH Sihem | ENSTA | MAA | Examinator |
| Mrs. SIZIANI Dhaouya | ENSTA | MCB | Supervisor |
| Mr. RECHIDI Youcef | Refinery of Algiers | INGENIER | Co-supervisor |

**Academic year 2023 –2024**

# Acknowledgments

First of all, we would like to express our deep gratitude to our thesis supervisor, **Mrs. SIZIANI**, for her guidance, patience and trust throughout this research work.

We would like to express our sincere thanks to our Co-Supervisor **Mr. RICHIDI Youcef** for his support, motivation, trust, valuable advice, expertise and unwavering support have been invaluable and have greatly contributed to the success of this project.

We would like to thank **Mr. ACHACHE Rafik** for agreeing to accompany us in this study. His help, his knowledge, his expertise enriched this work and allowed us to question and reorient our memory problem.

Our thanks also go to all the professors of the Department of Process Engineering of the NATIONAL SCHOOL OF ADVANCED SCIENCE AND TECHNOLOGY, for their quality teaching and the knowledge they passed on to me during my years of study. Their passion and dedication to research inspired and motivated us to pursue our own scientific inquiry.

Thank you also to **the members of the jury** of our thesis defense for agreeing to be part of the jury. Their comments and suggestions were valuable and allowed us to improve the quality.

Finally, we would like to thank all the people who, directly or indirectly, contributed to the realization of this thesis. Whether through enriching discussions, advice or simply by their presence, their contribution was invaluable.

This thesis is the result of a collective as well as a personal work, and we are deeply grateful to all those who accompanied us.

## Dedications

First of all, I would like to thank **GOD** for guiding me, helping me and giving me the strength and courage to do this modest work.

I dedicate this humble work to my dear parents. My sweet mother **Salima KADDOUR CHERIF** and my dear father **Omar SAOUDI**, they are my first teachers and my greatest supporters. Thank you for always believing in me.

I am grateful to my sisters **Manel** and **Amina**, as well as my little brother **Abderazak** and my sister's husband **AMROUCHE Mounir** for their patience and moral support. I fear that the words have escaped me, thank you for always being by my side,

My future husband, **ACHOUR Younes**, deserves my gratitude for his moral support, patience, encouragement and presence during difficult times. I thank you for agreeing to share my fears and happiness with me.

I am grateful to my conscientious, respectful, gentle and understanding partner **SEGHIER Nour El Houda** with whom I made this work possible.

My sincere thanks to **Nadi Souad**, my dear, for my support, for my courage, for being by my side and supporting me throughout my training.

I dedicate this project to **Mr. Moustapha**, my Mathematics and Physics teacher during my Bachelor's degree in 2019, whose intellectual generosity made me what I am today.

**SAOUDI Rania**

# Abstract

This thesis explores the treatment and desulfurization of liquefied petroleum gases (LPG), with a focus on the Merox process. It highlights the need to remove sulfur compounds from LPG to meet environmental and safety standards. The Merox process is detailed, showcasing its efficiency in converting mercaptans to disulfides for easy removal. The study also discusses the Algiers Refinery's capabilities in processing LPG and compares the Merox process with other desulfurization methods. The environmental and economic advantages of the Merox process are emphasized, underscoring its significance in the oil and gas industry for producing high-quality, compliant LPG products.



**Keywords:** processing, desulphurisation, liquefied petroleum gas (LPG), Merox process, sulphur, sulphur compounds, environmental and safety standards, mercaptans, disulfides, Algiers refinery, desulphurisation methods, environmental and economic benefits, oil and gas industry, high-quality LPG products.



# Résumé

Cette thèse explore le traitement et la désulfuration des gaz de pétrole liquéfiés (GPL), en mettant l'accent sur le procédé Merox. Elle souligne la nécessité d'éliminer les composés soufrés des GPL pour respecter les normes environnementales et de sécurité. Le procédé Merox est détaillé, montrant son efficacité à convertir les mercaptans en disulfures pour une élimination facile. L'étude discute également des capacités de la raffinerie d'Alger à traiter les GPL et compare le procédé Merox à d'autres méthodes de désulfuration. Les avantages environnementaux et économiques du procédé Merox sont soulignés, mettant en avant son importance dans l'industrie pétrolière et gazière pour produire des produits GPL de haute qualité et conformes aux réglementations.



**Mots-clés:** traitement, désulfuration, gaz de pétrole liquéfié (LPG), processus Merox, soufre, composés sulfurés, normes environnementales et de sécurité, mercaptans, disulfides, raffinerie d'Alger, méthodes de désulfuration, avantages environnementaux et économiques, industrie pétrolière et gazière, produits LPG de haute qualité.



# ملخص

تستكشف هذه الأطروحة معالجة ونزع الكبريت من الغازات البترولية المسالة(GPL) ، مع التركيز على عملية .Merox وتسلط الضوء على ضرورة إزالة مركبات الكبريت من GPL للامتثال للمعايير البيئية ومعايير السلامة. يتم تفصيل عملية Merox، موضحةً فعاليتها في تحويل الميركابتانات إلى ثنائي الكبريتيدات لإزالتها بسهولة. تناقش الدراسة أيضًا قدرات مصفاة الجزائر في معالجة GPL وتقارن عملية Merox بطرق نزع الكبريت الأخرى. كما يتم تسليط الضوء على الفوائد البيئية والاقتصادية لعمليةMerox ، مما يؤكد على أهميتها في صناعة النفط والغاز لإنتاج منتجات GPL عالية الجودة ومتوافقة مع اللوائح.



