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صادق أعضاء اللجنة العلمية على قبول المطبوعة المنجزة من طرف الأستاذ : زرقان السعيد

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- تحت عنوان : **Cryogenics Course**

وفق البرنامج المقترح لطلبة السنة الثالثة ليسانس طاقويات شعبة الهندسة الميكانيكية .

رئيس اللجنة العلمية للقسم

رئيس اللجنة العلمية لقسم الهندسة الميكانيكية

الأستاذ: مراوي موسى

Summary

This course manuscript serves as an educational resource for the cryogenics module aimed at third-year undergraduate students in the LMD program, energy option. Designed in line with the official curriculum, it aims to deepen understanding of cryogenics by utilizing knowledge of thermodynamics, heat transfer, and extremely low temperatures. It covers the main applications of the field as well as common techniques for producing cryogenic fluids, both for everyday uses and industrial needs.

The document also examines thermodynamic cycles used in low-temperature production, natural gas liquefaction processes, and the production of liquid compounds from air. Each chapter concludes with practical examples and solved exercises, making it easier to assimilate the concepts.

Presented as detailed lectures and illustrated with concrete examples, this manuscript facilitates a clear and progressive understanding of cryogenics.

Keywords

Cryogenics, Joule-Thomson expansion, cryogenic cycles, gas liquefaction, low temperature, gas separation.

Algerian People's Democratic Republic

Ministry of Higher Education and Scientific Research

Mohamed Boudiaf University – M'sila

Faculty of Technology

Department of Mechanical Engineering

1985

جامعة محمد بوضياف - المسيلة
Université Mohamed Boudiaf - M'sila

Cryogenics Course

Course Handout intended for students of the Bachelor's Degree in Energy Engineering

Prepared by Dr. Zergane Said

Preface

The work presented in the form of a course handout is a course material for the cryogenics module intended for third-year Bachelor's degree students in the LMD program. It is developed in accordance with the official program proposed for students in the energy option.

The objective of this document is to explicitly explore the field of cryogenics based on acquired knowledge in very low temperatures, thermodynamics, and heat transfer, examining their main applications as well as commonly used methods to obtain cryogenic fluids, whether in everyday life or in modern industry. The principal thermodynamic cycles applied in various processes for producing very low temperatures, techniques for natural gas liquefaction, and production of liquid compounds from air are explored and detailed in this course handout. At the end of each chapter, examples and exercises are provided with their solutions.

This manuscript presented in the form of detailed lectures with examples, facilitates a quick and simple understanding of cryogenics. It is structured into seven chapters as follows:

The first chapter: Serves as an introduction to cryogenics, covering the prerequisite basics of thermodynamics.

The second chapter: Presents gas cycles such as Brayton by studying the compressor.

The third chapter: Focuses on the study of compression and expansion steam turbine cycles (Rankine phase change cycle).

The fourth chapter: Describes the main industrial methods for obtaining low temperatures.

The fifth chapter: Gathers ideal thermodynamic cycles used in gas liquefaction and minimal work.

The sixth chapter: Illustrates different real cycles of gas liquefaction.

The seventh chapter: Addresses fundamental concepts related to gas separation by discussing descriptive aspects of some industrial processes for obtaining industrial gases.

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Chapter I

Thermodynamic review

I.1. Cryogenics

The term cryogenc is derived from :

Kruo (greek) = cold

Genisis (greek) = production

I.1.1. Definition

Cryogenic is the scientific discipline dedicated to investigating temperatures below 120 K, encompassing the generation, preservation, and application of extremely low temperatures in various industrial sectors. Its applications are diverse, notably in fields such as food, medicine, industry, physics, and livestock:

- **Food preservation**: Involves preserving food through rapid freezing, maintaining its original state, unlike conventional freezing methods that can cause surface dehydration and the formation of large ice crystals in the product.
- **Livestock breeding**: Aims to halt the progression of cells, allowing them to be reactivated later. It is used to preserve sperm, tissues, and as a last resort for individuals who can no longer be cured using current medical techniques.

- **Medical applications:** Preservation of blood cells, human and animal organs at cryogenic temperatures. It can also be used in the destruction of harmful tissues through freezing.

I.1.2. Cryogenic fluids

Are gases liquefied by cooling to a temperature below their boiling points. Among the gases listed in Table I.1, argon, helium, hydrogen, nitrogen, and oxygen are the most commonly used cryogenic gases, transported, handled, and stored in liquid form in the industrial sector

Table I.1 Boiling points of cryogenic fluids

Cryogenics gases	Boiling Temperature (K)
Acetylene	189
Hydrochloric acid	188
Nitrogen	78
Argon	88
Carbon dioxide	195
Helium 3	4
Helium 4	5
Hydrogen	21
Methane	112
Carbon monoxide	81
Oxygen	90
Boron trifluoride	173

I.1.3. Other application of cryogenics

Cryogenics is open to several areas of application such as:

- Food preservation using liquid nitrogen,
- The suspension of metabolism,
- The study of superconductivity (absence of electrical resistance),
- The study of superfluidity (absence of viscosity for a liquid),
- The transformation into a fine powder of all kinds of materials,
- Recovery of more than 90% of gases that destroy the ozone layer,

- The creation, from liquid nitrogen, of all kinds of snow.
- Rocket propulsion

I.1.4. Historical

Cryogenics was discovered around 1877 when oxygen was liquefied for the first time by caillet and pickel at a temperature of 90k, so the first cryogenic tests date back to the end of the 18th century; from this time, SO2 had also been liquefied by refrigeration using pressure. At the beginning of the 19th century “Faraday”, using pressure and refrigeration at the same time, succeeded in liquefying HBr, Hi, SiF_4, $C2H_4$. On the other hand, cryogenic fluids which are mainly gases, formerly called permanent gases, liquefaction tests date back to 1878 by “LINDE HAMPSON”, he was the first to liquefy the air in 1902; he was able to separate air-liquid, O_2-liquid, and N_2-liquid

I.2. Thermodynamic review

I.2.1. State forms of matter

In nature, there are three most well-known state forms that any substance can take, depending on the conditions of temperature and pressure. These forms are: solid form, liquid form and gas form. (Fig. I.1)

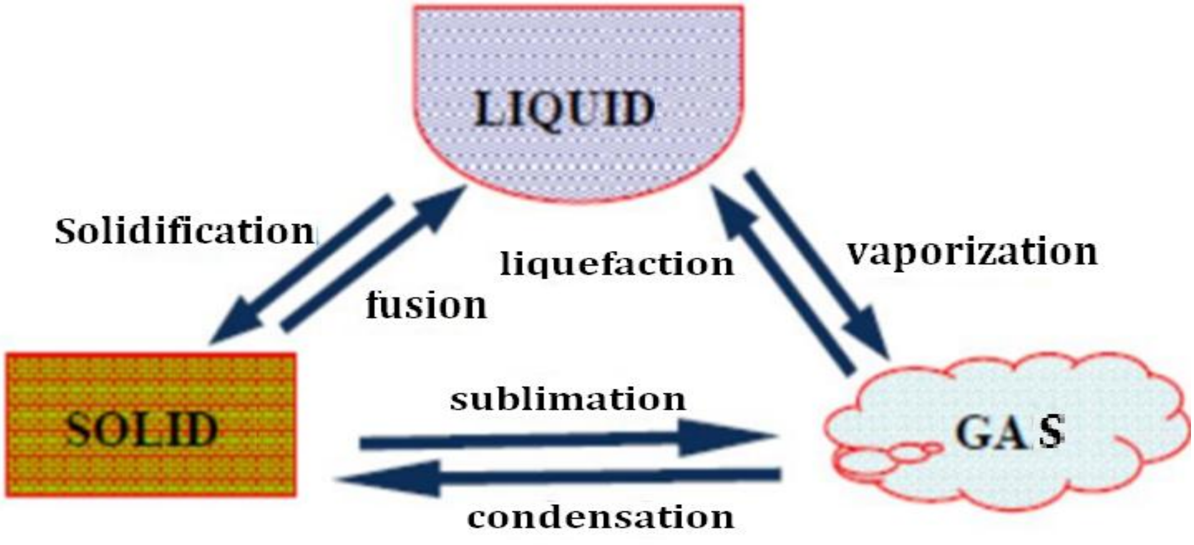

Fig. I.1 State forms of matter in nature

Another less known form of state of matter is also, paradoxically, the most widespread in the visible universe (99.99%) the stars, the intergalactic medium... is found in the plasma state. Plasma is a gas whose atoms, under the effect of temperature, have been dissociated. While in the other three states of matter (solid, liquid and gas) the nucleus and electrons of atoms are closely linked, they cease to be so in plasma.

The main comparisons of state forms of matter are shown in Table I.2

Table I.2 Comparisons of state forms

State	Condensed State	Fluid	Form	Volume	Compressibility	Diffusion capacity
Solid	Yes	No	definite	definite	Almost zero	Very slow
Fluid	Yes	Yes	Indefinite	definite	Very low	Slow
Gas	No	Yes	Indefinite	Indefinite	Very large	Very fast
Plasma	No	Yes	Indefinite	Indefinite	Extreme	Extreme

I.2.2. Phase diagram

Phase diagram is the phase equilibrium diagram, it represents the different phases of a pure body according to the variables: temperature/pressure. Figure I.2 shows the typical phase equilibrium diagram. The transition from one phase to another requires a heat input, whether sensible or latent heat.

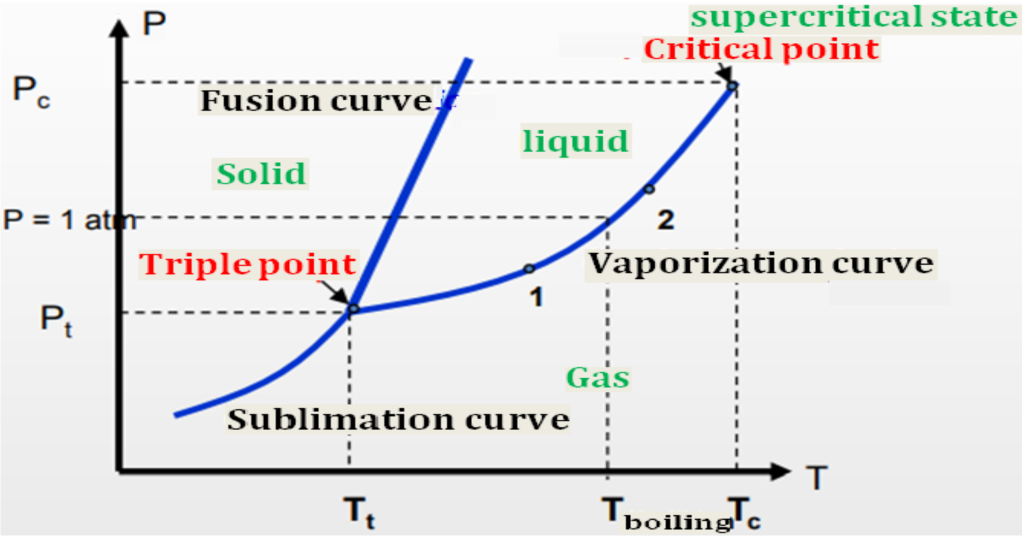

Fig. I.2 The typical phase equilibrium diagram

The phase diagram is established experimentally: the conditions are varied and the phase changes are observed. In this diagram, the three equilibrium curves correspond to a change of state.

