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Thème :

Simulation Comparative Study and Economic Analysis of BOG recovery processes- Case study: CP2K complex SONATRACK- SKIKDA.

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DEDICATION

This dissertation is dedicated to my beloved mother, whose unwavering love and support have been my guiding light. Your strength, wisdom, and encouragement have been the foundation upon which I have built my dreams.

To my father, whose steadfast support and belief in me have provided the strength I needed to persevere. Your guidance and love have been instrumental in my journey.

To my dear departed brothers, who remain forever in my heart. Your memories have been a source of inspiration and motivation throughout this journey. I hope to make you proud.

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To my grandmother, who wished to see me reach this milestone but is no longer with us. Your love and dreams for me have been a driving force in my life. I hope this achievement honors your memory.

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And to all those who have given me support, whether through words, actions, or simply believing in me—this work would not have been possible without you. Thank you for being my pillars of strength.

With deepest gratitude,

Raid Ziat

DEDICATION

A special dedication to my parents for their efforts throughout the academic path

Zouizi Abdelmadjid Walid

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Abstract

Currently, in the petrochemical industry, specifically in the polyethylene high density industry, a large amount of ethylene vapor in cryogenic storage tanks is sent to the flare. The aim of this study is to find the optimal method in terms of energy and cost for BOG ethylene recovery. To achieve that aim, a comparative study containing a group of refrigerants, represented by propane, propylene, nitrogen, and ammonia, was conducted using the simulation software Aspen HYSYS. V11.

From the comparative study, it was established that propane is the best refrigerant compared to other refrigerants, either on the technical or economic side. The use of propane as a refrigerant for ethylene BOG recovery yielded promising financial outcomes: total expenses incurred amounted to $664,868.5 with an annual profit of $5,630,525.5. This outcome underscores the economic viability and operational benefits of implementing a BOG recovery system, not only reducing waste but also enhancing profitability through effective resource utilization.

Keywords: ethylene, boil off gas, cryogenics, liquefaction, cryogenic processes, refrigeration loop, recovery, loss, investment.

Résumé

Actuellement, dans l'industrie pétrochimique, en particulier dans l'industrie du polyéthylène haute densité, une grande quantité de vapeurs d'éthylène dans les réservoirs cryogéniques est envoyée à la torche. L'objectif de cette étude est de trouver la méthode optimale en termes d'énergie et de coût pour la récupération du *BOG* (*boil-off gas*) d'éthylène. Les méthodes examinées dans cette étude étaient les cycles de Joule-Thomson et Claude pour la liquéfaction du BOG d'éthylène. Ces méthodes ont été mises en œuvre en utilisant le logiciel de simulation “Aspen Hysys V11”, qui a permis l'analyse comparative de différents réfrigérants, y compris le propane, le propylène, l'azote et l'ammoniac. La simulation a fourni des informations détaillées sur l'efficacité et la faisabilité économique de chaque option de réfrigérant. Sur la base d'une étude technique et économique, nous avons constaté que le propane est le réfrigérant optimal pour la récupération du BOG d'éthylène. Le propane a démontré une performance supérieure en termes d'efficacité énergétique et de rentabilité, ce qui en fait la meilleure option pour maximiser la récupération de l'éthylène *boil-off* tout en minimisant les coûts associés et en augmentant la productivité de la liquéfaction de l'éthylène.

Mots-clés : éthylène, *boil-off*, cryogénie, liquéfaction, procédés cryogéniques, boucle de réfrigération, récupération, perte, investissement.

TABLE OF CONTENTS

LIST OF ABBREVIATIONS

- CP1K: Petrochemical Complex No. 1 Skikda
- CP2K: Petrochemical Complex No. 2 Skikda
- PEHD: High-Density Polyethylene (HDPE)
- ENIP: National Petrochemical Industries Company
- FIR: Intervention and Reserve Force
- GL1K: Natural Gas Liquefaction Train of Skikda
- ENPC: Industrial Group of Plastics & Rubbers
- ENCG: National Fats Company
- B.O.G: Boil-Off Gas
- OMI: International Maritime Organization (IMO)
- PSV: Pressure Safety Valve
- SQUID: Superconducting Quantum Interference Device
- API: American Petroleum Institute
- TEMA: Tubular Exchanger Manufacturers Association
- Kuop: Oil Characterization Factor
- TBP: True Boiling Point Distillation
- ASTM: American Society for Testing and Materials
- PFD: Process Flow Diagram
- PID: Piping & Instrumentation Diagram
- USGC: U.S. Gulf Coast
- FCT: Full Containment Tank
- SCT: Single Containment Tank
- Pr: Prandtl Number
- Q: Heat Quantity [KW]
- M: Mass Flow Rate on the Shell Side (kg/h)
- ρ: Density (kg/m^3)
- Cp: Specific Heat at Constant Pressure (kJ/kg°C)
- Cv: Specific Heat of a Fluid at Constant Volume (kJ/kg°C)
- FLA: Location Factor

LIST OF TABLES

LIST OF FIGURES

General Introduction

GENERAL INTRODUCTION

Storage tanks play a pivotal role in safeguarding and managing liquefied gases like ethylene, serving as essential containers designed to withstand varying temperatures and pressures. Despite their robust construction, these tanks are susceptible to boil-off, a natural phenomenon where stored liquefied gases evaporate due to environmental conditions or operational factors. Effective storage tank design integrates insulation and pressure management systems to mitigate boil-off rates and uphold product integrity.

In the face of a looming energy crisis, companies are intensifying efforts to combat energy waste through tailored strategies. Energy conservation stands as a paramount concern for operators within the SONATRACH group, underscoring the critical importance of controlling, optimizing, and minimizing operational costs. Within this context, the management of boil-off ethylene gas flaring rates at the CP2K complex demands heightened attention and rigorous measures to curtail energy and raw material losses.

Efficient energy management, including optimizing ethylene recovery from BOG, enhances cost-effectiveness and profitability for industrial operations. Additionally, minimizing flaring through efficient recovery methods reduces greenhouse gas emissions and pollutants, aligning with global efforts to mitigate climate change and comply with regulatory standards.

The aim of this study is to identify the optimal method for energy-efficient and cost-effective recovery of ethylene from BOG. This research focuses on a comparative analysis of refrigerants—including propane, propylene, nitrogen, and ammonia—that are utilized in BOG recovery systems. The study comprises two main sections: the first is a theoretical exploration encompassing cryogenics, types of storage tanks, boil-off phenomena, and an overview of fluids and refrigerant cycles pertinent to the study.

The second section consists on an experimental investigation utilizing Aspen HYSYS V11 software to establish operational parameters, followed by a technical-economic assessment to determine the most suitable refrigerant for BOG recovery.

First Section: Bibliographic Review

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Bibliographic Review

INTRODUCTION

Storage tanks are integral components within various industries, particularly in the petroleum sector, facilitating the safe storage and distribution of crude oil and refined products. This chapter explores two primary types of storage tanks: fixed roof tanks and floating roof tanks. Fixed roof tanks maintain crude oil at atmospheric pressure but face challenges with temperature-induced pressure differentials, requiring specialized relief valves. Floating roof tanks, designed to store products with higher vapor pressures like gasoline and naphtha, offer unique advantages in vapor conservation and evaporation reduction.

Additionally, the chapter delves into essential maintenance practices for storage tanks, encompassing external protective coatings to combat corrosion and internal measures to prevent corrosion on tank bottoms and within the vapor space. It emphasizes meticulous procedures for emptying and gas-freeing tanks before maintenance tasks, prioritizing safety protocols to mitigate risks associated with flammable or toxic vapors. By understanding storage tank types, maintenance practices, and safety protocols, industry professionals can ensure the reliability, longevity, and safety of storage infrastructure.

I. Types of Storage Tanks

A storage tank is a container specifically designed to store liquids or gases at a controlled temperature, pressure, and environment. These tanks are crucial in various industries for storing substances such as crude oil, liquefied natural gas, chemicals, and other commodities, ensuring safe and efficient management of resources until they are ready for use or distribution [1].

There are two common designs:

1- The fixed roof tanks.

2- Floating roof tanks.

I.1 THE FIXED ROOF TANKS

Fixed roof tanks are utilized for storing crude oil under near atmospheric pressure conditions (Figure 1). Upon entry, the oil encounters an expanding plate that aids in the separation of any residual gas, which is then directed to a low-pressure flare system. Monitoring the oil level is facilitated by a float housed within a guide tube, with readings transmitted to the control room and regular checks performed through dipping. To maintain safety, the fire foam inlet is safeguarded by a delicate glass sheet, preventing gas leakage and designed to fracture if foam accumulates behind it. However, a notable challenge with fixed roof tanks arises from internal pressure variations due to temperature fluctuations, causing expansion or contraction of the tank contents. To counteract this, a combined pressure/vacuum relief valve is installed in the roof (as depicted in Figure 1), ensuring equilibrium and averting potential damage from excessive pressure or vacuum conditions [2] .