**الكلمات المفتاحية:** المعالجة ، إزالة الكبريت ، غاز البترول المسال (LPG) ، عملية Merox ، الكبريت ، مركبات الكبريت ، معايير البيئة والسلامة ، mercaptans ، ثاني كبريتيد ، مصفاة الجزائر ، طرق إزالة الكبريت ، الفوائد البيئية والاقتصادية ، صناعة النفط والغاز ، منتجات غاز البترول المسال عالية الجودة.

# TABLE OF CONTENTS


LIST OF FIGURES ..... i

INTRODUCTION ..... 1

Chapter one : **Generality LPG and acid Gaz** ..... 2

I. Liquefied petroleum gas LPG ..... 3

I.1 Definition ..... 3
I.2 Chemical composition of LPG ..... 3
I.3 Sources of LPG ..... 3
I.4 Use of LPG ..... 3
I.5 Characteristics of LPG ..... 4
I.6 Advantages and risks of LPG ..... 5

II. Thiols and sulphides ..... 5

II.1 Definition ..... 5
II.2 Physical and chemical properties ..... 5
II.3 Industrial hazards of sulfides ..... 6

III. Why $H_2S$ is dangerous in LPG ..... 6

Chapter Two: **The Refinery of Algiers** ..... 7

I. Presentation of the company ..... 8

I.1 Presentation of SONATRACH ..... 8
I.2 Presentation of the Algiers Refinery ..... 8

II. Geographical location of the Algiers Refinery ..... 8
III. Objective of the Algiers Refinery ..... 8
IV. The products of the refinery in Algiers ..... 9
V. Main units of the Refinery ..... 9
VI. LPG Processing and Production Units ..... 10

VI.1 RFCC-U530 Unit ..... 10
VI.2 MEROX-U600 Unit ..... 10
VI.3 ARU(580) Amine Regeneration Unit ..... 11
VI.4 SRU(590) Sulphur Recovery Unit ..... 11

Chapter three: **The Techniques of LPG desulphurization** ..... 12

I. Absorption and desorption ..... 13

I.1 Absorption ..... 13
I.2 Desorption ..... 14

II. Alkanolamines ..... 14

Chapter four : MEROX Process ..... 17

I. Equipment and Process Description ..... 18

**I.1** Amine Absorber 600-C-001 ..... 18
I.2 Amine Wash Water Decanter 600-D-002 ..... 18
I.3 Amine regeneration (desorption/stripping) ..... 19
I.4 L'extractor Plus C-002 ..... 19
I.5 The soda regeneration section ..... 20

II. Process reactions ..... 20

II.1 Réaction d'absorption par amines (DEA-H2S) ..... 20
II.2 Parameter influencing the balance of reactions ..... 21
II.3 Réaction d'extraction (Mercaptan-NaOH) : ..... 21

II.4 Réaction de régénération de la soude :..... 22
References ..... 21

# LIST OF FIGURES

*Figure 1unités production/traitement du GPL* ..... *11*
*Figure 2 schema illustratif des parametres de choix d'un solvant chimique* ..... *16*
*Figure 3 MEROX Unit simulation* ..... *18*
*Figure 4 Amine Absorber and Wash Water Decanter* ..... *19*
*Figure 5 Caustic acid mercaptan extraction column* ..... *19*
*Figure 6 Process for regenerating caustic soda* ..... *20*

# INTRODUCTION

The treatment of liquefied petroleum gases (LPG) is a crucial step in the oil and gas industry, aiming to purify these hydrocarbons for safe and efficient use. Among the various methods employed for this process, the Merox (Mercaptan Oxidation) process stands out for its effectiveness and its ability to remove sulfur compounds from LPG. This chemical process is essential not only for enhancing the quality of the final products but also for ensuring their compliance with environmental regulations and safety standards. In this introduction, we will explore the fundamental principles of the Merox process, its significance in LPG treatment, and its benefits for the industry.

Chapter one :

# Generality LPG and acid Gaz

# I. Liquefied petroleum gas LPG

LPG is the most widely used alternative fuel in the world. It has several economic and ecological advantages as well as its many uses in industry, transport, heating and electricity production. etc.

Indeed, LPG emits less $CO_2$ and no particles; and offers all the advantages of a gasoline engine, which is still much less popular than gasoline and diesel. Whereas before a few decades, LPG had a bad reputation related to the risk of explosion, due to its high flammability. Now, the regulations are stricter, the gas tank is much stronger and safer than that of the gas tank.

## I.1 Definition

Liquefied petroleum gas (LPG) is a combination of hydrocarbons, mainly propane and butane, that remains in gas form at room temperature. It can be liquefied under low temperatures and moderate pressure or higher pressures and ambient temperature.

LPG stores a large amount of energy in a small volume, making it easy to transport and market in steel cylinders. It is used as a fuel for vehicles and in various applications. The characteristics of LPG depend on its hydrocarbon content.

## I.2 Chemical composition of LPG

LPG is a blend of propane and butane, with additional compounds in trace amounts, which differ by country. It generally contains propylene, butene, methane, ethylene, pentane, and occasionally butadiene, acetylene, and methyl-acetylene [1].[1]

## I.3 Sources of LPG

Approximately 60% of LPG is sourced from natural gas fields, while the remaining 40% is obtained from oil fields during refinery processes. This includes recovery from crude oil in atmospheric distillation columns, conversion of heavy residues through catalytic cracking, and Petroleum Products Reforming units. [1][1]

## I.4 Use of LPG

LPGs are commonly used when natural gas networks are not available. They have various applications, including itinerant uses like catering, lighters, and lamps, domestic uses like electricity, air conditioning, and heating, and industrial uses like in petrochemicals, textile, and paper industries. They can also be used in agricultural applications as an alternative to chemicals for weed control and as a better alternative fuel for vehicles.