I.2.2.1. Triple point (P_t,T_t)

Is the coexistence of a three phases; solid, liquid and gas in equilibrium.

I.2.2.2. Critical point (P_c, T_c)

Beyond this point, there is no longer any difference between the liquid and the gas : monophasic supercritical state.

I.2.2.3. Vapor Pressure

It is the pressure of the gas in equilibrium with the liquid or the solid, this vapor pressure follows a law of the type:

$$\log(P)=-A/T+B \qquad (I.1)$$

where A et B are constants specific to the susbtance

By reducing the pressure on the bath through gas pumping, the temperature of the bath decreases.

Note: Helium does not have a solid-liquid-vapor triple point but an additional liquid phase called Superfluid (quasi-infinite thermal conductivity, nearly zero viscosity).

The transition from one phase to another requires a heat input, either sensible or latent heat:

- **Sensible heat (Q_s):** Amount of heat exchanged without a phase change but with a temperature change.

$Q_s = mC_p\Delta T$ (I.2)

- **Latent Heat (Q_s):** Amount of heat exchanged with a phase change at a constant temperature.

$Q_s = mL_v$ (I.3)

Where C_p is the specific heat, L_v is the latent heat of vaporization, and ΔT is the temperature difference.

I.3. Obtaining cooling

The idea is based on the use of a low temperature cryogenic fluid which heats up in contact with a solid body. Generally the types of cryogenic processes are based on isentropic expansion.

I.3.1. Joule-Thomson expansion

A gas of the state (P_1 V_1 T_1) enters an insulated pipe, through a valve it passes to an expansion in the state (P_2 V_2 T_2) or a sudden cooling is caused with a drop in pressure (T_1 is lower at T_2) (Fig. I.3)

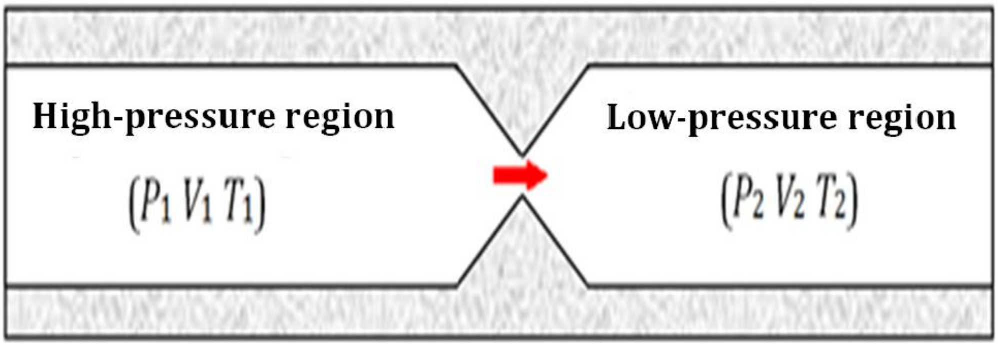

Fig. I.3 Expantion valve

The variation of the internal energy ΔU

$$\Delta U = Q + W = W_1 + W_2 \quad (I.4)$$

compression work W_1 (Wor received)

$$W_1 = -\int_{V_1}^{0} P_1 dv = P_1 V_1 \qquad (I.5)$$

Ralaxation work W_1 (assigned work)

$$W_2 = -\int_{0}^{V_2} P_2 dv = -P_2 V_2 \qquad (I.6)$$

So the variation of the internal energy

$$\Delta U = U_2 - U_1 = P_1 V_1 - P_2 V_2 \Rightarrow U_2 + P_2 V_2 = U_1 + P_1 V_1 \qquad (I.7)$$

$$U_2 + P_2 V_2 = H_2 \text{ et } U_1 + P_1 V_1 = H_1 \qquad (I.8)$$

We can conclude

$$H_2 = H_1 \Rightarrow \Delta H = 0 \qquad (I.9)$$

Or the isenthalpic transformation

I.4. Detailed properties of some cryogens commonly used in industry

- **Liquid Methane (LCH_4)** It boils at 111.7 K. It can be used as rocket fuel. Fuel in the form of liquefied natural gas (LNG) for transport.

- **Liquid Neon (LNe)** It is a clear, colorless liquid with a boiling point at 27.1 K. Neon is commonly used in neon advertising. Liquid neon is used commercially as a cryogen. It is compact, inert and less expensive than liquid helium.

- **Liquid nitrogen (LN2)** It boils at 77.36 K and freezes at 63.2 K. Resembles water in appearance – density 807 kg/m^3 (water - 1000 kg/m^3). Comes in 2 stable isotopes - N14 et N15 en proportion de 10000: 38. La chaleur de vaporisation est de 199,3 kJ (eau - 2257 kJ / kg) et il est produit par distillation de l'air liquide. N14 and N15 in the proportion of 10000:38. The heat of vaporization is 199.3 kJ (water - 2257 kJ/kg) and it is produced by distillation of liquid air. Nitrogen is mainly used to provide an inert atmosphere in the chemical and metallurgical industries. It is also used as a liquid to provide refrigeration. Preservation of food, blood, cell conservation. Superconductivity at high temperatures

- **Liquid Oxygen (LOX)** Blue in color - due to long O4 chains. Boils at 90.18 K and freezes at 54.4 K. Has a density of 1141 kg/m^3 (water – 1000 kg/m^3). O2 is slightly magnetic and exists in 3 stable isotopes - O16, O17, O18 in the ratio of (10000:4:20). Due to the unique properties of oxygen, there is no substitute for oxygen in any of its uses, it is widely used in industries and in medicine. It is widely used in the iron and steel manufacturing industry. Oxidizer propellant for spaceship rockets.

- **Liquid Argon (LAr)** It is a colorless, inert and non-toxic gas. It boils at 87.3 K and freezes at 83.8 K. It has a density of 1394 kg/m^3 (water – 1000 kg/m^3). Exists in the form of 3 stable isotopes - Ar35, Ar38, Ar40 and in a ratio of (338: 63: 100000).

- **Liquid air** For practical reasons, it is considered as a mixture of: 78% N2 + 21% O2 + 1% Ar + others. It has a boiling point of 78.9 K and a density of 874 kg/m^3, that of water being 1000 kg/m^3). Liquid air was previously used as a pre-cooler for low temperature applications. Liquid air is mainly used in the production of nitrogen, oxygen and rare gases**.**

Chapter II

Gas cycles (Brayton) – stady of the turbojet

II.1. Gas cycles (Brayton)

II.1.1. Definition

The gas turbine Brayton cycle, also known as the Joule cycle, is a thermodynamic cycle used in gas turbines and certain jet engines. This cycle involves compressing ambient air, mixing it with fuel, then igniting the mixture, causing its expansion and the production of work. Cooling is provided by the expansion of the gas in a turbine, while heat is extracted from the system in the form of mechanical work.

II.1.2. Functioning

The Brayton cycle allows for an increase in efficiency compared to certain other cycles. It is modeled by a closed cycle as depicted in Figure II.1.

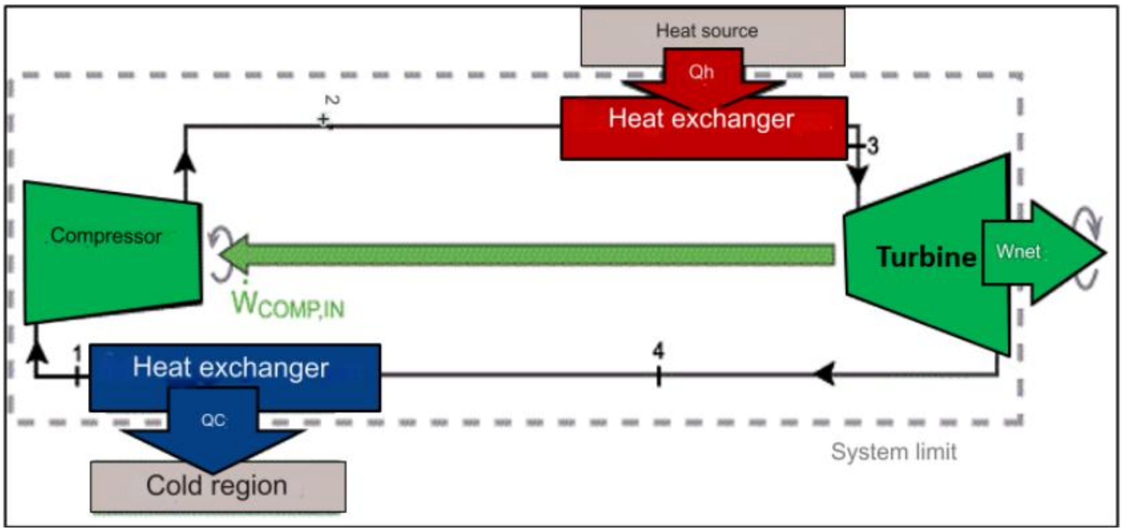

Fig. II.1 Closed cycle of Brayton

The Brayton cycle operates as follows:

1-2: Isentropic compression of fresh air

2-3: Isobaric heat addition during fuel combustion

3-4: Isentropic expansion to atmospheric pressure while producing energy.

4-1: Isobaric heat rejection

Assuming that in this cycle the fluids circulating in the gas turbine are perfect gases and that pressure losses are negligible, the (*T*-*S*) and (*P*-*V*) diagrams are represented in Figures II.2 and II.3.