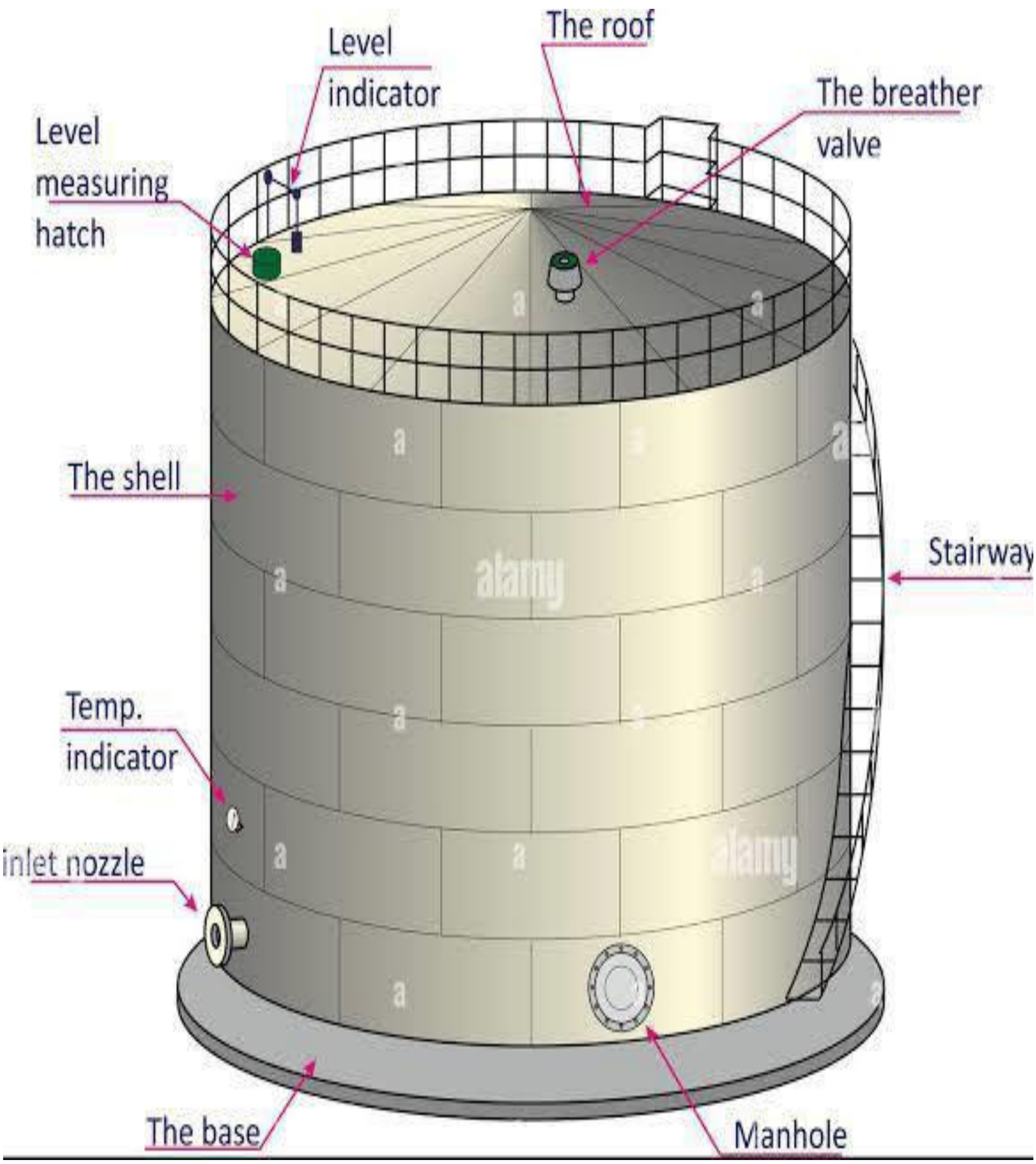

Figure 1: Fixed Roof Tank and Accessories

Pressure / Vacuum Safety Valve (Double Breather)

The double breather valve illustrated in Figure (1) is specifically adjusted to release pressure into the surrounding atmosphere if the internal pressure surpasses 20 mm of water. Conversely, it draws in ambient air when a vacuum of 10 mm of water is formed internally [3]

I .2 THE FLOATING ROOF TANKS

Floating roof tanks derive their name from the fact that their roofs rest on the liquid surface, effectively eliminating the vapor space above the liquid. This design feature enables the storage of products with higher vapor pressures, such as gasoline and naphtha. There are two main types of floating roof tanks: pontoon roof and hard top pan roof tanks. These tanks are widely utilized due to their ability to significantly reduce expensive evaporation losses from the stored products[4].

I.2.1 The Pontoon Roof Tanks

The floating roof is equipped with a circular array of pontoons, as depicted in Figure (2), encircling a central single deck. To ensure a secure seal, the rim of the roof is fastened using shoes pressed against the sides, which are held in place by either weights or springs, as illustrated in Figure[5] .

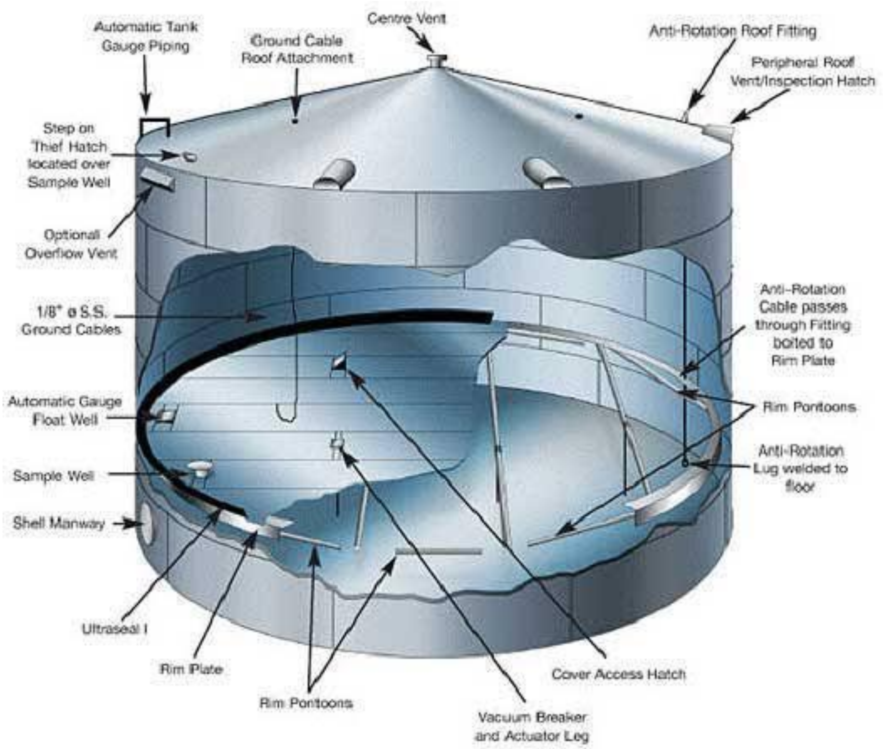

Figure 2: Pontoon Roof Tank

Figure 3: Floating Roof Tank Sealing Method

I .2.2 The Hard Top Pan Roof Tanks

This variant of the floating roof, illustrated in Figure 4, combines the benefits of a pontoon roof for vapor conservation with enhanced fire safety measures. Additionally, it features a fixed cone roof, providing added protection to the floating roof components. Unlike other designs, this floating roof type eliminates the need for roof water drainage, contributing to cost savings, particularly for tanks with diameters below 100 feet. Structurally, the floating roof takes the form of an inverted shallow pan crafted from single-thickness steel, ensuring full contact with the liquid surface. Moreover, automatic vents are integrated into the hard top pan roof design, enhancing

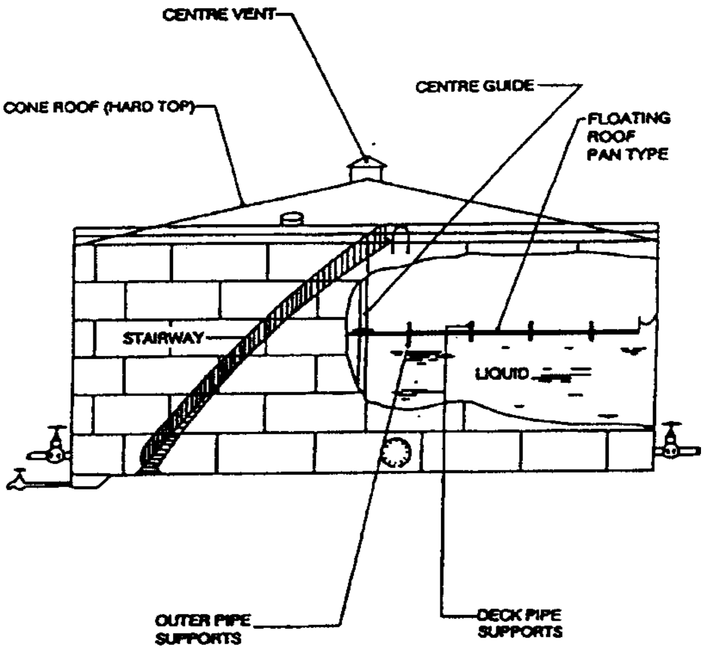

Figure 4 : Hard Top Pan Floating Tank

operational efficiency and safety. Figure (4) visually demonstrates the typical sealing method employed for hard top pan floating roofs [6].

I .3. TANK MAINTENANCE

Regular maintenance of storage tanks is essential for ensuring operational integrity and preventing potential leaks or failures. Conducting monthly or weekly walk-arounds of tanks is recommended, during which stains on steel should be carefully inspected for indications of leaks. It's crucial to check valve function, nozzle welds, and associated piping for any signs of damage or deterioration. Additionally, attention should be given to the tank's foundation to detect wash-out or deterioration. Keeping thorough records of product inflow and outflow is important for monitoring usage and identifying any discrepancies. Tanks should be opened at least every two years for a visual inspection inside, focusing on weld deterioration, corrosion, and the condition of coatings, if present. Records of inspections and their results should be diligently maintained. For tanks equipped with internal containment liners, weekly checks of leak monitors are necessary to ensure their effectiveness. Furthermore, it's advisable to conduct an API-653 inspection every five years, as recommended by TFI, to assess the overall condition and compliance of the tank with industry standards. By adhering to these maintenance practices, tank operators can mitigate risks and ensure the continued reliability of their storage infrastructure [7].