## I.5 Characteristics of LPG

Understanding the characteristics of LPG is crucial for its use, performance evaluation, and environmental impact assessment. These characteristics encompass vehicle compatibility, performance-influencing properties, safety during handling and storage, and environmental advantages over conventional fuels. By studying these features, we can make informed decisions regarding sustainable mobility and responsible energy resource use.

Key Characteristics:

- Density: LPG is lighter than water in its liquid state and heavier than air in its gaseous state.
- Vapor pressure: The vapor pressure of LPG determines its evaporation rate. Higher temperatures result in increased pressure. At 15°C, the vapor pressure is 7.5 Bars for propane and 1.7 Bars for butane.
- Smell and color: LPG is colorless and odorless, but it is odorized for leak detection purposes by adding a Sulphur compound called mercaptan.
- Coefficient of expansion: LPG has a high coefficient of expansion in its liquid state, which must be considered during storage.
- Boiling temperature: LPG changes from a liquid to a gaseous state when heated. The boiling temperature for butane is -0.6 °C, propane is -40 °C, and LPG is -25°C.
- Higher calorific value: LPG's calorific value measures the heat released during combustion. LPG has a higher calorific value, making it more efficient. Examples include PCS (iC4) at 29460 kcal/kg and PCS (C3) at 22506 kcal/kg.
- Latent heat: The amount of energy required for LPG to change states is its latent heat. Propane has a latent heat of 84.78 Kcal/kg, while N-butane has 90.01 Kcal/kg.
- Chemical hazard properties: LPG is extremely flammable and can form explosive mixtures with air. It is corrosive to certain materials and lacks lubricating properties. Inhaling LPG can lead to anesthetic and narcotic effects.

These characteristics highlight the importance of proper handling and precautions when using LPG to ensure safety and efficiency.

### I.6 Advantages and risks of LPG

LPG has several advantages, including its eco-friendliness and compliance with strict emission standards. Compared to petrol and diesel, LPG emits less $CO_2$, reducing greenhouse gas emissions and combating climate change. It also generates fewer air pollutants such as fine particles, carbon monoxide, nitrogen oxides, and unburned hydrocarbons. LPG-powered vehicles often meet the strictest environmental standards. In terms of equipment safety, LPG tanks have safety valves to release excess pressure, minimizing the risk of leakage and explosion. Additionally, LPG is stored in specialized tanks designed to withstand accidents and bumps. However, there are risks associated with LPG, such as the risk of leakage, explosion, and fire. LPG can easily evaporate into flammable vapors, and it contains acidic impurities that can be harmful. Combusting non-desulphurized LPG can release sulfur dioxide, which is toxic to catalysts used in refining processes.

## II. Thiols and sulphides

### II.1 Definition

Thiols, also known as mercaptans or thioalcohols, are organic compounds with sulfhydryl (–SH) groups. They have a strong and unpleasant smell even at low concentrations. Thiols can form mercaptides when the hydrogen in the (–SH) group is replaced by mercury or other heavy metals. Hydrogen sulfide ($H_2S$), also called sulphur hydride, is a colorless acid gas that reacts with basic aqueous solutions and metals. It is part of the sulfide group formed by sulfur and metallic elements.

### II.2 Physical and chemical properties

$H_2S$ is a gas with the smell of rotten eggs. It is flammable and decomposes when burned. In the presence of excess oxygen, it ignites spontaneously at 260 °C. As a strongly reducing compound, it reacts with oxidants to cause corrosion of oxidizable metals and alloys. Complete combustion of $H_2S$ produces sulfur dioxide, a toxic, polluting gas. $H_2S$ is soluble in certain solvents and water to form a weakly acidic solution called hydrogen sulfide. It is heavier than air and tends to accumulate in poorly ventilated areas. It can be liquefied at -60.2 °C, which is also its boiling point. The melting point of $H_2S$ is 187 K. The specific gravity of this liquid at 60 °C and 1737 kPa is 0.960 g/l. The triple point is -85.5 °C, and the critical point is 8.937 MPa and 100 °C. The molecular weight of H2S is 31.08 g/mol.

### II.3 Industrial hazards of sulfides

Industrial processes using mercaptans present several types of problems, including fire and explosion hazards and possible adverse effects on workers' health.

- Fire and explosion

Mercaptans have a lower explosion limit of 4% by volume. The risk of fire is higher in the presence of heat sources; the autoignition temperature is 250 °C.

- Health risks

Mercaptans in contact with liquids or vapors can cause irritation to the skin, eyes and upper respiratory tract mucous membranes.

Accurate exposure of workers to high concentrations of mercaptans can, depending on the intensity (above 50 ppm), produce serious effects ranging from mild to severe: muscle weakness, nausea, dizziness and anesthesia, poisoning, respiratory paralysis, unconsciousness, and even fatal consequences.

## III. Why $H_2S$ is dangerous in LPG

$H_2S$ is highly undesirable in liquefied petroleum gas (LPG) for the following reasons:

- Storage: $H_2S$ can cause corrosion in expensive tanks when produced LPG is stored for further distribution.
- Polymer yields: Sulfides can degrade polymer properties in polyolefins such as polypropylene.
- Catalysts: $H_2S$ is known to poison catalysts in reactions using LPG as a starting material.
- Emissions: When propane or other liquefied gases are burned, $H_2S$ oxidizes to form $SO_2$, a particularly harmful emission.[2]

# Chapter Two:
# The Refinery of Algiers

# I. Presentation of the company

## I.1 Presentation of SONATRACH

Sonatrach is an oil and gas company located in Algeria. The date of its founding was December 31, 1963. It is a major player in the oil sector. SONATRACH is ranked the top company in Africa.[3]

The Sonatrach oil and gas group is engaged in the extraction, processing, pipeline transportation, marketing, and exploration of hydrocarbons and their derivatives.