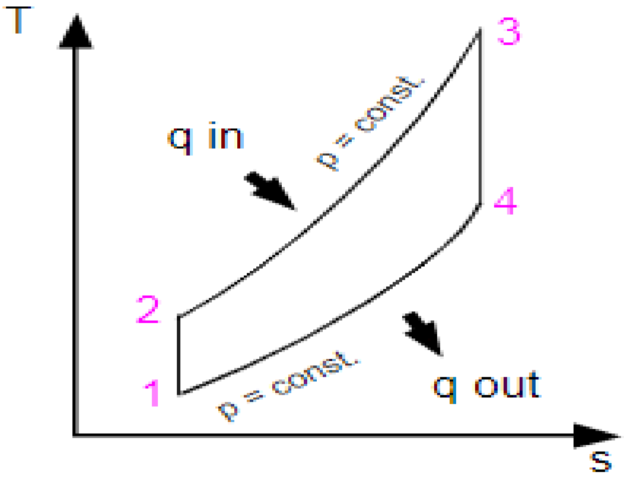

Fig. II.2 Diagram (*T S*)

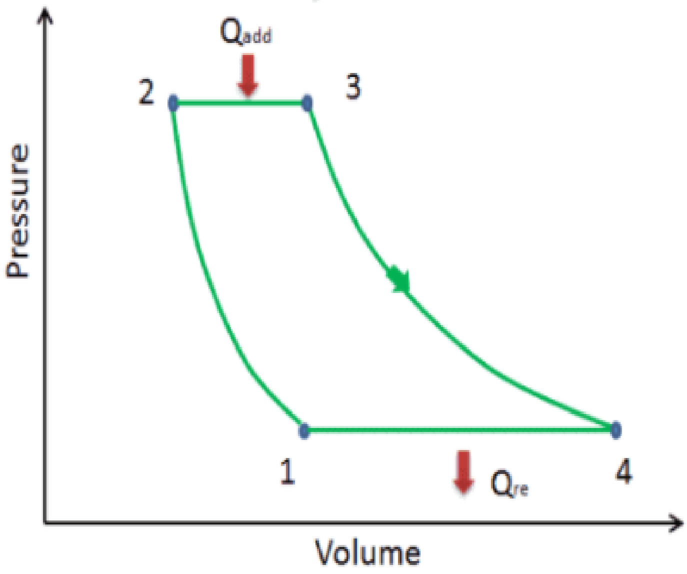

Fig. II.3 Diagram (*P V*)

II.1.3. Energy balance

Pour le cycle fermé de Brayton, la variation de l'énergie interne est nulle

$$\Delta U_{cyc}=\sum W+\sum Q=0 \qquad \text{(II.1)}$$

Alors pour les transformations selon le cycle de Brayton :

- Isentropic compression $Q_{12}=0$

$$h_2-h_1=W_c=C_p(T_2-T_1) \qquad \text{(II.2)}$$

- Isobaric combustion $W_{23}=0$

$$h_3-h_2=Q_{23}=C_p(T_3-T_2) \qquad \text{(II.3)}$$

- Isentropic expansion $Q_{34}=0$

$$h_4-h_3=W_{34}=C_p(T_4-T_3) \qquad \text{(II.4)}$$

- Isobaric heat rejection $W_{41}=0$

$$h_1-h_4=Q_{41}=C_p(T_1-T_4) \qquad \text{(II.5)}$$

So, the thermal efficiency of the theoretical cycle η_{th}

$$\eta_{th} = \frac{Q_2 + Q_1}{Q_2} = 1 + \frac{Q_1}{Q_2} = 1 - \frac{(T_4 - T_1)}{(T_3 - T_2)} = 1 - \frac{T_1}{T_2} = 1 - \left(\frac{P_1}{P_2}\right)^{\frac{1-\gamma}{\gamma}} \qquad (II.6)$$

In general, increasing the pressure ratio is the most direct way to increase the overall thermal efficiency of the Brayton cycle, as the cycle approaches the Carnot cycle. According to the Carnot principle, higher efficiencies can be achieved by increasing the gas temperature. However, there are also limits on the pressure ratios that can be used in the cycle.

The maximum temperature within the cycle is reached at the end of combustion and is limited by the maximum temperature that turbine blades can withstand. As is typically the case, metallurgical considerations (around 1700 K) impose upper limits on thermal efficiency. In the two diagrams (T S) of Brayton cycles with the same turbine inlet temperature but different compressor pressure ratios, it is evident that, for a constant turbine inlet temperature, the net work per cycle decreases according to the following relationship:

$$W = W_T - W_c \qquad (II.7)$$

Cycle A exhibits the highest efficiency. On the other hand, Cycle B generates a higher net work output per cycle (enclosed area in the diagram), thus a greater net output produced per unit mass flow rate. The work produced by the cycle, multiplied by the mass flow rate per cycle, equals the output power produced by the gas turbine. Consequently, with less work output per cycle (Cycle A), a higher mass flow rate (thus a larger system) is required to maintain the same output power, which may not be economical (Fig. II.4). This is a key consideration in gas turbine design, as engineers must balance thermal efficiency and compactness. In most common designs, the pressure ratio of a gas turbine varies from around 11 to 16.

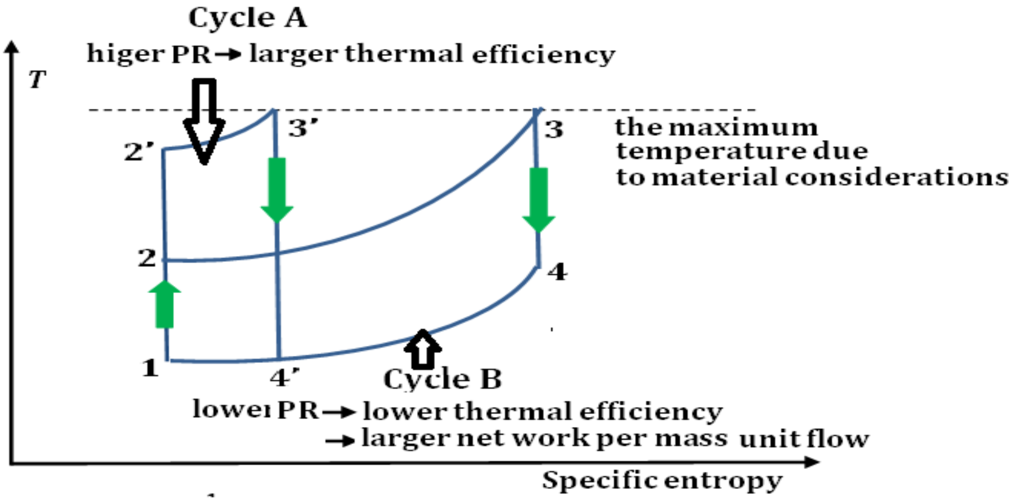

Fig. II.4 Ideal Brayton cycles with different pressure ratios and the same turbine inlet temperature

II.2. Turbojet

A turbojet engine is a propulsion machine that converts the chemical potential energy contained in a fuel, combined with an oxidizer which is ambient air, into kinetic energy. This kinetic energy is then used to produce a reaction force in a compressible medium, opposing in the direction of ejection.

II.2.1. composition

A turbojet engine consists of a tube inside which are arranged a multi-stage compressor, a combustion chamber placed on the same axis, a gas turbine, and an exhaust nozzle (Fig. II.5).

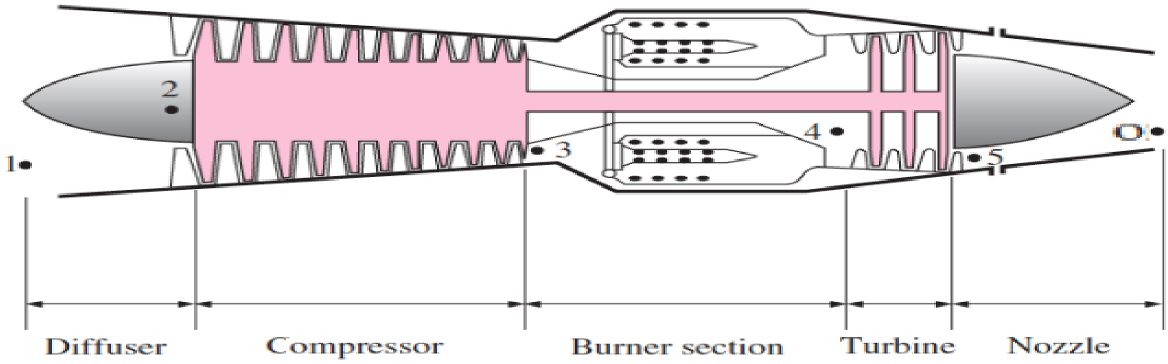

Fig. II.5 A turbojet

II.2.2. Operating principal

A turbojet engine operates on a similar principle. Air enters the engine through the inlet nozzle located at the front. It is first compressed and directed towards the combustion chamber, where it is then mixed with kerosene before being ignited. The speed difference between the incoming and outgoing air sets the engine in motion, while the principle of gas turbines forms the basis of thrust.

They operate according to the following cycle:

- 0-1-2: Isentropic compression
- 2-3: Isobaric combustion
- 3-4-5: Isentropic expansion in the turbine, then in the nozzle
- 5-0: Isobaric exhaust

So, we can present this cycle on the $(P\ V)$ diagram as illustrated in Figure II.6.

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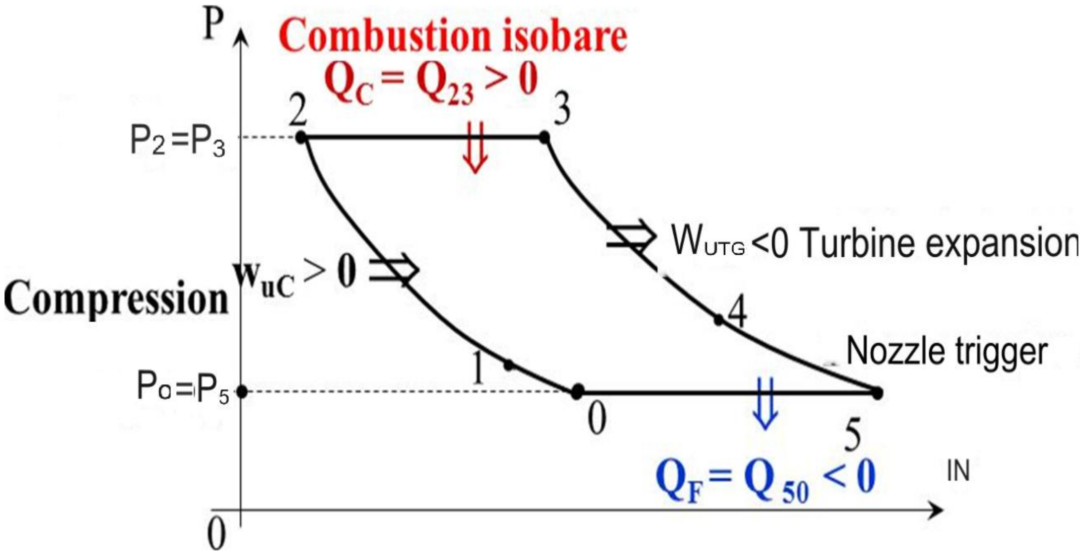

Fig. II.6 Diagram $(P\ V)$ of turbojet

And the diagram $(T\ S)$ in Figure II.7.