I .4. TANK FAILURES – COMMON CAUSES

The predominant cause of welding-related issues in storage tanks is often the lack of proper weld fusion, which ranks as the most common concern. This deficiency can lead to compromised structural integrity and increased vulnerability to leaks or failures.

Additionally, employing welders who lack certification and haven’t undergone testing for welding procedures can exacerbate these challenges, further risking the quality of welds and overall tank integrity.

Another critical factor contributing to the deterioration of welded seams is corrosion, particularly evident in the lower horizontal and vertical welds. Corrosion weakens the steel, rendering it susceptible to failure over time. Furthermore, the occurrence of brittle fractures in steel presents a significant concern, highlighting the importance of ensuring the robustness and resilience of tank materials through proper fabrication and maintenance practices.

A crucial aspect often overlooked is the absence of certified inspections, which are vital for identifying and addressing potential issues before they escalate into more significant problems.

Without rigorous inspections conducted by qualified professionals, underlying defects or weaknesses may go unnoticed, posing serious safety and environmental risks.

Moreover, the competence of tank erectors plays a pivotal role in upholding industry standards and specifications, particularly those outlined by the American Petroleum Institute (API). Companies lacking adequate knowledge of API requirements may prioritize cost-saving measures over adherence to regulatory guidelines, potentially compromising the quality and safety of tank installations. Hence, it is imperative to engage contractors well-versed in API Specifications and procedures to ensure compliance and mitigate the likelihood of subpar workmanship [8].

I .5. PROPER INSPECTION PROTOCOL

To ensure the structural integrity of storage tanks, a comprehensive inspection and testing regimen is imperative. This includes visually inspecting welds, plates, and appurtenances for any signs of damage or deterioration. Additionally, Ultra-sonic Thickness (UT) testing should be conducted on shell courses, floor, and roof to assess thickness and detect any potential weaknesses. Vacuum testing of all floor weld seams is recommended, except for those coated with epoxy. It's crucial to identify and address bottom-side corrosion on floors promptly. Settlement surveys should be performed to check for planar tilt and detect any floor bulges or depressions that may compromise stability. Finally, providing calculations for safe or maximum fill height is essential for ensuring the structural capacity of the tank is not exceeded. These measures collectively contribute to maintaining the reliability and safety of storage tank infrastructure [9].

Figure 5: Weld deteriorarartion and four-way junction

Figure 6: Evidence of interior shell corrosion

Figure 7 : Floor plate corrosion floor

Figure 8: Floor top side corrosion [7]

Figure 9 : Severe roof corrosion

I.6 Future Trends and Innovations in Storage Tanks Technology

I.6.1 Advanced Materials

Future storage tanks may incorporate advanced materials such as composites, polymers, and nanomaterials. These materials offer advantages like increased strength, corrosion resistance, and lighter weight compared to traditional materials like steel [10].

I.6.2 Smart Tanks

Integration of sensors and IoT (Internet of Things) technology allows for real-time monitoring of tank conditions such as temperature, pressure, and levels of stored substances. This data can be used for predictive maintenance, improving safety, and optimizing operations [10].

I.6.3 Automated Maintenance

Robotics and automated systems will play a larger role in tank maintenance, inspection, and cleaning processes. Drones equipped with sensors and cameras can inspect tanks for defects without human intervention, reducing downtime and safety risks [10].

I.6.4 Flexible Storage Solutions

Flexible and collapsible tank designs will become more popular, especially for temporary or mobile storage needs. These tanks can be easily transported, assembled, and disassembled, providing flexibility in various applications such as disaster relief, military operations, or remote construction sites [10].

I.6.5 Environmental Sustainability

Future storage tank designs will focus more on environmental sustainability, with features such as double-walled construction, leak detection systems, and measures to prevent soil and groundwater contamination in case of spills or leaks [11].

I.6.6 . Scalable Designs

Modular tank systems that can be easily expanded or reconfigured to accommodate changing storage requirements will gain popularity. These designs offer scalability and cost-effectiveness, allowing companies to adapt to fluctuating demand or operational needs [11].

I.6.7 Integration with Renewable Energy

Storage tanks may be integrated with renewable energy systems such as solar panels or wind turbines to power auxiliary equipment or provide backup power for critical operations. This integration helps reduce reliance on fossil fuels and lowers overall carbon footprint [11].

I.6.8 Data Analytics and AI

Advanced data analytics and artificial intelligence algorithms will be used to optimize storage tank operations, improve efficiency, and predict maintenance needs. AI-driven decision-making can help optimize inventory management, scheduling of deliveries, and resource allocation.

These trends indicate a shift towards more efficient, sustainable, and technologically advanced storage tank solutions that can meet the evolving needs of industries worldwide[11

II .1 Cryogenic Storage tanks

Cryogenic product storage tanks provide a controlled environment for safe storage of chemicals, reducing risks and possible degradation, so constant and reliable control of storage temperatures requires solutions that guarantee accurate monitoring and the optimal choice of insulation and refrigerant.

The manufacturer’s expertise in cooling technologies is accompanied by its ability to identify BOG solutions that are characterized by minimum maintenance costs, maximum energy savings and the greatest ease of installation, depending on the customer’s needs, ammonia or hydrocarbon-based refrigerants as well as liquid propane, propylene and ethylene are stored in special low-temperature tanks. The ambient heat increases this temperature. The vapours thus generated must be evacuated in order to avoid pressure formation. They are processed into liquid and returned to the storage tank [12].

II.2 The fields of cryogenics

From a physical standpoint, the study of cryogenics allows us to investigate and understand the behavior of matter at low temperatures. At these temperatures, molecules no longer follow the classical rules of quantum physics established until then. Cryogenics thus enables the study of various domains, such as**:**

Research Domain

-Measurements at very low temperatures (materials, solid-state physics).

-Instrumentation development (SQUID).

-Accelerators and particle physics: Magnets, cavities, detectors.

-Controlled nuclear fusion: Magnetic confinement.

-Astrophysics: Observation sensors on Earth and in space.

Industrial Domain

- Electronics (detectors, components...).

- Electrical engineering (alternators, limiters...).

- Liquefaction and refrigeration: Fluid storage - liquefaction of LNG and LPG.

- Space: Propulsion (fuel and engines).

-Medical: MRI Cryosurgery, cryopreservation [13].

II.3 Types of cryogenic liquid storage tanks

The main aspects related to storage in a cryogenic facility are the chosen containment technology and the total storage capacity.

When it comes to containment technology, cryogenic storage tanks are divided into three broad categories: Underground Storage Tanks, Aboveground Storage Tanks (ASTs), in-ground Storage Tanks. The figure presents the three categories of cryogenic liquid storage tanks, as used by the industry.

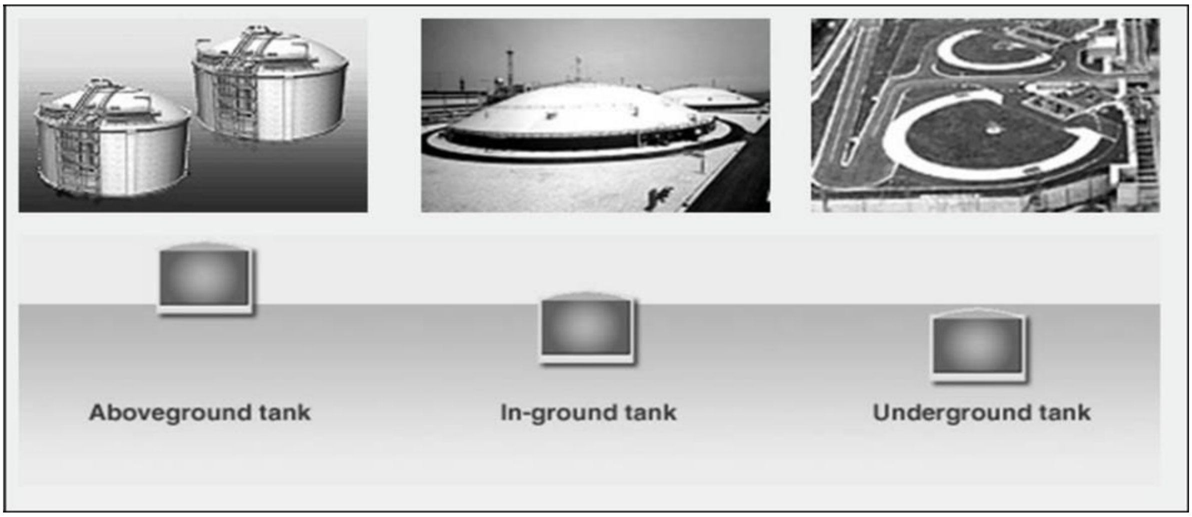

Figure 10: Categories of storage tanks

The aboveground or self-supporting cryogenic storage tank is the most widely used technology in the industry. This technology can be subdivided as follows based on its structural characteristics:

- -Single Containment Tank (SCT).
- -Double Containment Tank (DCT).
- -Full Containment Tank (FCT).