In addition, Sonatrach is growing its mining, petrochemical, power generating, new and renewable energy, and saltwater desalination operations. [4]

## I.2 Presentation of the Algiers Refinery

Constructed in 1959, the refinery in Algiers started operating on April 15, 1964.It covers the needs for necessities like LPG, diesel, gasoline, and more. in addition to the products that form the basis of the petrochemical sector.

95% of the fuel requirements of the Central area of Algeria are met by the 3.6 million tons of Saharan crude oil processed annually by the Algiers refinery.[5]

The refinery installed its RFCC Block for catalytic cracking (associated LPG treatment, acid water treatment, amin regeneration, and Sulphur recovery) and its MS Block for the production of components for the manufacture of gasoline (naphtha hydro processing, CCR reforming, and isomerization) between November 2019 and February 2020.[6]

# II. Geographical location of the Algiers Refinery

The refinery in Alger is located 5 km south of EL Harrach and 20 km east of Alger, occupying an area of 182 hectares. This location was chosen after a soil study and the discovery of a water tank needed for the supply of cooling systems.

The refinery of Algiers is located in Sidi Arcine in the commune of Barraki, 20 km east of Alger and is located at an altitude of 20 m. The site of the refinery in Algiers occupies a total area of 182 hectares (built and fenced 96 hectares) and is delimited.[7]

# III. Objective of the Algiers Refinery

The main task of the Algiers Refinery is to process the crude oil from the Hassi-Messaoud field, as well as the condensate from the Hassi-R'Mel fields. These operations make

it possible to obtain different oil cuts for the production of various derivatives such as gasoline, diesel, oil, and many others.

## IV. The products of the refinery in Algiers

The refinery has a wide range of products that meet national and international standards which are:

- Commercial butane and propane: used as fuel in gas vehicles & for domestic heating.
- Naphtha (90% gasoline + 10% total solvent): a raw material mostly used in petrochemicals MS Block + exported.
- Lead-free essences and gas-oil: are used in vehicle motors.
- Kerosene: is used as fuel in aviation.
- Heavy fuel is exported feed RFCC Unit.

## V. Main units of the Refinery

Sonatrach consists of several units where crude oil is transformed from prime to different finished products:

- Atmospheric distillation unit ″Topping″ (U 100).
- Liquefied gas separation unit "gas-plant" (U 300).
- MS block section: is divided into three units:
  - NHT Naphtha Hydrotreatment Unit (U 500).
  - Naphtha Isomerization unit (U 510).
  - CCR Catalytic Reforming Unit (U 520).
- RFCC catalytic cracking unit (U 530).
- Block Sulphur section: break down into four units:
  - Acid gas (fuel-gas) treatment unit with amine (U 560).
  - Acid water stripping unit (U 570).
  - Amin Regeneration Unit (U 580).
  - Sulphur Recovery Unit (U 590).
- Utilities consists of several units on site; Raw Water Unit, Fire Water unit, Demineralized water unit, The torch... etc.
- Storage Park consisting of 53 cylindrical tanks with a total capacity of 474500 m3 for the storage of the various products and 9 spherical reservoirs with a capability of 15106 m3 to store propane and butane.

- Laboratory the laboratory performs on the various intermediate or finished products a number of conventional tests to control the specifications of the petroleum products according to the standards and to detect anomalies in the operation of the process to optimize the parameters. The laboratory department is part of the technical subdivision and consists of two departments:
    - Control Service : As its name suggests, it is responsible for controlling the quality of products and for this purpose performs different types of analyses:

    Distillation to verify the starting and end point of the oil cut, The measurement of density, The measurement of the TVR, Verification of the following points: freezing, disturbance, and lightning point of diesel and kerosene and/or A1 jet, Measurement of the conductivity of kerosene and or A1, Checking the color of certain products, Measurement of the gasoline index using a CFR engine.
    - Chemical department : The department responsible for performing qualitative and quantitative analyses on the various finished products and process waters.[7]

# VI. LPG Processing and Production Units

## VI.1 RFCC-U530 Unit

The RFCC unit is designed to produce a lighter distillate with better value and maximum efficiency. Indeed, the RFCC unit processes a total feed rate of 1,000,000 t/year of the RCO + HGO heavy crude oil fractions from the ADU unit (unit 100).

The products from this section are acid fuel gas, acid LPG and light gasoline, which are processed at high temperature and medium pressure in the presence of a finely divided silica and alumina catalyst.

## VI.2 MEROX-U600 Unit

The MEROX unit is designed primarily to decrease the sulfur content of the acid LPG. Container in the load carried by the mixed flow of LPG C3/C4 of the RFCC unit, precisely of the 530-D-045 debutanizer head. Before being separated into propane and butane products in the C3/C4 530-C-045 separator. The treatment occurs in two stages:

- Elimination of $H_2S$ by absorption with amine.
- The elimination of mercaptans by caustic extraction.

The planned capacity of the MEROX Unit is 1172 Sm3/day (48.8 Sm3/h) of a C3/C4 mixed feed, corresponding to the maximum fuel mode of the RFCC Unit.

The purpose of the Merox Unit is to ensure that Sulphur levels meet the specifications for propane and butane products.

As the process of the Merox Unit is fully integrated with the RFCC Unit (U530), the utilities are common to both units. All common installations in this block of units are referred to by unit number 535

The Merox U600 Unit is designed to produce a treated C3/C4 LPG product that will be directed to the C3/C4 530-C-045 separator of the RFCC unit.