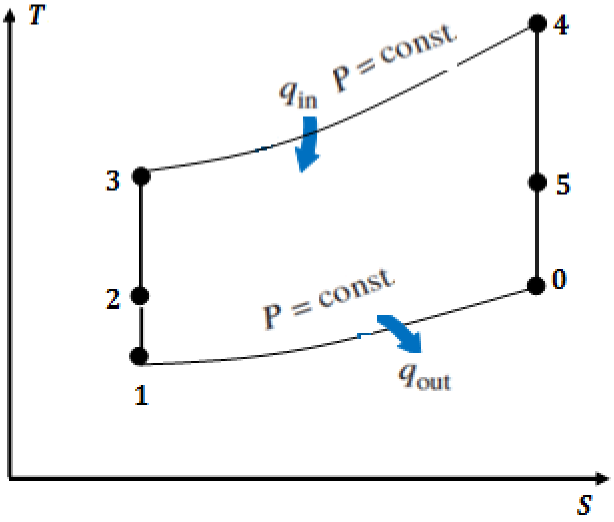

Fig. II.7 Diagram ($T\,S$) of turbojet

Chapter III

Phase change cycles (Rankine)

III.1. Rankine cycle

The Rankine cycle, or Rankine vapor cycle, is an ideal thermodynamic cycle of a heat engine that involves a phase change. It constitutes the fundamental operating cycle of steam power plants (Fig. III.1). At constant pressure, it converts some of the heat into mechanical work. Heat is supplied from outside to a closed loop, which typically uses water (in liquid and vapor phases) as the working fluid. This fluid undergoes a phase change, transitioning from the liquid state to the vapor state and vice versa. The Rankine cycle was invented by William John Macquorn Rankine (1820-1872), who gave it its name.

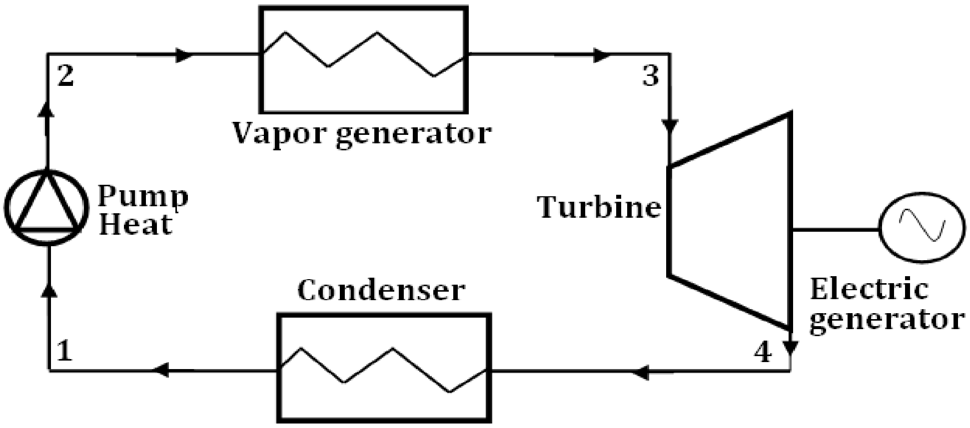

Fig. III.1 Rankine cycle

The Rankine cycle can occur in two forms:

- The open Rankine cycle, where water vapor is discharged into the atmosphere. This was the case with old steam locomotives, which required the transport of large quantities of water as well as coal.
- The closed Rankine cycle, as used in thermo-electric power plants. In this type of cycle, the residual heat from steam condensation can be recovered through cogeneration.

III.1.2. Fonctioning

The Rankine cycle represents the ideal model for a basic thermal power plant. It also serves as a basis for understanding the operation of steam engines. In this cycle, a fluid, typically water, undergoes transformations involving heat exchanges with two heat sources at constant temperature. These exchanges can result in transitions between the liquid and vapor phases.. The stages that compose this cycle are:

- 1-2 : The isentropic compression occurs in the pump. The working fluid is pumped from low to high pressure. Since the fluid is in a liquid state at this stage, the pump requires little input energy.
- 2–3 : The high-pressure liquid enters the boiler. It is heated at constant pressure through an isobaric process by an external heat source to become saturated dry steam. During this phase, a phase change of water from liquid to gas occurs, and both points are located on the water saturation curve..
- 3–4: Isentropic expansion in turbine: Saturated dry steam expands through a steam turbine, generating energy. From a thermodynamic perspective, this results in a decrease in the temperature and pressure of the steam, and some condensation may occur as a result.

- 4–1 : Heat rejection at constant pressure in the condenser, isobaric process: Wet steam enters a condenser, where it condenses at constant pressure to become saturated liquid.

In an ideal Rankine cycle, the pump and turbine would be isentropic, meaning they would not generate entropy and thus maximize the net work output. Processes 1-2 and 3-4 would be represented by vertical lines on the T-S diagram (Fig. III.2) and would more closely resemble the Carnot cycle.

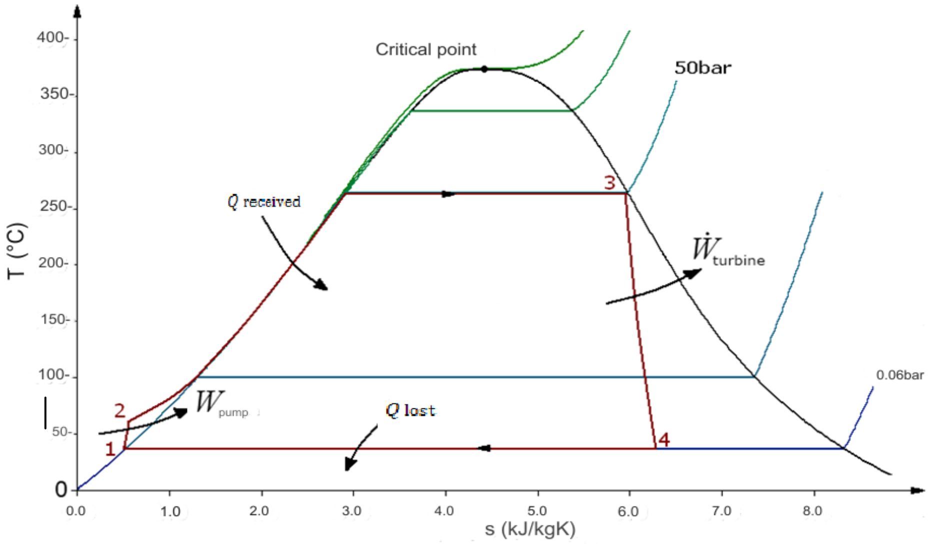

Fig. III.2 T S diagram of the Rankine cycle

The Rankine cycle illustrated here prevents the working fluid state from reaching the superheated vapor region after expansion in the steam turbine. In this case, the energy extracted by the condensers is reduced. The actual steam production cycle differs from the ideal Rankine cycle due to irreversibilities caused by fluid friction and heat loss to the environment. Consequently, the heat loss reduces the net work efficiency and requires the addition of a hot steam source.

III.1.2. Energy balance

The Rankine cycle is characterized by a closed system where the quantity of circulating water remains constant. Thus, the mass flow rate of water, represented by $\dot{m}$, through the different components such as the pump, boiler, turbine, and condenser remains constant. However, the various thermal machines integrated into this cycle are open thermodynamic systems.

- In pump (1-2): Isentropic compression of water

$$W_{12} = h_2 - h_1 \quad \text{(III.1)}$$

- In boiler (2-3): Isobaric heating of water, which involves vaporization in the boiler.

$$Q_{23} = h_3 - h_2 \quad \text{(III.2)}$$

- In turbine (3-4): Isentropic expansion in the turbine, the work transferred by the steam in the turbine is :

$$W_{34} = h_4 - h_3 \quad \text{(III.3)}$$

- In condenser (4-1): Isobaric liquefaction cooling in condenser. The heat lost by the steam in the condenser during the transformation is:

$$Q_{41} = h_1 - h_4 \quad \text{(III.4)}$$

The Rankine cycle is a closed system, so we can apply the first law of thermodynamics to it, which states:

$$\sum Q_{cyc} + \sum W_{cyc} = 0 \quad \text{(III.5)}$$

So, the thermodynamic efficiency

$$\eta_{th} = \frac{Q_{23}+Q_{41}}{Q_{23}} = 1 + \frac{h_1 - h_4}{h_3 - h_2} \quad \text{(III.6)}$$

III.2. Improvements to the Rankine cycle

To achieve good thermodynamic efficiency, it is essential to design a Rankine cycle with the highest possible steam pressure (HP) and the lowest possible pressure (BP). However, the selection of these values is constrained by a critical factor: HP and BP pressures must be carefully chosen to maintain moisture content in the turbine below 10%, in order to avoid corrosion issues and consequent efficiency reduction. Challenges related to moisture resulting from increasing HP or decreasing BP can be overcome through improvements to the Rankine cycle. One such improvement involves superheating the steam exiting the boiler. This process, known as the Rankine cycle with superheat or Hirn cycle, addresses moisture challenges. Currently, the maximum allowable temperature for this superheat is around 600°C.

III.2.1. Hirn cycle

The Hirn cycle (or Rankine cycle with superheat) is a variant of the Rankine cycle, in which the steam leaving the boiler is superheated to a temperature higher than the critical temperature before being expanded in the turbine. This variant is used in power plants for electricity production (Fig. III.3).