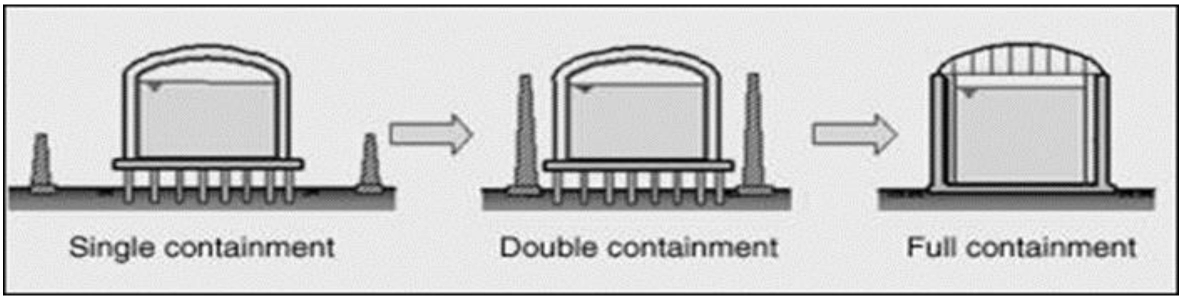

Figure 11: Structure of storage tanks

Over the years, as shown in Figure 11, the trend has been shifting from single containment to full containment, via double containment, due to increased safety measures and reduced plot space. The full containment type of confinement is widely used in LNG receiving terminals. However, in liquefaction plants, the confinement technology used tends to be more project-specific.

The following sections describe each of the above-ground cryogenic storage tank technologies, detailing their structural specifics [14].

II.3. 1 Single Containment Tank

The single containment above-ground storage tank consists of an inner tank made of suitable cryogenic metal (9% nickel steel) designed to hold the cryogenic liquid, an outer tank made of carbon steel, and a steel roof.

The inner tank is surrounded by insulation to control heat leakage through the tank wall; however, the outer tank is not designed to meet low-temperature ductility requirements to contain the cryogenic liquid in case of a leak from the inner tank.

In the event of an inner tank rupture, a secondary means of containing the cryogenic liquid is typically provided, such as an earth safety berm capable of holding 110% of the total tank volume capacity. The drawback of this type of storage tank is the need for a large storage yard area because the space required for the earth berm significantly increases the total land usage [15].

II.3.2 Double Containment Tank (DCT)

The double containment storage tank is essentially a single containment tank surrounded by a closed reinforced concrete outer tank designed to contain any potential leakage from the inner tank but not the vapour released during a spill.

In addition to the outer carbon steel wall, the DCT design also includes a concrete outer tank that serves as a secondary means of liquid containment. The outer container is a reinforced concrete cylinder surrounding the carbon steel outer wall and is designed to contain the full volume of the tank plus an additional safety margin .

II.3.3 Full Containment Tank (FCT)

Similar to SCT and DCT, the Full Containment Tank (FCT) consists of an inner tank made of appropriate cryogenic metal (9% nickel steel) designed to hold the cryogenic liquid, with a reinforced concrete outer tank and a reinforced concrete roof. The outer concrete tank is also designed to contain the liquid in case of leakage or rupture of the inner tank. Insulation surrounds the inner tank to control heat leakage through the tank wall.

Different types of insulation are used in different parts of the tank. Generally, the annular space between the inner and outer tanks is filled with bulk perlite. Additionally, an elastic cover, such as fiberglass, is installed outside the inner tank. The cover provides resilience to the perlite. The reinforced concrete roof is coated with carbon steel, with the coating also serving as a framework for the concrete.

Heat leaks from the tank roof are limited by installing insulation on the suspended deck (directly suspended from the roof). There is no insulation immediately beneath the roof, and the vapor space between the suspended deck and the tank roof is close to ambient temperature. For bottom insulation, most cryogenic tanks use cellular glass (foam glass) .

II.4 Materials and Insulation

When it comes to maintaining temperatures like those used for operating and storing LNG or other cryogenic fluids, it is of the utmost importance to have properly sized insulation to reduce heat ingress into the tank. Therefore, insulation is one of the main determining factors influencing the production of BOG (Boil-Off Gas) in a cryogenic system.

The three fundamental factors determining the overall suitability of insulation materials are thermal conductivity, density/weight, and the cost of labor and materials. These factors will be presented for each studied insulation material.

Cryogenic tanks typically feature different materials for the bottom, walls, and roof, constituting a studied assortment of materials providing both structural resistance to the tank and thermal insulation to the cryogenic fluid.

Below is a brief description of the materials commonly used in cryogenic tanks for insulation and structure:

- Concrete: It is intended to provide structural resistance to the tank and withstand weather conditions.

- 9% Nickel Steel: Standard ferrous construction steels are unsuitable for extreme cryogenic temperatures due to an increased risk of brittle fractures and insufficient toughness. 9% nickel alloy steel is the material meant to be in direct contact with the cryogenic liquid. It possesses the required mechanical and physical properties for the construction of storage tanks and cryogenic pipelines, withstanding temperatures down to -196°C while offering the necessary structural integrity.

- Sand: A layer of sand is typically placed between the 9% nickel steel layer and the foam glass insulation.

- Asphalt: A thin layer of asphalt is usually placed between foam glass insulation layers to seal and waterproof the layers so that the system is vapour-tight, and no additional vapour barrier is required.

- Foam Glass: This waterproof material is designed for industrial applications requiring high load capacity, combining high compressive strength with low thermal conductivity. Its characteristics make it suitable for the bases of cryogenic tanks. Polyurethane can replace foam glass as insulation, but it generally proves to be more expensive.

- Expanded Perlite: As a natural siliceous volcanic rock, perlite can be expanded four to twenty times its initial volume by heating it to over 900°C with two to six percent combined water, turning trapped water molecules into steam and creating countless small glass bubbles that allow the raw rock to crack and expand. Expanded perlite, besides its thermal properties, is easy to install, relatively inexpensive, non-combustible, and does not shrink, swell, deform, or sag, often being the primary insulation material chosen for cryogenic tanks.

- Aluminium: This material is typically an alloy that receives special treatment to develop a temper that ensures the required intergranular and exfoliation corrosion resistance, as well as temperature resistance without the risk of brittle fractures. It is often used on cryogenic tanks as the material for supporting the suspended insulation platform (deck) attached to the roof, often used as an alternative to welded nickel steel, as it represents a lighter and safer strength-to-weight ratio than previous technologies [16].

II.5 Application of liquefaction cryogenics

II.5.1 Cryogenic cycles

A cooling cycle is used to cool a product through the refrigeration transfer of a refrigerator in the evaporator in order to achieve a phase change and reach a desired temperature.

To create a refrigeration circuit, at least five components are required:

- A refrigerant (cooling source): which undergoes state changes to absorb or release its latent heat mainly at the desired location (Example: Propane, ethanol).

- A compressor (pressure increase): which provides mechanical energy to the refrigerant to allow it to evolve.

- A pressure reducer (expansion - through an expansion valve or turbo-expander), often improperly called a throttle valve, which lowers the boiling point of the refrigerant.

- An evaporator (heat exchanger): where the refrigerant evaporates, absorbing the necessary energy from the medium to be cooled.

- Condenser (condensation): it condenses to reach the refrigerant in liquid state [17].

II.5.2 Cryogenic thermodynamic processes

Cryogenic refrigeration and liquefaction cycles involve combinations of para-isothermal compressions, cooling, thermal regenerations, and isenthalpic or adiabatic expansions of fluids.

Four main families of cryogenic thermodynamic processes can be distinguished:

- Joule-Thomson isenthalpic expansion processes.

- Brayton reverse cycles with isentropic expansion.

- Mixed processes combining isenthalpic and isentropic expansions (Claude cycle).

- Classical or integrated cascades [14].

II.5.3 Joule-Thomson isenthalpic expansion process

The Joule-Thomson effect is defined, at a given temperature and pressure, by the difference in enthalpies at this temperature between the gas at low pressure (theoretically zero: ideal gas) and the gas at the considered pressure. In practice, the low pressure is often atmospheric pressure.

This "free expansion" (as opposed to "expansion with production of external work" when done in a machine) is usually accompanied by cooling. It should be noted that if the gas is an "ideal gas", there is no cooling. The refrigerating production obtained by simple expansion, or by the Joule-Thomson effect, will therefore depend on the imperfection of the gas. This "imperfection," resulting from the potential energy of molecular attraction, increases with the density of molecules: the Joule-Thomson effect will be all the more significant as the pressure is high and the temperature is low.