## VI.3 ARU(580) Amine Regeneration Unit

The purpose of the ARU unit is to process a combined load of 180 T per year of sulfur-rich amine from the FGATU (U-560) and Merox (U-600) units. The amine in circulation is di-ethanol amine (DEA) in solution of 25% by weight. The regenerated lean amine must comply with limit values: 0.03 moles $H_2S$/mol DEA max. The amine regeneration unit consists of the following sections:

- Rich amine vaporization flask section
- Amine regeneration section
- Lean amine storage tank/circulation pump section/filtration section
- Amine unloading/dilution plants/transfer section
- Closed amine purge section
- Chemical unloading, storage, dilution and injection plants

## VI.4 SRU(590) Sulphur Recovery Unit

The objective of the sulfur recovery unit is to convert the sulfur species present in the sour gas stream of the ARU-580, SWS-570 refinery units and the flow of future units in order to comply with the environmental requirements of minimizing the air pollution of the refinery. The Sulphur recovery unit consists of the following sections:

- Section Claus.
- Tail gas treatment section.
- Incinerator and chimney section.
- Degassing section

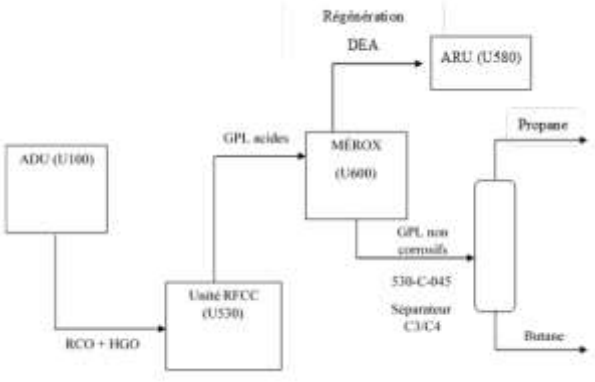



***Figure 1:*** *LPG production/processing units*

Chapter three:

# The Techniques of LPG desulphurization

Petroleum gas desulphurization and oil cutting remains very necessary for low sulfur content in combustion and refining processes, in order to avoid equipment damage (corrosion) and to ensure the quality of finished products (to ensure the required specifications of gas/liquid products, as well as compliance with environmental standards).

Acid gas treatment processes are diverse, including adsorption, catalytic oxidation, hydrodesulphurization, extraction and removal by absorption. The choice of these processes depends on the composition of the gas mixtures, the material transfers and the characteristics of the reactants, with the aim of achieving the desired characteristics for the final product.

This chapter deals with a theoretical approach on one of the desulphurization processes used in the MEROX process of the Algiers refinery: liquid-liquid absorption by alkanolamines.

# I. Absorption and desorption

## I.1 Absorption

Absorption consists of bringing a mixture of gases (solute) and a liquid (solvent) into contact in order to preferentially solubilize a compound. It consists of shifting the thermodynamic equilibrium, and promoting the transfer of matter from the gas phase by the selective retention capacity of liquid solvent. The recovery of the substance that has dissolved in the liquid is called desorption.

High pressures and low temperatures promote absorption. Depending on the type of solvent, the gas is absorbed by physical dissolution (physical absorption) or chemical reaction (chemical absorption). In most cases, a desorption step for solvent regeneration follows the absorption step to separate the gas components present in the solvent. High temperatures or low pressures reduce the solubility of gases in the solvent, resulting in the expulsion of gases.[8]

### I.1.1 Types of absorption

- ❖ Physical absorption (without chemical reaction):

The solvent in the physical absorption process has a certain affinity for the constituent to be absorbed ($CO_2$ or $H_2S$) in such a way as to form physical Van der Waals bonds after contact between the solvent and the gas to be purified. This process gives best results at low temperatures and high $CO_2$ partial pressure, and is often used to treat gases with high carbon dioxide levels (syngas).

- Physical solvents

The first historical physical solvent is water, but acid gases have too low a solubility in water for this solvent to be effective. Methanol and propylene carbonate are the oldest solvents on the market. The most well-known and widely traded physical solvents [19] .

- ❖ Chemical absorption:

Through the action of the difference in the partial pressure of acid gases between the gas phase and the so-called chemical solvents, the latter absorb the acid gases, which gives rise to a very exothermic reaction. These solvents are weak bases that react with the GA in a reversible way, which allows the reaction to be reversed (desorption) and reused in a closed cycle. These solvents absorb negligible amounts of hydrocarbons compared to physical solvents. They have a good treatment capacity, especially when the partial pressures of the contaminants are low[18] .

- chemical solvents

Chemical solvents can be: washing with caustic soda, aqueous solutions of alkanolamines, or amines with steric crowding.

Chemical solvents commonly used for $H_2S$ desulphurization or acid gas removal are alkanolamines [20].

## I.2 Desorption

Desorption is the reverse transformation of sorption (adsorption or absorption), by which the absorbed molecules detach from the substrate. Thermal desorption such as incineration, drying and heating. This method is often used when the solvent is volatile and has a high vapor pressure at higher temperatures.

Chemical desorption: Chemical desorption refers to the removal of an adsorbed substance by specific chemical reagents on the surface of a material by
chemical reactions.

In many processes, when alkanolamines that have been used to absorb $H_2S$ are regenerated, for example, the solution is regenerated by heating it; the desulphure decomposes then by releasing the amine and $H_2S$ which desorpes [21] .

# II. Alkanolamines

Several commercial processes are used to soften liquid light hydrocarbons, the most common being amine treatment systems, caustic washes, and molecular sieves.

In the case of large quantities of dissolved acid gases, a caustic wash may not be the best option due to the cost of caustic soda, waste disposal issues, and the efficiency of the process in meeting the sales specifications of the liquids. The disadvantages of molecular sieves are high investment and operating costs, the undesirable formation of SOC in the presence of $H_2S$ and $CO_2$, and the inability to meet ppm concentrations in the products sold. Therefore, amine-based treatment is generally the most cost-effective and technologically sound choice for liquid softening when significant amounts of $CO_2$ are present[26].