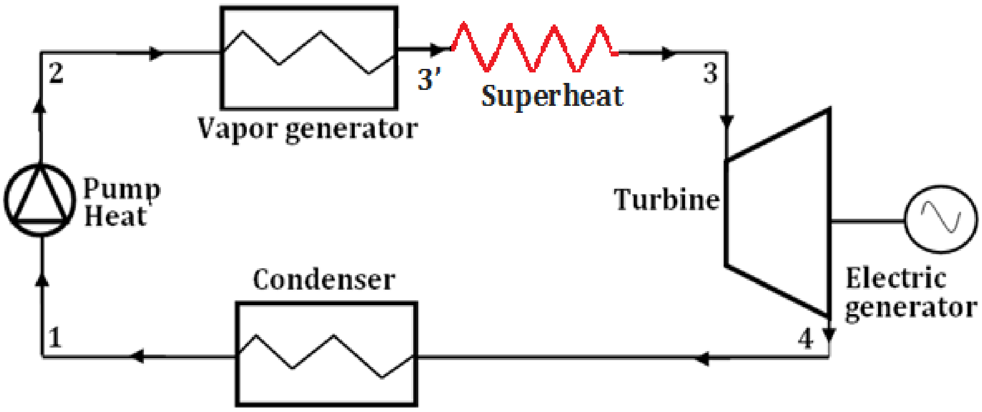

Fig. III.3 Hirn cycle

In this cycle, steam is superheated, thus transitioning from a state of dry saturated vapor (3) to a state of superheated vapor (3'), while maintaining constant pressure. The first two phases are characteristic of the simple Rankine cycle, whereas the third phase is specific to the Hirn cycle (Fig. III.4).

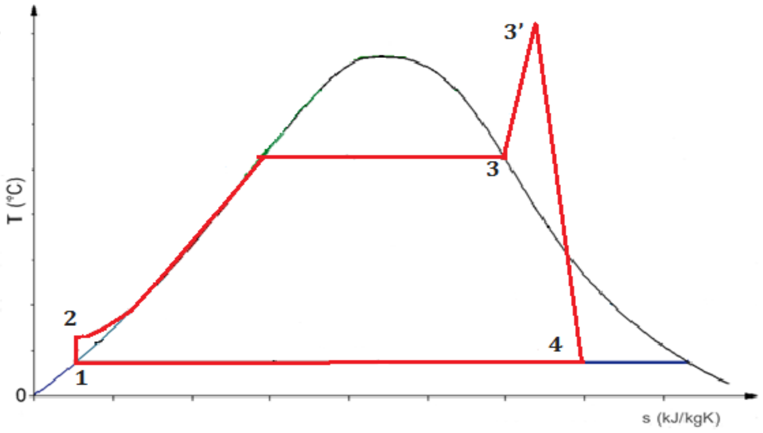

Fig. III.4 $T\,S$ diagram of the Hirn cycle

Chapter IV

Main industrial methods for obtaining low temperature

Introduction

The processes of refrigeration and cryogenic liquefaction involve the combined use of compression, cooling, thermal regeneration, and expansion.

In this field, it is possible to distinguish the following methods:

- Isenthalpic Joule-Thomson expansion.
- Reversed Brayton cycles with isentropic expansion.
- Mixed process combining isenthalpic and isentropic expansion (Claude cycle).
- Classic or integrated cascades.

IV. 1. Isenthalpic Joule-Thomson expansion

The isenthalpic Joule-Thomson expansion is a technique used for liquefying gases to separate gas mixtures. It enables the liquefaction of gas mixtures such as air as well as atmospheric gases like oxygen, nitrogen, and argon on an industrial scale. It can also be used in refrigeration for temperatures ranging between 77 and 100 K. Its first industrial application was developed by Carl Von Linde (Linde cycle).

The Linde cycle includes the following steps:

1. Compression: The gas is compressed at high pressure using a compressor.
2. Preliminary cooling: The compressed gas is cooled to a temperature close to ambient temperature using a heat exchanger.
3. Isenthalpic expansion: The cooled gas is then rapidly expanded through an expansion valve, causing a temperature drop without phase change.
4. Final cooling: The expanded gas is further cooled to an even lower temperature using another heat exchanger.
5. Liquid collection: At this stage, some of the gas liquefies, and the liquid is collected. The remaining uncondensed gas is recycled back into the system. The Linde cycle was one of the first effective industrial methods for gas liquefaction on a large scale. It paved the way for many industrial applications, particularly in the production of liquid nitrogen, oxygen, and argon, as well as in the field of cryogenics.

For example, refer to Figure IV.1 for air.

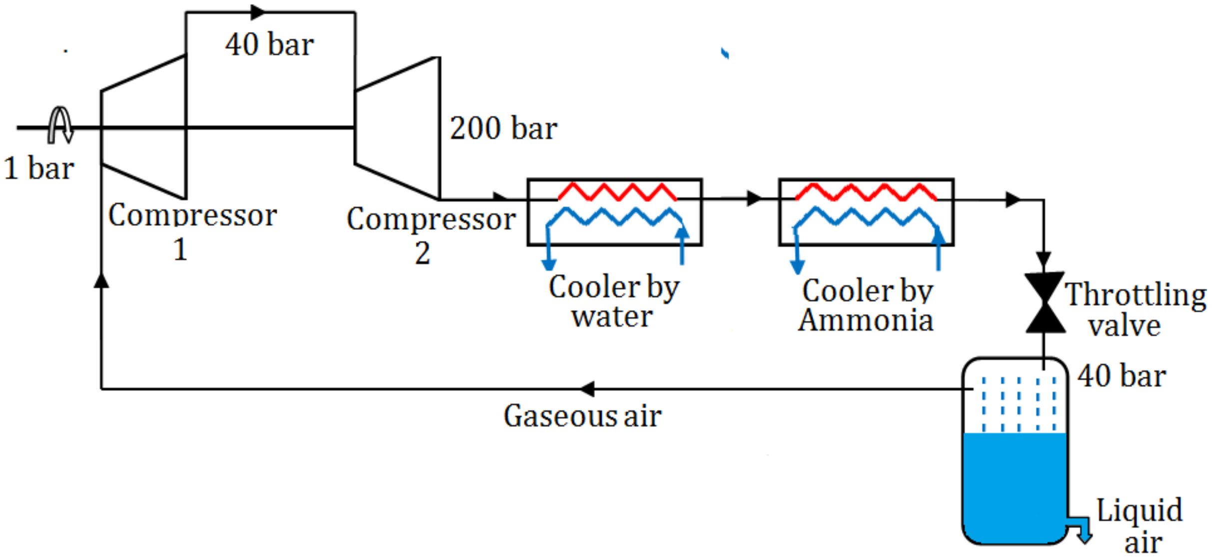

Fig. IV.1 Linde cycle

The dehydrated air is compressed from 1 atm to 40 atm in compressor C, then from 40 atm to 200 atm in compressor C'. It is then cooled in heat exchanger R to ambient temperature by water, and then to 213 K by liquid ammonia (NH3). Afterwards, it passes through coil s and undergoes expansion through valve r until it reaches 40 atm. The liquid is collected at point 7, while the unliquefied portion returns to compressor C' by passing through coil S

IV. 2. Reversed Brayton cycle with isentropic expansion

It is a cycle that achieves refrigeration by reversing the Brayton cycle, meaning a gas compressed in a machine increases its temperature, and a gas expanded in a machine, producing work (turbine or piston machine...), decreases its temperature.

This cycle operates according to the following stages (Fig. IV.2):

- (1-2) Adiabatic compression
- (2-3) Isobaric cooling in a condenser
- (3-4) Adiabatic expansion in a turbine
- (4-1)Evaporation

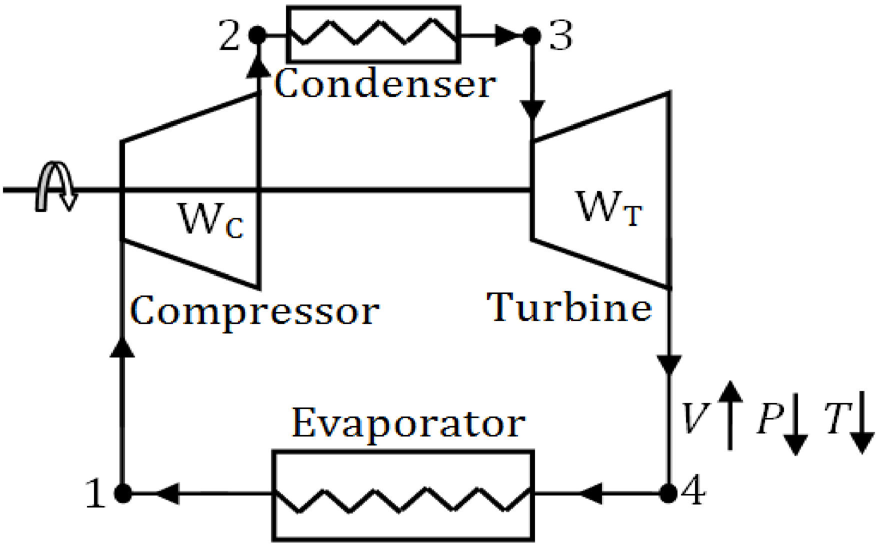

Fig. IV.2 Reversed Brayton cycle

The (h S) diagram is represented in figure IV.3

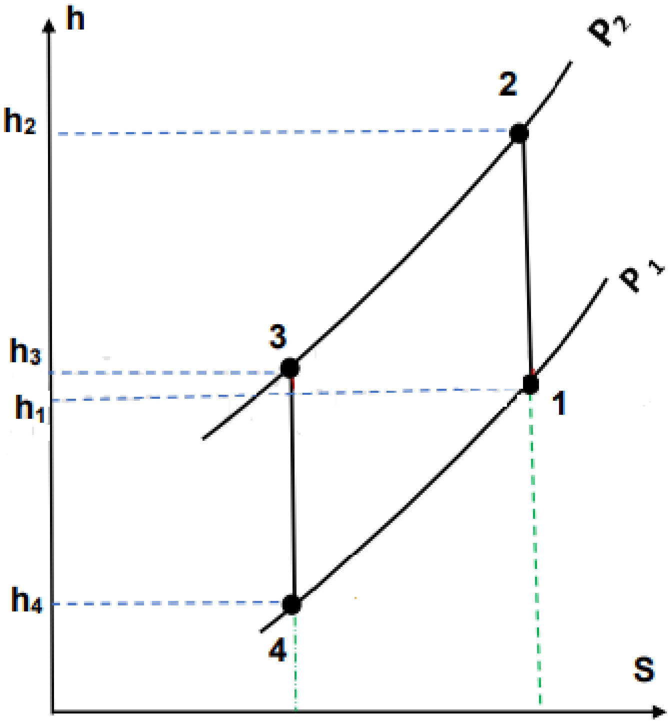

Fig. IV.3 ($h \quad S$) Diagram of reversed Brayton cycle

In inverse Brayton cycles, cold is obtained through the adiabatic expansion of the working fluid (typically a gas) through a turbine. As the fluid expands in the turbine, its temperature decreases, allowing for the extraction of heat from the surrounding environment or a low-temperature heat reservoir, thus producing a refrigerating effect. Subsequently, heat is typically rejected in a condenser, where the fluid is cooled and returns to a liquid state. This liquid is then pumped to the evaporating pressure, where it absorbs heat from the low-temperature environment again, and the cycle repeats. So, for the energy balance :