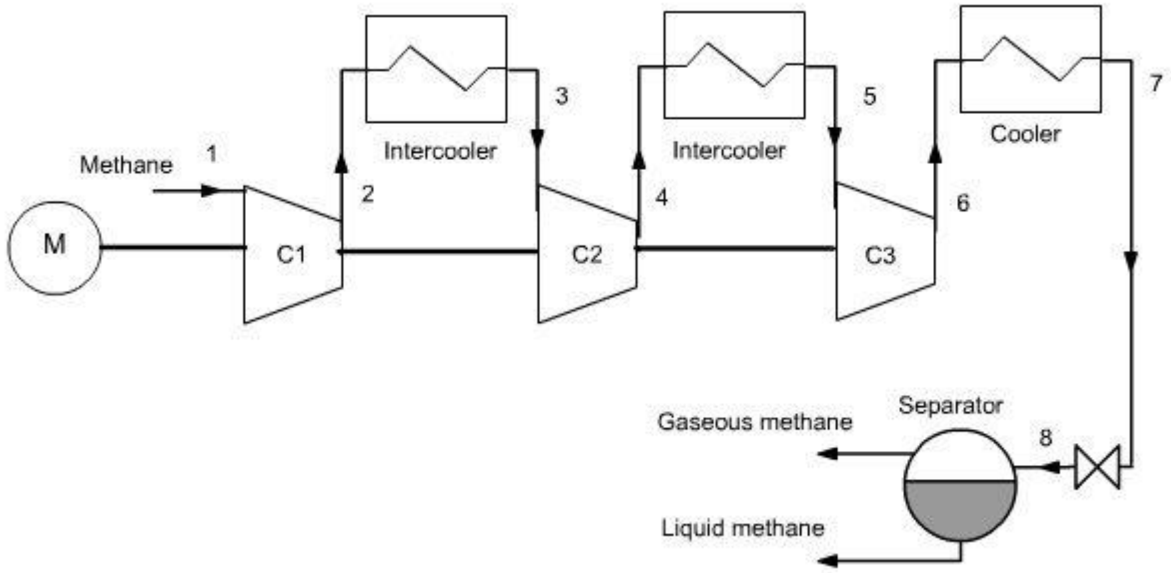

Figure 12 : Simple liquefaction cycle

- Linde cycle

In a Linde cycle (see below), two improvements are made to the previous cycle:

- The gaseous methane after isenthalpic expansion is recycled.

- A heat exchanger is introduced between this gaseous methane and the methane exiting the cooler, in order to cool the compressed gas not to 210 K but to 191 K.

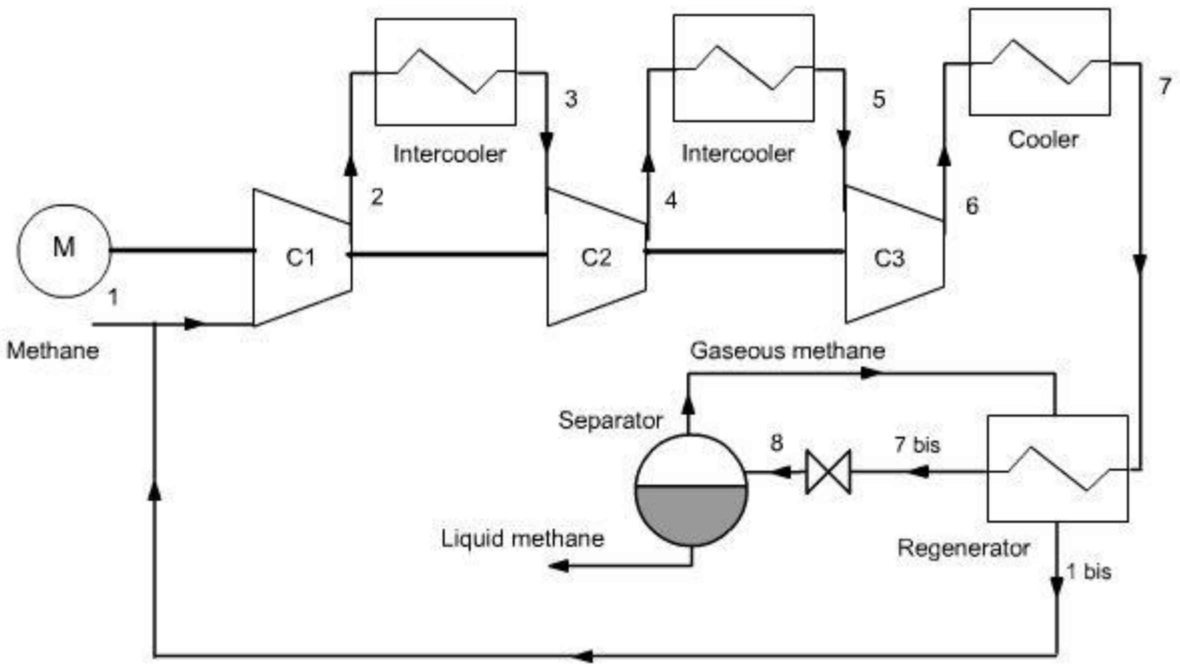

Figure 13: Linde Cycle

For these new conditions, the compression work per kilogram of liquefied methane becomes equal to 1.91 MJ, which is simply 43% of the previous value. The performance improvement mainly comes from the decrease in temperature at the inlet of the expander, which reduces the vapour fraction at the outlet and therefore increases the flow rate of the liquid phase. Additionally, the decrease in temperature at the inlet of the first compressor reduces the compression work, but this effect is less significant than the first one [18].

II.5.4 Inverse Brayton cycle

Inverse Brayton cycle does not involve the Joule-Thomson effect; therefore, it can be implemented with an ideal gas. Cold is produced by the expansion of the gas in a machine. Heat is extracted from the system in the form of mechanical work. It's noteworthy that the lowest temperature in the system is that of the machine's exhaust. As the name suggests, an inverse Brayton cycle achieves a refrigerating effect by reversing the Brayton cycle, that is, the gas turbine cycle: a gas is compressed, cooled, and then expanded (see figure below). Since the temperature at the end of the expansion is low, this gas can be used to cool an enclosure, either by direct contact, especially if it is air, or through a heat exchanger.

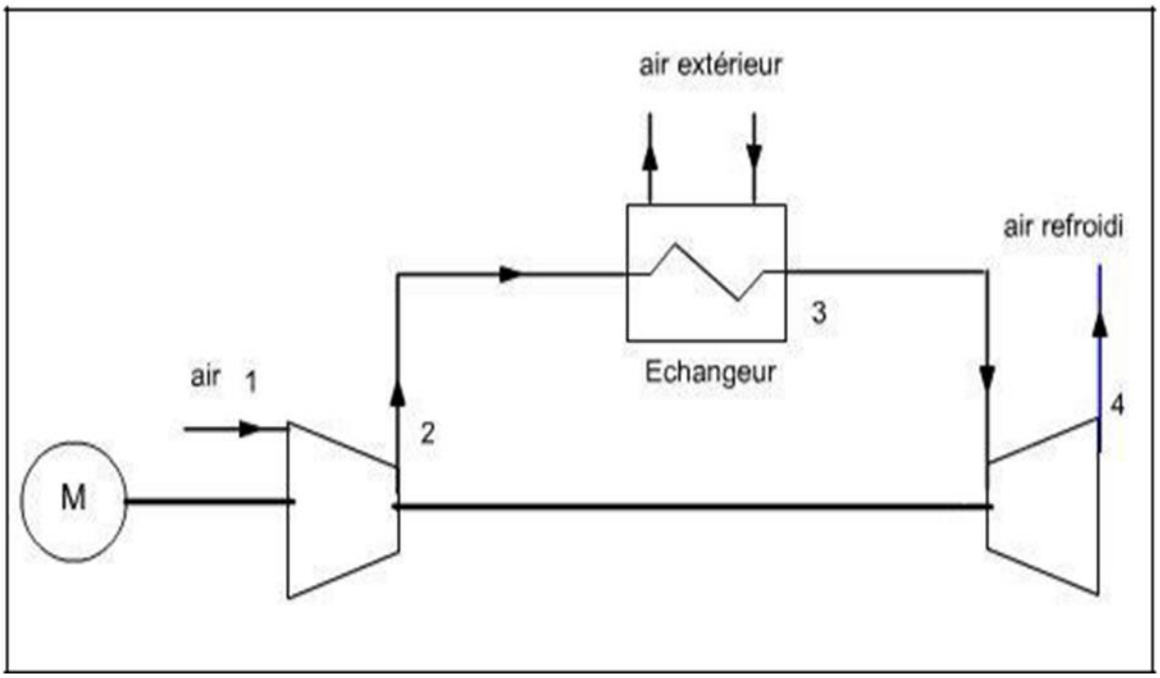

Figure 14 : Diagram of an open inverse Brayton cycle

Until recently, the air-based inverse Brayton cycle was widely used in airplanes to provide cabin air conditioning during flight [19].

II.5 .5 Mixed Processes - Claude Cycle

The Linde cycle uses an isenthalpic expansion, which has two disadvantages: firstly, the expansion work is lost, and secondly, cooling can only be achieved if the thermodynamic state of the fluid is such that the Joule-Thomson expansion results in a decrease in temperature.

Claude, on the other hand, proposed a cycle that involves both a turbine and an expansion valve and has the particularity that the installation operates with a single fluid compressed at a single pressure level, as shown in the figure below. The Claude cycle has been used in numerous air liquefaction installations.