They are therefore derivatives of ammonia in which the hydrogen atoms are replaced by an alcohol group (e.g. methanol, ethanol). The hydroxyl group of alkanolamines increases the solubility in water and decreases the vapor pressure of the aqueous solution

Alkanolamines have two types of functions: an amine function that ensures the basicity of the molecule and an alcohol function that ensures a high solubility of the amine in water.

Amines can be classified into three main families:

— Primary amines: Monoethanolamine (MEA), Diglycolamine (DGA).

— Secondary amines: Diethanolamine (DEA), Dispropanolamine (DIPA).

— Tertiary amines: Methyldiethanolamine (MDEA).

$H_2S$ is more soluble in amines than hydrocarbons. Thanks to the acid-base contact which makes them more suitable for the treatment of acid gases. The high affinity of ethanolamines with $H_2S$ is due to the nature of the amine and according to their steric size and the degree of nitrogen substitution.

The choice of amine has another as an absorbent differ mainly from a few characteristics:

— Solubility: that it be very selective towards the absorbat.

— Low volatility (so as not to be dragged)

— Low viscosity (increase in absorption rate, faster flow) since a less viscous solvent is preferred in order to avoid clogging and pressure drop in the pumping device.

— Is not very corrosive to the materials

— Either non-flammable Not very alterable

— Low freezing point

— Low price[25].

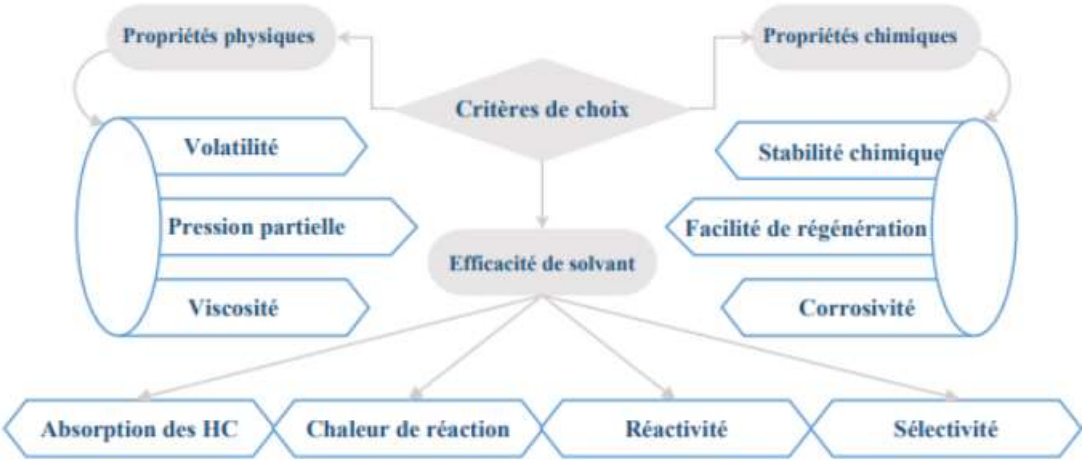



*Figure 2 schema illustratif des parametres de choix d'un solvant chimique*

Chapter four :

# MEROX Process

The MEROX process (MERcaptan OXidation) is an industrial softening process used for the chemical treatment of petroleum distillates with oxidative catalytic agents to remove acidic products (mainly mercaptants, COS,$H_2S$ ) or transform them into disulfides. The merox process goes through two main steps:

1. Softening of liquid hydrocarbons by removing mercaptans in an extraction column enriched with NaOH caustic soda.

The operation is preceded by an essential pre-stage of $H_2S$ removal, passing through an alkanolamine absorption column.

2. Regeneration of Amine (the absorption solvent)

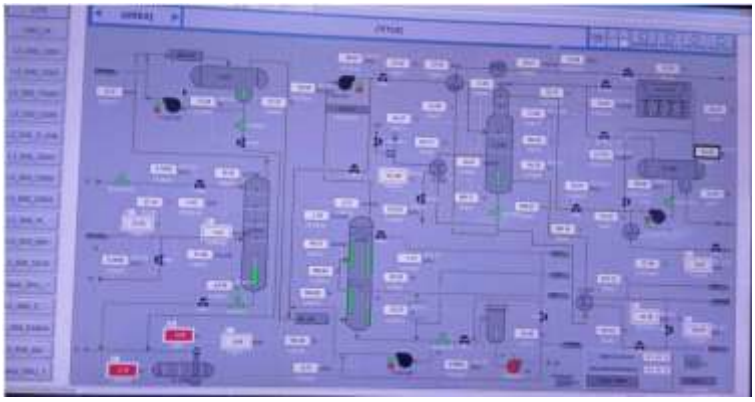


***Figure 3:*** *MEROX Unit simulation*

# I. Equipment and Process Description

## I.1 Amine Absorber 600-C-001

The amine absorber is a 10-plate absorption column, whose role is to remove $H_2S$ from the LPG from the RFCC debutanizer (530-C-044), by counter-current contact of a stream of an alkanolamine solution (DEA) to produce the absorption reaction. The amine absorber is a vertical tank consisting of a series of specially designed perforated trays. Each tray has an amine inlet tank with an inlet weir separating this tank from the central mixing area.

## I.2 Amine Wash Water Decanter 600-D-002

The wash water decanter is a horizontal tank installed to remove traces of solubles and/or entrained amines from the LPG stream downstream of the amine absorber. The water is left to settle into the wash water tank and then is recycled back to the inlet for later contact. The fresh water injection rate must be adjusted to achieve the desired concentration of amine in the wastewater.