- The work received be gas in compressor

$$W_c = h_2 - h_1 \tag{III.1}$$

- The energy exchanged in condenser

$$Q_{32} = h_3 - h_2 \tag{III.2}$$

- The work provided to the turbine by the gases

$$W_T = h_4 - h_3 \qquad \text{(III.3)}$$

- The energy exchanged in evaporator

$$Q_{14} = h_1 - h_4 \qquad \text{(III.4)}$$

And the net work is :

$$W_{net} = (h_2 - h_1) - (h_4 - h_3) \qquad \text{(III.5)}$$

IV. 3. Mixed process combining isenthalpic and isentropic expansion (Claude cycle).

The Claude cycle is characterized by the fusion of a Brayton cycle comprising one or more stages and a Joule-Thomson cycle. It involves an isentropic expansion in the turbine, followed by an isenthalpic expansion in the only relaxation phase leading to gas liquefaction. The beginning of the cycle is similar to that of Linde's: compression of the gas to be liquefied, then cooling to ambient temperature. Its operation is described as follows (Fig. IV.4) :

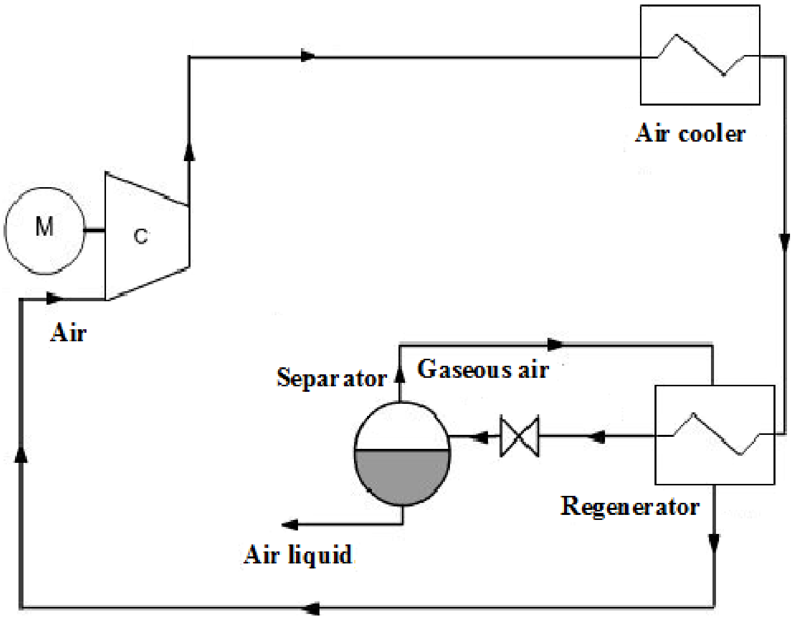

Fig. IV.4 Claude cycle

- Compression: The refrigerant gas is compressed at high pressure in a compressor, thus increasing its temperature and pressure.
- Condensation: The compressed gas passes through a condenser where it transforms into liquid, releasing heat. This heat is then rejected outside the system.
- Expansion: The high-pressure liquid is expanded through an expansion valve, reducing its pressure and temperature.
- Evaporation: The low-pressure and low-temperature liquid is directed to an evaporator where it absorbs heat from the environment, causing its evaporation and thus cooling the space to be refrigerated.
- Recompression: The evaporated gas is drawn back into the compressor, initiating a new cycle.

This process is repeated continuously to maintain the desired temperature in the refrigeration system as represented in figure IV.5.

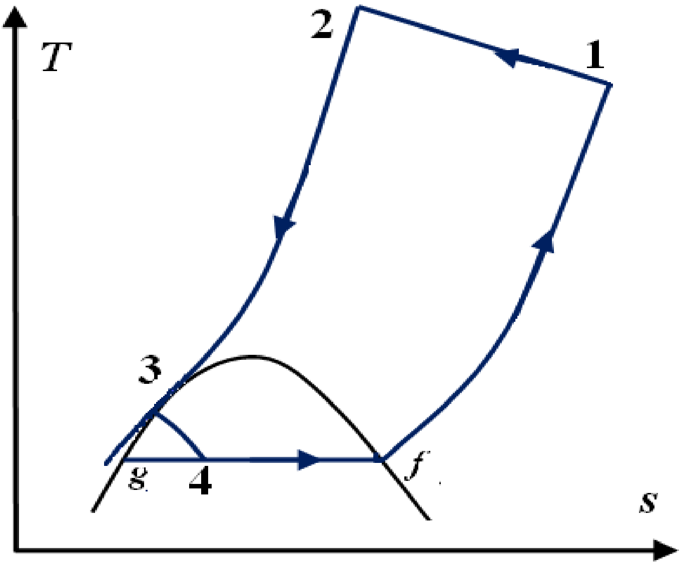

Fig. IV.5 (T s) diagram of Claude cycle

IV.4. Classic or integrated cascades

A cascade system is a type of refrigeration that uses multiple simple refrigeration units, each with different refrigerants. In this system, the cold source of one unit acts as the hot source for the next unit. For example, to liquefy nitrogen as illustrated in Figure IV.6:

- Ammonia is condensed at 20°C under pressure and then vaporized at -43°C after expansion.
- Ethylene is condensed at -43°C under pressure due to the evaporation of ammonia, and then vaporized at -100°C after expansion.
- Methane is condensed at -100°C under pressure and then vaporized at -161°C after expansion.
- Finally, nitrogen is condensed at -161°C under pressure.

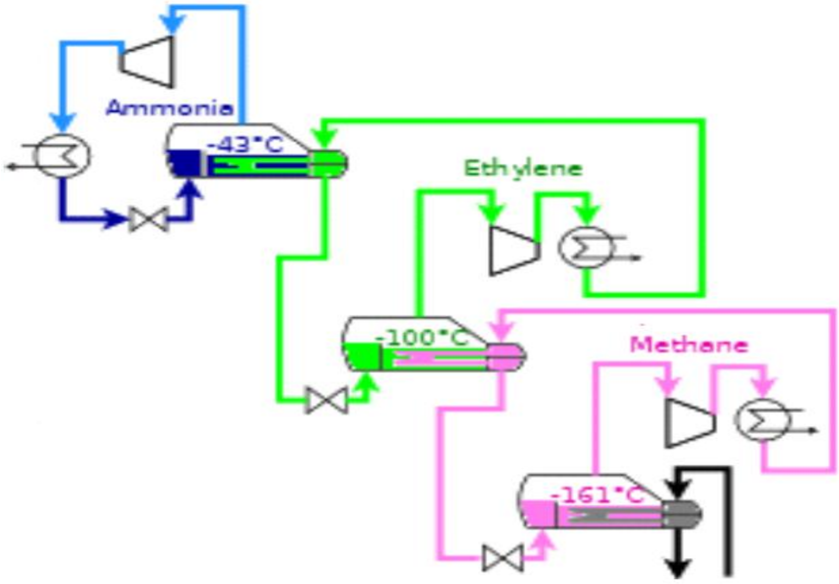

Fig. IV.6 Cascade system

A cascade system offers specific advantages compared to other cooling methods. In a cascade system, the compression ratio of each stage is reduced, which improves the volumetric efficiency at each level and makes the entire system much more efficient. Additionally, it is important to note that a cascade cooling system also requires a smaller compressor displacement.

Chapter V

Ideal liquefaction cycles and minimal work

Introduction

The ideal thermodynamic cycle for gas liquefaction is impractical in reality, leading to the use of modified cycles. This ideal cycle serves as a benchmark for evaluating various liquefaction processes by comparing their effects, such as ratios and certain defined functions.

Liquefaction is a process that converts a gas into a liquid, representing the reverse of vaporization. Although the term "condensation" is commonly used to describe this phenomenon, it is not entirely accurate from a thermodynamic perspective. Liquefaction allows gases to be stored and transported in small-volume containers and also facilitates the attainment of very low temperatures through the evaporation of the liquid. When a gas's critical temperature is higher than the ambient temperature, it can be liquefied simply by compressing it. For example:

- Sulfur dioxide liquefies at 20 °C when compressed to 4 bars

- Ammonia (NH_3) liquefies under a pressure of 9 bars.

Gas liquefaction is crucial in industry, particularly for the production of pure gases through fractional distillation.

The ideal liquefaction system that we will model is that of the first processes of the Carnot cycle, a reversible isothermal compression followed by a reversible isentropic expansion

V.1. Carnot liquefaction cycle

The Carnot liquefaction cycle is a theoretical model that illustrates an ideal gas liquefaction process, based on the Carnot cycle, which is a reversible thermodynamic cycle that achieves maximum efficiency in heat-to-work conversion systems. This cycle is used as a reference in thermodynamics to assess the maximum efficiency of a heat engine or refrigeration system. Although the ideal Carnot cycle is primarily used to compare and evaluate the efficiency of real liquefaction processes, it is challenging to implement perfectly due to technical limitations and the irreversibilities inherent in real processes. Nevertheless, it provides a valuable framework for understanding the fundamental principles of liquefaction and for comparing the performance of various liquefaction cycles used in industry.

The Carnot cycle includes a compressor, an expander and a reservoir (Fig. V.1).

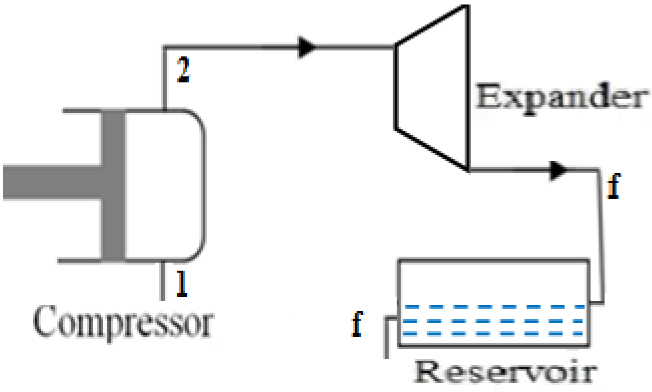

Fig. V.1 Carnot cycle

The evolution of this cycle is as follows:

The liquefied gas is reversibly and isothermally compressed from the ambient state, point 1, to a certain pressure, point 2. This pressure is chosen so that the gas is in the saturated liquid state at point f, following a reversible isentropic expansion through the expander. At the final state at point f, the pressure is the same as the initial pressure, at point 1.