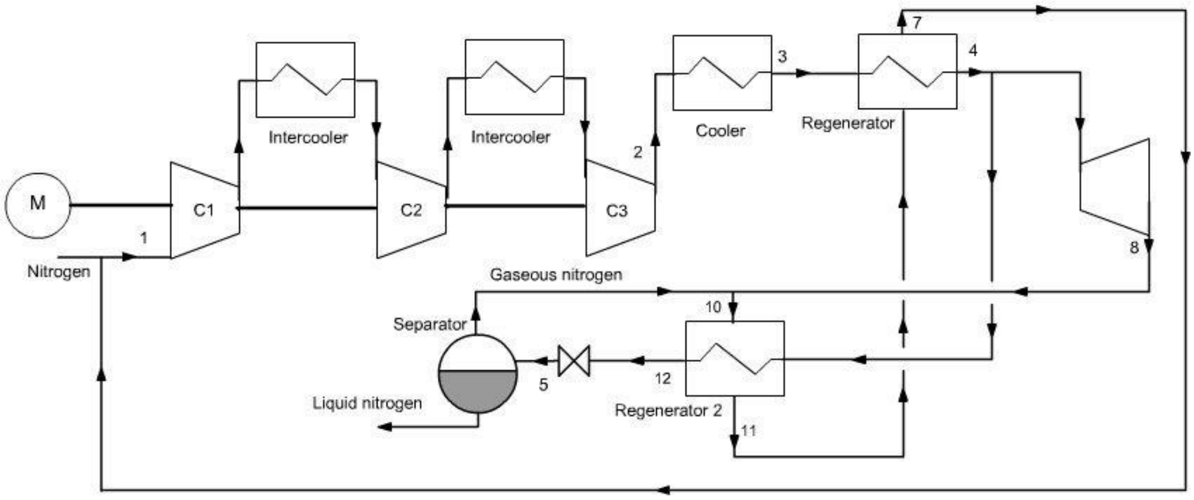

Figure 15: Diagram of the Claude cycle

The advantage of this cycle is that the compression ratio can be significantly lower than in the case of the Linde cycle. One difficulty is that the expansion machine can only operate with good efficiency if the fluid remains in the vapor zone or maintains a high vapor quality. The originality of the Claude cycle is therefore to combine isentropic expansion in the turbine and isenthalpic expansion in the single expansion valve leading to gas liquefaction [20].

II.5 .6 Cascade Cycles

It is also possible to use cascade refrigeration cycles, where the evaporator of one serves as the condenser for another, and so on (see figure 16). The different refrigeration circuits are then independent hydraulically but thermally coupled by their evaporators and condensers.

A widely used variant nowadays in natural gas liquefaction units is to use a so-called "incorporated" cascade, which employs a single thermodynamic fluid composed of a mixture of methane, ethane, propane, butane, and pentane.

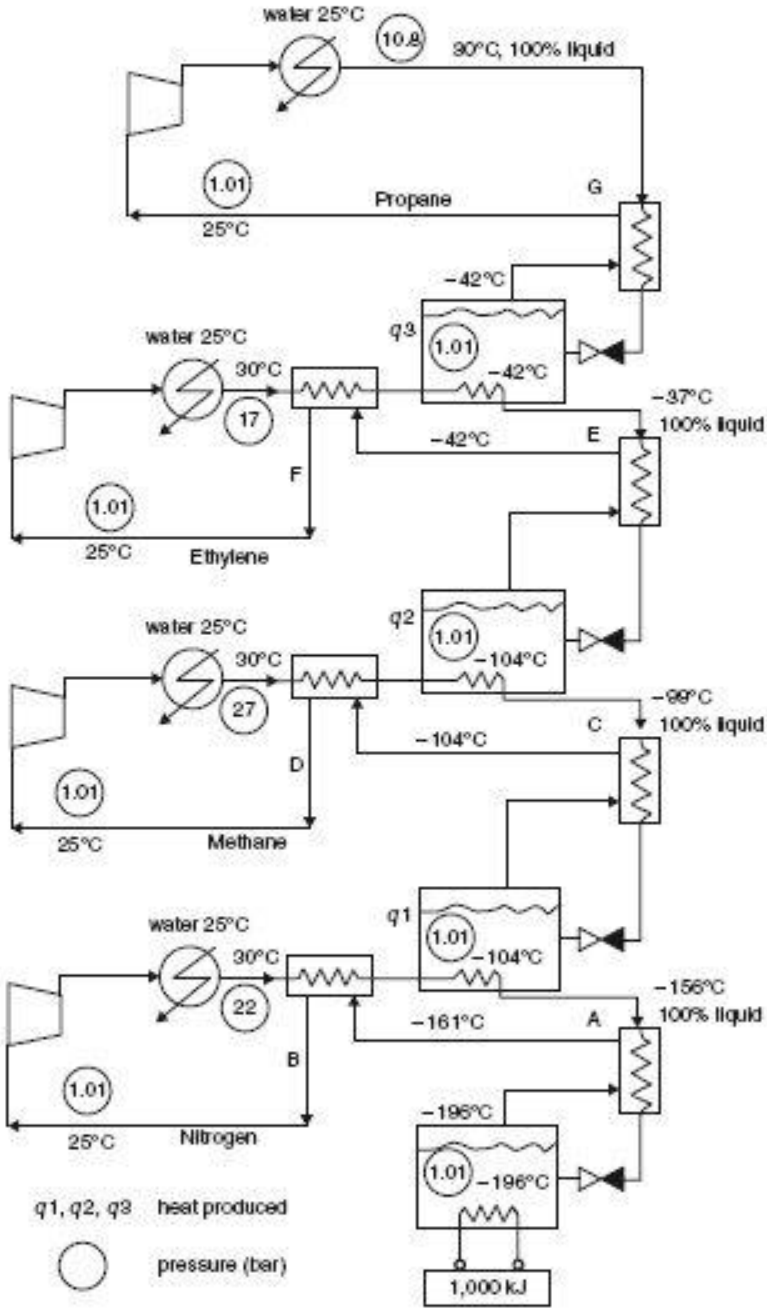

Figure 16 : Diagram of a Classic Cascade

II.6 Ethylene Tank Features

A storage tank is determined by its shape, geometric dimensions which determine the contained volume, its pressure, and the temperature of the stored product, which is also related to its pressure by the law of saturated vapour. The spherical shape is best suited for insulation, but for capacities exceeding 12 to 20,000 m3, cylindrical shape is always preferred. Assuming that heat exchanges have the same intensity per unit of lateral surface, bottom, and roof, it is demonstrated that the most favourable shape of a cylindrical tank satisfies the equality: Height = Diameter.

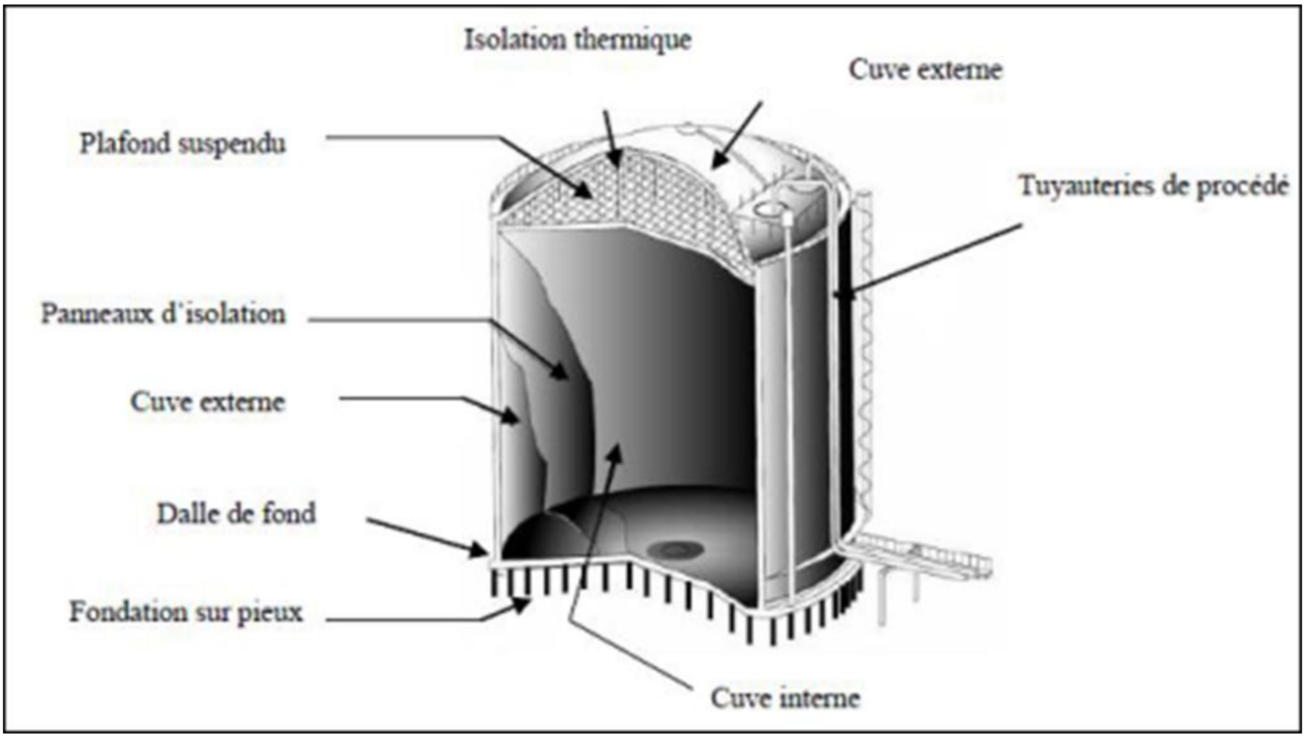

Figure 17: Simplified diagram of a cryogenic storage tank.

Ethylene is stored in double-walled insulated tanks, with perlite insulation under a gas atmosphere at temperatures around -104°C and at pressures slightly above atmospheric, at its bubble point. It consists of 2 envelopes:

- An inner flexible envelope made of 18-8 type stainless steel, a material resistant to low temperatures.

- An outer envelope made of pre-stressed reinforced concrete, which provides mechanical strength.

The inner roof is typically flat and suspended from the domed roof of the outer tank.

The annular space between the two envelopes is filled with a substantial thickness of insulation material, approximately 0.5 m thick, made using perlite (a volcanic rock).

The gas atmosphere is typically nitrogen (an inert and non-condensable gas on the cold wall) under a pressure that at the top is maintained a few millibars above atmospheric pressure.