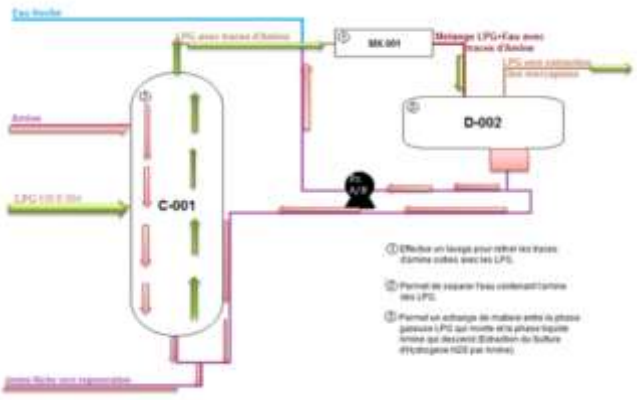



***Figure 4:*** *Amine Absorber and Wash Water Decanter*

## I.3 Amine regeneration (desorption/stripping)

The rich amine is delivered to the 580-D-001 spray bottle. From the 580-D-001 Rich Amine Vaporizer Flask, the Rich Amine is pumped by the flow controlled feed pumps of the 580-P-008-A/B regenerator, reset by level control of the vaporization tank, to the 580-C-001 Amine Regeneration Column after preheating in the 580-E-001-A/B Lean/Rich Amine Heat Exchangers. The regenerated lean amine from the bottom of the regeneration column is pumped by the downhole pumps of the 580-P-003-A/B regenerator to the 580-E-001-A/B lean/rich amine heat exchanger to exchange heat with the liquid rich amine on the tube side and cool it to 77°C.

## I.4 L'extractor Plus C-002

The Extractor Plus is a combined column with pre-treatment, extraction and post-processing sections. -The caustic soda pre-wash section is located in the lower part of the tank. Because of their difference in density, the hydrocarbon flows upwards while the caustic soda flows downwards.

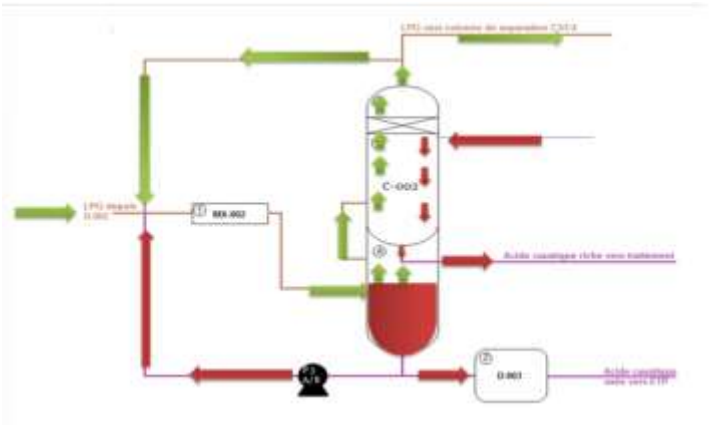


***Figure 5:*** *Caustic acid mercaptan extraction column*

### I.5 The soda regeneration section

The mercaptan-rich caustic solution containing the MEROX WS reactive catalyst is drawn from the bottom of the extraction section of the Extraction Plus column and sent to the regeneration section of the unit. The mercaptan-rich solution is lightly heated and carefully mixed with a regulated amount of air before entering oxidizer 600-D-004. The mixed air, caustic solution and desulphurised oil phase is then directed to the 600-D-006 disulfide separator, where these elements are separated.

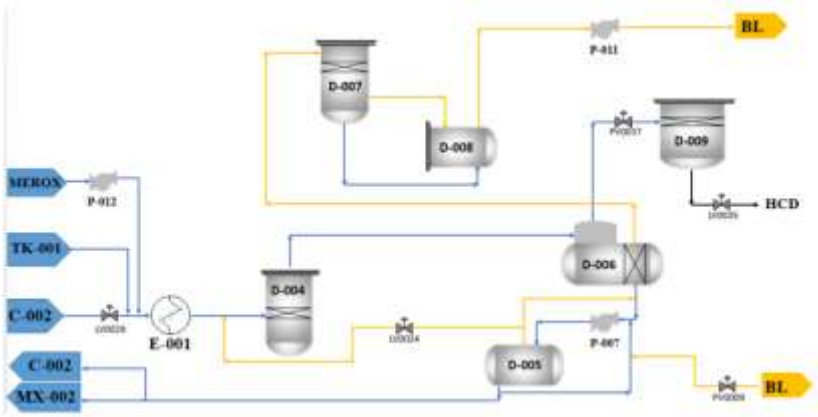



***Figure 6:*** *Process for regenerating caustic soda*

## II. Process reactions

### II.1 Réaction d'absorption par amines (DEA-H2S)

The process of absorbing $H_2S$ using an aqueous solution Diethanolamine (DEA) which has a high affinity for $H_2S$ and a low solubility in hydrocarbons,

Hydrogen sulfide ($H_2S$) is a weak acid that weakly ionizes in water to form hydrogen ions and sulfide ions, as shown in the following reaction:

$$H_2S \rightleftharpoons H^+ + HS^-$$

DEA is a weak base and ionize in water to form amine ions and hydroxyl ions:

$$(CH_2OHCH_2)_2\,NH + H_2O \rightleftharpoons (CH_2OHCH_2)_2\,NH^{2+} + OH^-$$

The dissolution of $H_2S$ in the amine solution forms a weakly bound salt, and the sulfide ion is thus absorbed by the amine solution, as shown in the reaction:

$$(CH_2OHCH_2)\,2\,NH_2{}^+ + HS^- \rightleftharpoons (CH_2OHCH_2CH_2)_2\,NH_2SH$$

The reversibility of the reaction thus allows the amine solvent regeneration process and the continuous removal of $H_2S$ by the regenerated amine solvent.