The pressure reached at the end of isothermal compression for nitrogen, as an example, is extremely high, around 70 to 80 GPa. In practice, it is very difficult to achieve such pressures in a liquefaction system, which partly explains why this type of process is not used in liquefaction facilities.

The (T s) diagram of this cycle is presented in Figure V.3.

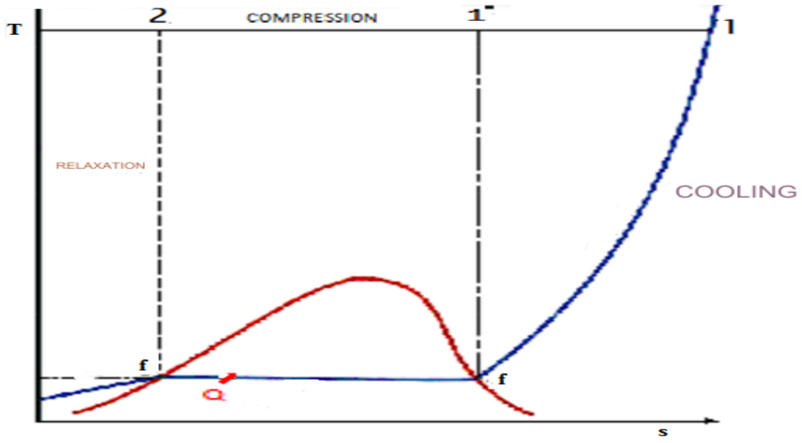

Fig. V.3 Diagram (T s) of Carnot cycle

The work required to cool the gas to its liquefaction temperature TfT_fTf, transitioning from state 1 to state *f*, corresponds to the actual liquefaction work.

V.2. Minimum liquefaction work

The work *W* is the value defined by the reversible process from 1 to *f*. The variation of internal energy :

$$W - Q = U_f - U_1 \tag{V.1}$$

The work required to go from point 1 (P_1, V_1) to point f (P_1, V_f) (the area 1, 2 and *f*).

$$W = Q + U_f - U_1 = T_1(S_1 - S_2) + U_f - U_1 \tag{V.2}$$

Part of the work provided

$$W' = P_1(V_1 - V_f) \tag{V.3}$$

So the minimum work to produce is:

$$W - W' = T_1(S_1 - S_2) - (H_1 - H_f) \tag{V.4}$$

The minimum work W-W' is represented by the area 1 2 f. In practice, isothermal compression is difficult to achieve. It is replaced by adiabatic compression followed by cooling at constant pressure and isenthalpic expansion is replaced by adiabatic expansion through a valve.

Note: Point 1 is normal gas conditions at ambient conditions, and point 2 is chosen so that the fluid gases reach the saturated liquid state.

By applying the first thermodynamic principle to the 'compressor and expander' system we will have:

$$Q_r - W = m(h_l - h_1) \tag{V.5}$$

Where :

Q_r : Heat transfer from the compressor [kJ],
W : Work required for liquefaction [kJ],
m : Mass of the fluid flowing in the system [kg],
h_l : Enthalpy of the liquid phase [kJ/kg],
h_1 : Enthalpy of the gas [kJ/kg].

and by the second thermodynamic principle we obtain:

$$Q_r = mT_1(S_2 - S_1) \tag{V.6}$$

by combining equations (V.5) and (V.6) we obtain

$$(Q_r - W) - Q_r = m(h_l - h_1) - mT_1(S_2 - S_1) \tag{V.7}$$

Where :

S_2 =S_l: Entropy of the gas leaving the compressor [kJ/kg.K]

S_l : Entropy of the liquid [kJ/kg.K]

S_1: Entropy under normal conditions [kJ/kg.K]

The work per unit mass becomes:

$$W/m = T_1(S_2 - S_1) - (h_l - h_1) \quad \text{(V.8)}$$

The ideal work required depends only on the pressure and temperature at point 1 and the type of gas to be liquefied, generally point (1) is taken under ambient conditions.

In the following table (Table 1) we find the list of some ideal works required for some gases and for a point (1) taken at 101.3 kpa and at 300K.

Table. V.1 Boiling point and the ideal work of liquefaction of some gases

Gas	Eullition temperature (K)	Ideal liquefaction work (kJ/kg)
He4	3.19	8178
He3	4.21	6819
H_2	20.27	12019
N_2	77.36	768.1
Air	78.80	738.9
CH_4	111.7	1091
O_2	90.18	635.6

Chapter VI

Real liquefaction cycles

Introduction

The natural gas liquefaction industry encompasses a growing variety of processes, with the most commonly used being classic cascade cycles and integrated cycles.

VI.1. Classic cascade liquefaction cycles

A classic cascade liquefaction cycle is a process used to liquefy natural gas in several successive stages. It relies on the principle of refrigeration by compression and expansion of multiple refrigerants, each with a boiling point lower than the previous one. This process is employed in Arzew (Oran) in three units of CAMEL (Compagnie Algérienne de Méthane Liquéfié), commissioned in 1963, with a capacity of 0.5 × 10^9 Nm3/year (normal cubic meters per year)

This cycle is characterized by:

Multiple refrigerants: Several refrigerants are used, typically three, with each fluid having a lower boiling point than the previous one. The first fluid, at a higher temperature, cools the natural gas to a certain temperature. The second fluid takes over to further lower the temperature.

Finally, a third refrigerant further reduces the temperature until the conditions where natural gas liquefies are reached, which is around -162°C.

Compression and expansion: Each refrigerant is compressed to increase its pressure and temperature, then cooled by heat exchange before being expanded in an expander, causing a sudden drop in temperature. This process allows for the gradual cooling of natural gas.

Energy efficiency: This cascading cycle is designed to be energy-efficient by avoiding large temperature differences between the natural gas and the refrigerants, which reduces energy consumption.

This process is used for the production of liquefied natural gas (LNG), which is easier to transport and store than natural gas in its gaseous form.

Figure V.1 illustrates an example of cascade liquefaction, with three stages of propane, four of ethylene, and three of methane. The first stage consists of a propane cycle that is compressed to 10.8 bars in order to be condensed at 30°C in the water refrigerant. During this condensation, the propane transfers a certain amount of heat to the water.

- This first cycle ensures the transfer of cold between the water temperature and that of -42°C
- The second cycle, consisting of ethylene compressed to 17 bars, ensures the transfer from -42°C to -104°C.
- The third cycle, consisting of methane compressed to 17 bars, ensures the transfer from -104°C to -161°C.

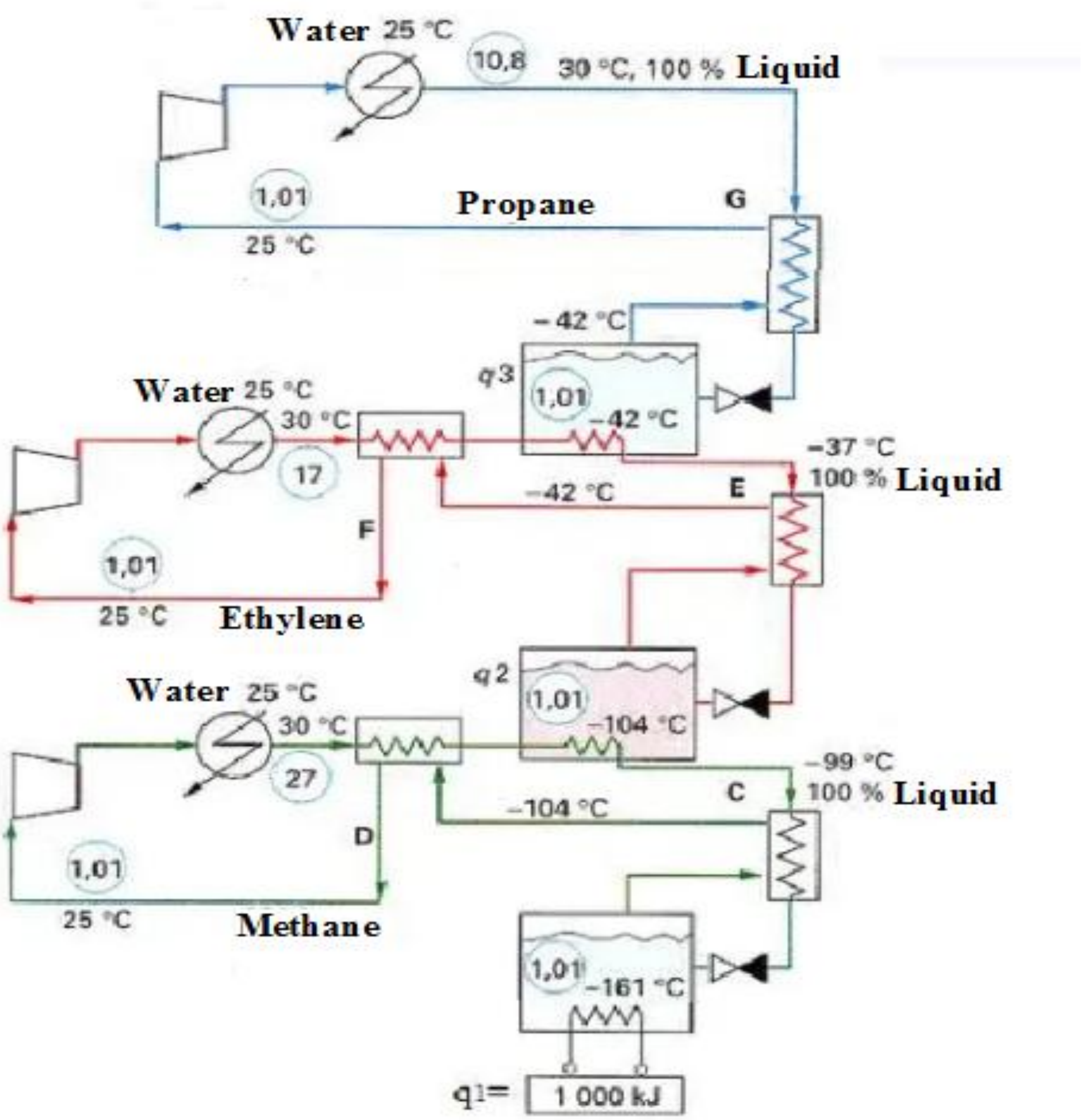

Fig. VI.1 Classic cascade liquefaction cycle

VI.1.1. Thermodynamic efficiency

The thermodynamic efficiency η of this cycle is the ratio between the system's efficiency and Carnot efficiency.

$$\eta = \frac{\varepsilon}{\varepsilon_C} \tag{VI.1}$$

knowing that :

$$\varepsilon = \frac{W_2}{W} \tag{VI.2}$$

And

$$\varepsilon_C = \frac{T_1}{T_2 - T_1} \tag{VI.3}$$

VI.2. Integrated liquefaction cycle

The integrated cascade liquefaction cycle is a process where multiple refrigeration cycles are combined to liquefy natural gas. Each cycle uses a different refrigerant, typically in three stages, such as propane, ethylene, and methane, allowing the gas to be cooled to progressively lower temperatures. The term "integrated" means that these cycles are optimized and combined into a single system to maximize energy efficiency and minimize operational costs. This process is commonly used in natural gas liquefaction plants to achieve temperatures as low as -162°C.