The low-temperature storage of the product continuously causes slight evaporation, which helps maintain a constant temperature. The quality of insulation is therefore reflected in the evaporation rate, typically expressed as a percentage per day, ranging from 0.05% to 4%. Furthermore, these tanks must meet both mechanical and thermal conditions.

II.7- Impacts of BOG on the environment

II.7.1- the main gases influence the environment

Refrigerant fluids are crucial for cooling systems (refrigeration and air conditioning) due to their high heat absorption capacity. However, their release into the atmosphere, primarily through leaks during equipment charging, use, or disposal, poses significant environmental risks. Chlorinated gases (CFCs and HCFCs) contribute to ozone depletion when emitted. Previously, chlorofluorocarbons (CFCs and HCFCs) were widely used for their safety and good thermodynamic performance. Additionally, fluorinated gases (HFCs, PFCs, and SF_6) have a warming potential far greater than CO_2 and are used in various applications, including refrigeration, air conditioning, insulation foams, aerosols, semiconductor industry, and electrical transmission equipment. Major emitting sectors include transportation, buildings, household consumption, energy production, and industry [21].

II.7.2 the greenhouse effect and global warming

The greenhouse effect is the warming of the atmosphere due to solar radiation trapped by certain gases. The Global Warming Potential (GWP) measures a gas's ability to contribute to this effect, considering its lifetime in the atmosphere and production levels. Some gases, although present in small quantities (less than 1%), act like glass panes by absorbing terrestrial infrared radiation while being transparent to solar radiation. They trap emitted energy and re-emit it as infrared radiation toward the Earth's surface, causing additional warming. Analogous to a gardener's greenhouse, these gases are termed greenhouse gases. This natural greenhouse effect is crucial; without it, the average surface temperature would be -18°C, whereas with it, it is +15°C [21].

III.1 Definition of boil-off gas (BOG)

Any input of heat into equipment or an installation containing cryogenic liquid leads to its partial vaporization, known as boil-off gas or "evaporation gas." If not removed, the boil-off gas accumulates, resulting in an increase in pressure. In terminals, under normal operation, compressors maintain stable pressure in storage tanks; they evacuate the boil-off gas to re-incorporation units.

The daily evaporation rate with a typical tank is between 0.05 to 1% [17].

III .2 Origin of Boil-Off

As seen earlier, ethylene is stored and transported in cryogenic tanks in liquid form, meaning it's liquid at a temperature below its boiling point. However, due to temperature differences between the tanks, pipes, and the surrounding atmosphere, whenever the tanks are filled, loaded, or unloaded, or due to heat exchange, boil-off gas is generated, usually with a volume assumed to be 600 times greater than that in liquefied form. These vapors are generated in two ways:

III.2.1 Boiling in the Holding Mode

The holding mode refers to the interval between loading and unloading operations, during which ethylene is stored, meaning the penetration of heat into the storage and piping from the environment. There are three main sources of BOG [17]:

III .2.1.1 Boil-off from the storage tank

Although ethylene tanks are designed and prepared to maintain cryogenic temperatures of ethylene through multi-layer insulation, heat transfer still occurs through the walls, roof, and floor of the tanks, via convection, radiation, and conduction. Thus, while these are intended to maintain the liquid temperature so that vaporization is less than 0.05% of the total tank content per day, the daily BOG flow rate variation can range between 0.02 and 0.1%.

III .2.1.2 Boil-off from Pumps and Pipes

During the holding mode, to maintain cryogenic temperature on the loading/unloading system, a small portion of stored ethylene circulates through the pipelines, pumps, and the entire circuit, absorbing heat from the environment as well as heat generated by pumping, turbulent flow, and line friction. As ethylene circulates, more BOG forms in the tanks, which can cause a pressure drop, lowering the liquid's boiling point. To compensate for this pressure drop, the temperature in the tank must decrease by approximately 0.1°C per 0.01 bar of pressure drop; however, this option increases the BOG rate because the only way to lower the temperature is to regasify a portion of the liquid [17].

III.2.1.3 Unpumpable Liquid Level

In the event that the tank reaches a minimal stock without replenishment, meaning the level of unpumpable liquid ethylene equivalent to 300 tons, this quantity will be added to the total BOG.

III.2.2 Boiling During Loading/Unloading Mode

This period corresponds to the time when the ethylene carrier docks at the jetty unloading ethylene into the storage tanks, with the connection made by insulated pipelines and loading arms. The BOG generated during the loading and unloading process can reach values 8 to 10 times higher than those observed for the terminal operating in the holding mode. The main reason for this increase is that the liquid replaces the volume of the empty tank entirely occupied by ethylene vapor. This increase is attributable to the need for a vapor return line from the replenishment installation, which drains the storage tanks [17].

III.3 Characteristics of Boil-off Exiting the Tank

III.3.1 Overview of Ethylene

Ethylene, also known as ethene, is a hydrocarbon molecule composed of two carbon atoms and four hydrogen atoms (C2H4). It is a colorless, flammable gas with a faintly sweet odor. Ethylene is a crucial industrial chemical widely used in the production of plastics, fibers, and other organic chemicals. Its physical properties include a boiling point of -103.7°C (-154.7°F) and a melting point of -169.2°C (-272.6°F), making it a gas at standard temperature and pressure conditions. Chemically, ethylene is highly reactive due to its double bond between carbon atoms, allowing it to participate in polymerization reactions to form polyethylene and in various organic synthesis processes. Its composition of carbon and hydrogen atoms gives it a simple molecular structure yet versatile chemical properties, making it indispensable in modern industrial processes. [22].

III.3.2 The Significance of ethylene Storage in HDPE Production

Ensuring reliable and safe storage of acetylene is paramount for maintaining uninterrupted production cycles and meeting quality standards in HDPE manufacturing facilities. Proper storage practices mitigate safety risks associated with acetylene's flammability and ensure a stable supply chain for consistent HDPE production. Effective management of acetylene storage contributes significantly to the operational efficiency and sustainability goals of HDPE production companies.

Table 2: Molar Composition of Ethylene [23]

Feed Composition	**Molar fraction**
Ethylene	0,9988
Methane	0,0005
Ethane	0,0002
Hydrogene	0,0005

Table 3: Conditions and properties of ethylene gas [23]

Conclusion

The theoretical part of this dissertation has extensively explored critical aspects of storage tanks and cryogenic technologies essential for industrial operations. It systematically examined various types of storage tanks, emphasizing the necessity of stringent maintenance and inspection protocols to ensure operational reliability and safety. Future trends in tank technology, including advancements in materials, smart systems, and sustainable practices, were identified as pivotal areas for innovation.

Within the realm of cryogenics, the study provided detailed insights into the design and applications of cryogenic storage tanks, highlighting their crucial role in handling liquefied gases under extreme temperatures and the significance of effective insulation materials. Environmental impacts associated with refrigerants, such as greenhouse gas emissions and ozone layer depletion, were also discussed, emphasizing the imperative of adopting sustainable practices in storage operations.

Property	**Value**
Temperature (°C)	-74
Pressure (kg/cm^2g)	0
Flow rate (avg) Kg/h	500
Flow rate (max) Kg/h	1100
Discharge flow rate Kg/h	5000

Moreover, the theoretical exploration encompassed the concept of boil-off gas (BOG), analyzing its origins, characteristics, and strategies for management during storage and handling. This comprehensive analysis establishes a robust understanding of storage tank technologies, outlining opportunities for advancements that prioritize safety, efficiency, and environmental stewardship in industrial contexts.

Part II: Simulation Comparative Study and Economic Analysis of BOG recovery processes- Case study : CP2K complex SONATRACK- SKIKDA.

SECOND SECTION:

SIMULATION COMPARATIVE STUDY AND ECONOMIC ANALYSIS OF BOG RECOVERY PROCESSES- CASE STUDY: CP2K COMPLEX SONATRACK-SKIKDA.

INTRODUCTION

Our internship was conducted at Sonatrach-Skikda CP2K unit for 15 days. Boil-off gas (BOG), primarily composed of ethylene, represents a loss of valuable resources and poses environmental and economic challenges in CP2K complex. To address this issue effectively, this experimental study focuses on identifying the optimal refrigerant for liquefying BOG ethylene, thereby facilitating its recovery and minimizing BOG emissions.

Central to this exploration are detailed descriptions of ethylene liquefaction processes utilizing propane (R290), propylene (R1270), ammonia (R717), and nitrogen (R728) as refrigerants. Each process is meticulously examined from a technical standpoint, focusing on practical considerations such as equipment configurations, operational parameters, and performance metrics derived from simulations conducted using the HYSYS software.

The primary objective of these simulations is to assess the feasibility and efficiency of each liquefaction process in recovering ethylene from BOG. Technical calculations encompass critical aspects such as energy consumption, refrigerant efficiency, and system reliability, crucial for determining the practical applicability and operational robustness of each method.

Moreover, this section includes a comprehensive technical-economic study that evaluates investment costs, utility expenditures, and maintenance considerations associated with implementing ethylene liquefaction technologies. Results from these analyses provide insights into the economic viability and sustainability of adopting specific liquefaction processes at CP2K.

I. The geographical location of the CP2K

The CP2k complex is located inside the Skikda industrial zone, with an area of 16.68 hectares, 10% of which is built.

CP2k is located on the coast 06 km east of the capital of the wilaya of Skikda and at an average height of approximately 06 m above the sea.

Geographical position limited as follows:

- To the North: the Mediterranean Sea.
- To the south: the main road of the industrial zone.
- To the East: FIR (The intervention and reserve force).
- To the West: CP1K (plastic material complex).