## II.2 Parameter influencing the balance of reactions

The absorption of $H_2S$ in the amine solution is promoted by:

— Low temperatures:

The lower the temperature of the lean amine solution, the better the removal of $H_2S$ when processing a hydrocarbon gas. However, the temperature of the lean amine is limited by the temperature of the gas to be processed.

The temperature of the lean amine should be maintained between 3 and 6 °C higher than that of the gas supply stream to avoid any possible condensation of these vapours.

— Loading of acid gas:

An effective means of eliminating acid gases depends on a good regeneration of the amine solution, as we will see later. However, this will also depend on limiting the concentration of $H_2S$ in the rich amine to favor the forward direction of the reaction given in equation (3).

— A high concentration of amines:

The concentration of the uncombined amine ion is favoured by a high concentration of amine, good regeneration and absence of strong acids.

This is based on a lower heat requirement for desired $H_2S$ removal, lower chemical losses, and for fewer operational issues.

The concentration of migrated free amine ions is affected by the efficiency and control of amine regeneration. The fewer sulfide ions there are in the lean amine, the higher the concentration of free amine ions available for $H_2S$ removal.

In most cases, lean amine should contain no more than 0.03 moles of $H_2S$ per mole of amine and no more than 0.1 moles of $CO_2$ per mole of amine

## II.3 Extraction reaction (Mercaptan-NaOH):

The Merox process includes catalytic oxidation of mercaptans at ambient temperatures and pressures, in disulfide in the presence of oxygen and an alkaline medium. The air ensures the oxygen supply, but the alkaline medium is provided by the caustic soda. The overall reaction can be written:

$$\mathrm{R{-}SH} + \tfrac{1}{4}\,\mathrm{O_2} \rightleftharpoons {}_2\,\mathrm{RSSR} + \tfrac{1}{2}\,\mathrm{H_2O}$$

Most oil fractions are composed of a mixture of mercaptans insofar as the R chain could have an atom with ten or more carbon atoms in the chain.

When this reaction occurs, two different mercaptans can enter the reaction. This is indicated by the display of R and R' in the reaction. The reaction is then written:

$$2\,RSH + 2\,RSH + O_2 \rightleftharpoons RSSR + 2\,H_2O$$

The degree of completeness of the extraction of mercaptan depends on the solubility of a mercaptan in the alkaline solution, which in turn depends on the following:

— Molecular weight of mercaptan.

— Degree of branching of the mercaptan molecule.

— Concentration of caustic soda.

— Temperature of the system.

The following equation illustrates the mechanism of mercaptan extraction:

$$RSH + NaOH \rightleftharpoons NaSR + H_2O$$

## II.4 Soda regeneration reaction:

The regeneration process is based on the ability of a catalyst composed of ferrous metal chelates in an alkaline environment to promote the oxidation of mercaptans to disulfides using air as a source of oxygen

The ability of the MEROX process to completely regenerate caustic depends on the following equation:

$$NaSR + \tfrac{1}{4}\,O_2 + \tfrac{1}{2}\,H_2O \rightleftharpoons \tfrac{1}{2}\,RSSR + NaOH$$

The amount or molecular weight of the mercaptan present cannot be controlled, as it is a function of the raw source and the distillation cut of the feedstock, however, for a mercaptan of the same molecular weight, the primary mercaptan will be the most completely extracted, the secondary mercaptan will be less completely extracted, and the tertiary mercaptan will be the least completely extracted. This too is a function of the raw material.

# CONCLUSION

The Merox process plays a vital role in the treatment of liquefied petroleum gases (LPG), significantly contributing to the purification and enhancement of these hydrocarbons. Through specific chemical reactions, this process efficiently removes sulfur compounds, making LPG safer for transportation and use while meeting stringent environmental standards.

In conclusion, the Merox process represents a critical technological advancement for the oil and gas industry. It ensures not only the quality and safety of LPG but also optimizes the profitability of refining operations. As environmental and safety requirements continue to evolve, the role of the Merox process in LPG treatment will remain indispensable, enabling the industry to meet future challenges with efficiency and sustainability.

# References


1. ABDERRAOUF, F., N. OULED JAAFRI, and O. KHELIFI, *Désulfuration de GPL au niveau de la raffinerie d'Adrar*. 2022, UNIVERSITE AHMED DRAIA-ADRAR.
2. Veerakumar, U., et al. *Innovation and Technology Advancements in Measurement of Ultralow Sulfur in Natural Gas Products*. in *Abu Dhabi International Petroleum Exhibition and Conference*. 2017. SPE.
3. Boubaker, L., M. Djebabra, and S. Saadi, *Contribution of stakeholder theory in the management of environmental quality of Algerian firms: case study of the SONATRACH group, Algeria.* Management of Environmental Quality: An International Journal, 2014. **25**(3): p. 335-351.
4. SANDOULY, P., *Les 500 premières entreprises africaines.* Jeune Afrique, 2008.
5. Shammas, P., *Algeria: Review of petroleum, politics and risks.* Energy exploration & exploitation, 1999. **17**(1): p. 1-65.
6. Tayeb, B. and L. Akli, *Etude d'Automatisation et de Régulation de la pression dans le ballon de gaz 500-D-002 à la raffinerie d'Alger SONATRACH*. 2014, Université Mouloud Mammeri.
7. Farid, K. and K. Yazid, *Etude, amélioration et automatisation du thermo-circulateur de la raffinerie de Sidi-Arcine (Alger)*. 2018, Université Mouloud Mammeri.
8. MOHAMED, M., *L'AMINE.* 2004.