Figure 18 : Satellite view of the Skikda industrial zone

I.1 Production of CP2K

HDPE production at the CP2K level in previous years is presented in the following table:

I.1.1 Design and Standards of CP2K Ethylene Cryogenic Storage Tank

The ethylene cryogenic tank described in the project data adheres to API STD 620 Appendix Q standards for cryogenic storage. It is designed with an inner tank capable of storing up to 12,000 metric tons of ethylene at a project temperature of -104°C and a project pressure ranging from 2000 mmH_2O to 50 mmH_2O. The external tank, which is designed for nitrogen gas storage, features a project pressure range from +50 mmH_2O to -25 mmH_2O.

The inner tank's design includes specific severity parameters of 0.57, indicating its robustness to handle cryogenic temperatures and pressures. The tank is designed without provision for project wind pressure, ensuring stability even under environmental loads up to 270 KG/m2. It features a nominal thickness for the inner tank of 0.0924 g, with no relaxation of stresses and corrosion tolerance set at 0 mm.

The envelope joint rendering for the inner tank is specified at 80%, indicating a high degree of welding efficiency and integrity, whereas the external tank's joint rendering is set at 50%. These parameters collectively ensure that the ethylene cryogenic tank meets stringent safety and operational standards for storing ethylene and nitrogen gas in industrial applications.

I.2 History of Boil-off within CP2K

The history of Boil-off at the CP2K level in previous years is presented in the following table:

1.3 Description of the HYSYS simulator

HYSYS is chemical engineering process simulation software, developed by the Canadian company HYPROTECH. It has been designed to enable the treatment of a wide range of problems ranging from simple two- and three-phase separation to distillation and chemical transformation. HYSYS software is a sizing tool used to ensure optimal designs are identified. It is also used to model existing units and ensure that equipment is efficient by specification, thus evaluating and improving existing processes. Engineers engaged in design engineering use HYSIS software to make rapid calculations using efficient models and optimal techniques. Simulation by HYSYS reduces engineering costs by:

- Rapid calculations of different designs using efficient models and optimal techniques to ensure that process equipment is correctly specified to deliver the desired product characteristics at the desired production yields.
- Creation of models that can be applied during the operation of the unit from design concept to details: Estimation, training and optimization.

To define these bodies, HYSYS requires you to fill in a table of values to be used during calculations. Furthermore, to characterize complex hydrocarbon mixtures, it is possible to use the results of standardized analyzes such as TBP, ASTM, Kuop…etc.

The HYSYS will subsequently use this data to generate a finite number (chosen by the user) of pseudo bodies identified by Their normal boiling points to represent these mixtures. Optionally, the simulator can read other databases such as DDB, DIPPR, API, GPA, etc. This option also allows you to use physical properties already stored in the HYSYS database.

II. DESCRIPTION OF PROCESSES

Among the processes known in the field of liquefaction, two processes have been chosen for Boil-Off recovery, shown as follows:

1- The cascade method using a single refrigerant process for each loop; the refrigerants used are: propane (R290); propylene (R1270); ammonia (R717).

2- Claude's cycle method using nitrogen (R 728).

II.1 The liquefaction of ethylene by propane (R290) as a refrigerant

The liquefaction module will be subdivided into two systems as follows:

II.1.1 Ethylene cycle

At the outlet of the ethylene condenser E-102, the saturated liquid stream is divided into two streams. One fraction is routed to the ethylene economizer E-103 through the throttling valve of ethylene V-2. The remaining fraction is subcooled in the E-103 ethylene economizer. This subcooled liquid flow is then expanded by the ethylene valve V-1 before being sent to the Ethylene Storage Tank.

II.1.2 Refrigerant cycle

The refrigeration cycle serves as the heat sink for ethylene condensation. The refrigerant is vaporized and superheated in the E-102 ethylene condenser as it exchanges heat with the ethylene. The superheated flow is drawn off and compressed by the K-PR-101 refrigeration compressor. The compressed stream is discharged into the E-PR-104 refrigerant condenser, where it is condensed by heat exchange with cooling water. This subcooled liquid stream is then expanded at the outlet of the refrigerant condenser through the refrigerant valve V-3 before being sent back to the ethylene condenser E-102. There, it evaporates and superheats, exchanging heat with ethylene, thus triggering a new refrigeration cycle.

Figure 20: Propane Cycle PFD (Process Flow Diagram) for liquefaction of ethylene

Table 6 : PFD (Process Flow Diagram) of Propane Cycle for ethylene liquefaction.

II.2 The liquefaction of ethylene by Propylene (R1270)

For the liquefaction of ethylene, propylene can be used as a refrigerant while keeping the same principle of the previous liquefaction of ethylene with propane (R290). The proposed scheme is shown in the figure below.

Figure 21: PFD of Propylene Cycle for ethylene liquefaction.

Table 7 : PFD (Process Flow Diagram) of Propylene Cycle for ethylene liquefaction

II.3 The liquefaction of ethylene by ammonia (R717) as a refrigerant

For the liquefaction of ethylene we also used ammonia as a refrigerant and we kept the same principle of the previous liquefaction of ethylene with propylene (R1270)and propane (R290).

The process diagram is as follows:

Figure 22 : PFD of Ammonia Cycle for ethylene liquefaction.

Figure 23: Nitrogen Cycle PFD for ethylene liquefaction

The characteristics of the flows indicated in the simulation are given in the following table

Table 9: Nitrogen Cycle PFD (Process Flow Diagram) for ethylene liquefaction.

III. The technical-economic study

The technical-economic study is the first step in carrying out a new project; it is a study which consists of verifying that the project is technically feasible and economically viable.

III.1. Technical calculation

The technical calculation for a cooling loop is done by the following steps:

1. Set the compressor discharge pressure in the refrigeration cycle;

2. Determine the refrigerant flow rate;

3. Deduct the flow of ethylene sent to storage;

4. Calculate the specific power of liquefaction.

Table 10 : the different technical parameters.

III.2 The economic calculation

III.2.1 Financial valuation of the Boil off

The aim of this study is to estimate the cost of annual boil-off losses since the shutdown of the ethylene unit. The evolution of annual ethylene losses is illustrated in the following table:

III.2.2 Calculates investment costs for equipment for different processes and utility costs using HYSYS software

The software allows us to estimate the investment cost and the utility cost, the results obtained given in the following table:

Table 12: Calculation of investment costs for equipment for different processes and utility costs.

III.3 Calculation of maintenance cost

The order of magnitude of the maintenance cost of a petrochemical plant is approximately 5% of the investment per year « Maintenance cost = investment cost × 5% » The calculation of the maintenance cost is mentioned in this table [17]:

Table 13: Calculation of maintenance cost.

III.4 The impact on the environment

Table presents the ASHRAE 34 based safety properties and environmental properties of the selected fluids.

Table 14: represents the safety and environmental properties of proposed refrigerants

Global warming potential (GWP) is a measure of the contribution of a given mass of gas to global warming. GWP is a relative scale that compares the amount of heat trapped by greenhouse gases to the amount of heat trapped in the same mass of carbon dioxide. The GWP of carbon dioxide is 1 by definition. The ozone depletion potential (ODP) of a chemical compound is the relative amount of degradation it can cause to the ozone layer.

III.5.Refrigerant availability

The availability of refrigerants is noted in the following table:

III.6 The comparison between the proposed refrigerants

The comparison is made according to the following different criteria :

With :

(+): very low;

(++): Low;

(+++): High;

(++ ++): very high.

IV. Results and interpretation

IV.1. Calculation of the Payback period

Payback period = Investment / Profit

Profit = Income-Expenses

IV.2 Final investment cost of ethylene liquefaction using Propane (R290)

IV.2.1 Factors that may be project specific

- Means of access: roads, ports, airports;

- Temporary site installations;

- Off-site intermediate bases;

- Telecommunications.

IV.2.2 Political-economic factors

- Local monopolies – imposed suppliers;

- Exchange rate;

- Local competition;

- Taxation.

IV.2.3 Income

Table 17: Annual Income

GENERAL CONCLUSION

Storage tanks are integral to the process of storing liquefied gases like ethylene. However, the storage of such gases inevitably leads to the generation of BOG due to heat ingress and the natural boil-off of the stored product. BOG represents a significant loss of valuable ethylene gas, which is currently being burnt as waste at CP2K. The installation of an ethylene boil-off gas recovery unit is therefore crucial to mitigate these losses and improve operational efficiency.

In this context, we have examined the feasibility of re-liquefying the BOG using several refrigerant fluids (propane; propylene; ammonia; nitrogen). We have chosen the cascade process, which consists of creating cold by isenthalpic expansion of gas already compressed on a Joule-Thompson valve, followed by a separation of the gas / liquid which is done in a flash balloon, while we used the Claude process for nitrogen. The latter is based on the creation of cold by isentropic expansion of the gas in the turbine.

In this work we used the ASPEN HYSYS V-11 software to simulate the different ethylene vapor recovery circuits, while we used the ASPEN Capital Cost Simulator V11 extension to estimate the investment capital of the processes. proposed, and the study was completed with an evaluation of the losses caused by the boil-off phenomenon.

From the comparative study, it was concluded that propane is the best compared to other refrigerants either in the technical or economic side. The use of propane as a refrigerant for ethylene BOG recovery yielded promising financial outcomes: total expenses incurred amounted to $664,868.5 with an annual profit of $5,630,525.5. This outcome underscores the economic viability and operational benefits of implementing a BOG recovery system, not only reducing waste but also enhancing profitability through effective resource utilization.

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