This "integrated" cycle means that the different refrigeration cycles are combined and optimized to operate together smoothly, thereby reducing energy losses and increasing the overall efficiency of the process.

VI.2.1. Operating principal

The operating principle of the integrated cascade liquefaction cycle is based on a series of progressive cooling steps, carried out using several distinct refrigerants, to transform natural gas into a liquid. Here are the main steps of the process (Fig. VI.2):

1. **Initial compression of natural gas**: Natural gas is first compressed to increase its pressure, thereby facilitating the subsequent cooling steps.
2. **Stepwise cooling with refrigerants**: The natural gas passes successively through several refrigeration cycles using different refrigerants (such as propane, ethylene, and methane). Each refrigerant is selected based on its ability to absorb heat at a specific temperature:
    - Propane is used for initial cooling at moderately low temperatures.
    - Ethylene is used to further lower the temperature.

   - Methane or another refrigerant is used for the lowest temperatures, allowing the necessary cooling levels for liquefaction to be reached.

3. **Successive expansion steps**: In each cycle, the refrigerant is compressed, cooled, and then expanded to absorb heat from the natural gas and lower its temperature.
4. **Condensation and liquefaction**: As the temperature of the natural gas decreases, it reaches the point where it transitions from a gaseous state to a liquid state, usually at a temperature of around -162 °C.
5. **Storage of the liquefied gas**: Once liquefied, natural gas is stored in cryogenic tanks for transport or use.

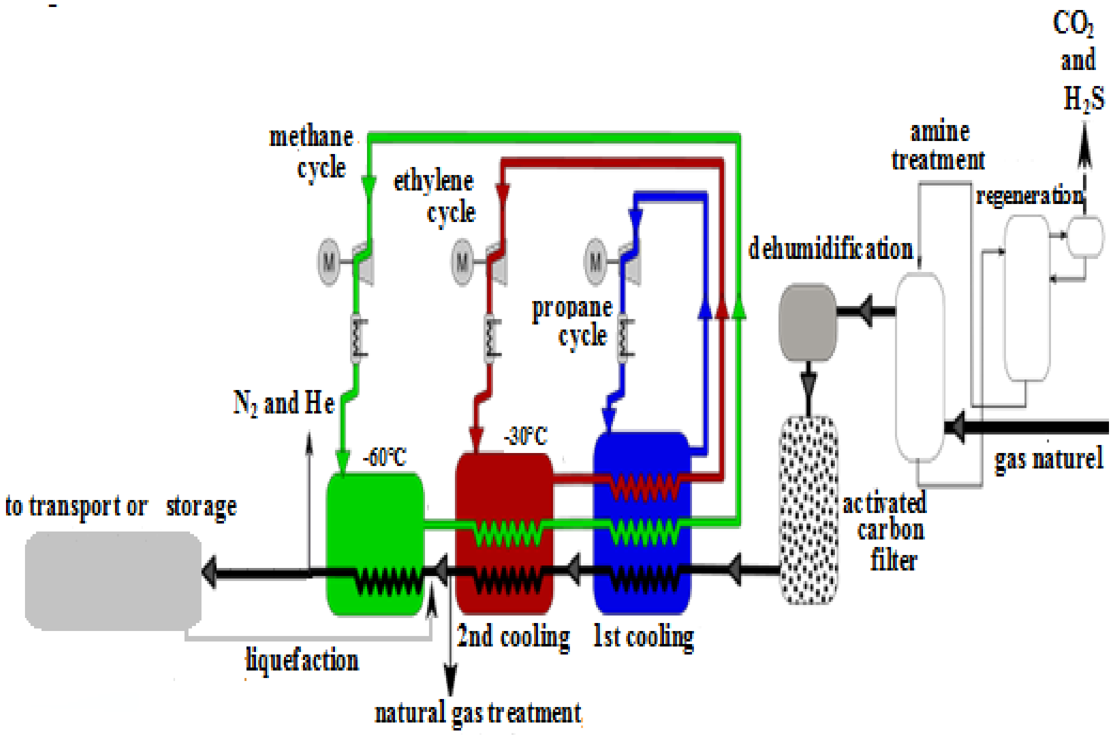

Fig. VI.2 Integrated liquefaction cycle

Compared to other systems, this cycle stands out for its low energy consumption and higher efficiency (see Table VI.2).

Table VI.2 Comparison of the cascade cycle with other cycles

Cycle	energy consumption at -195,8°C	Eficiency
Cascade	7.44	44.6%
Linde	21.5	15.4%
Claude	9.25	35.9%

However, it presents some complications:

- Difficulty in adjustment,
- Requires a large-scale installation,
- Involves a large number of cycles.

Chapter VII

Gas liquefaction and separation

Introduction

Several methods allow the separation of gas mixtures without changing their state, whether at ambient or lower temperatures. However, the most common industrial processes rely on liquefaction at low temperatures, such as distillation and fractional condensation.

In some cases, separation is combined with liquefaction to produce substances in a liquid state. Liquefaction may also be necessary, for example, for the transport of natural gas or the use of hydrogen as rocket fuel.

The main industrial techniques include permeation, adsorption, absorption, distillation, and fractional condensation, based on the physical and physicochemical properties of gases. This document focuses on industrial facilities, excluding those used for research or small-scale operations.

VII.1. Gas separation techniques

The gas separation techniques consists of isolating the different components of a gas mixture based on their physical and chemical properties. These methods are essential in industry to produce high-purity gases such as oxygen, nitrogen, argon, hydrogen, and others. Here are the main methods used to separate gases.

VII.1. 1. Cryogenic distillation

This is the most common method for separating air gases (such as oxygen, nitrogen, and argon) (Fig. VII.1).

- **Principle**: Based on the difference in boiling points of gases. The air mixture is first liquefied by intense cooling (cryogenics), then the gases are separated by fractional distillation.
- **Steps**:
    - Air is compressed and purified to remove impurities (water vapor, carbon dioxide).
    - It is then cooled until it liquefies.
    - The gases are separated in a distillation column where each gas evaporates and condenses at different temperatures. For example, nitrogen has a boiling point of -196°C, while oxygen evaporates at -183°C.
- **Applications**: Oxygen production for hospitals, liquid nitrogen for industrial processes.

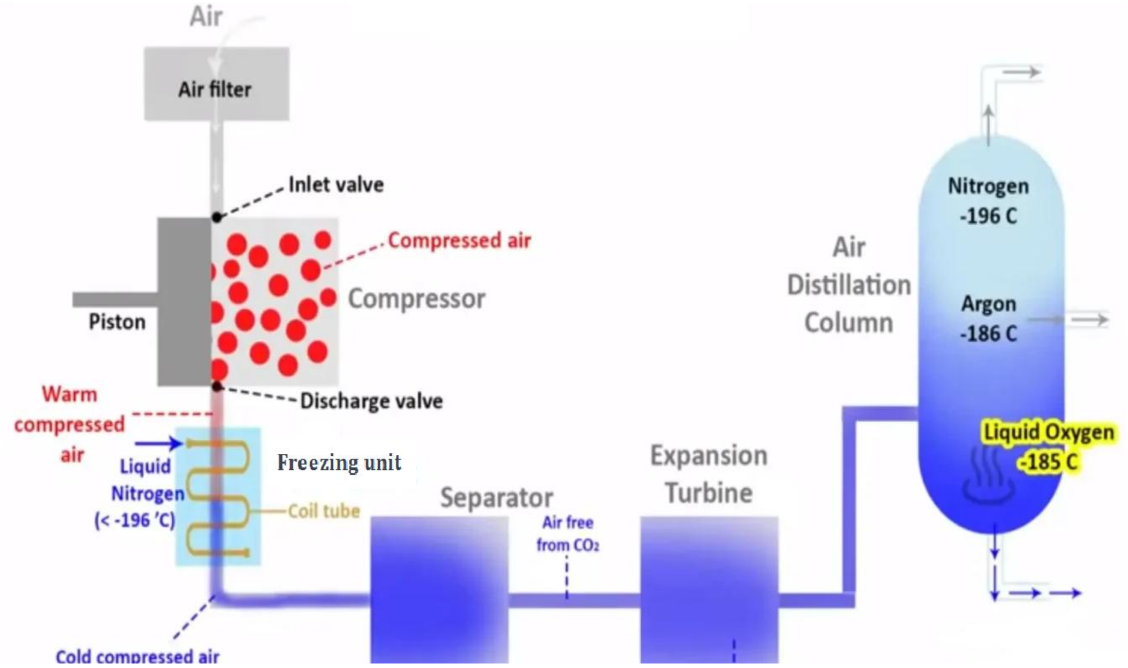

Fig. VII.1 Cryogenic distillation method

VII.1.2. Pressure swing adsorption

A non-cryogenic method that uses adsorbent materials like zeolite to capture specific gas components (Fig. VII.2).

- **Principle**: The gas mixture is compressed and brought into contact with an adsorbent material that captures a specific component (e.g., carbon dioxide or moisture), while other gases pass through. By changing the pressure, the adsorbed component is released and recovered.
- **Steps**:
  - At high pressure, the adsorbent captures certain molecules.
  - At low pressure, these molecules are released and recovered.
- **Applications**: Oxygen and nitrogen production, hydrogen purification.

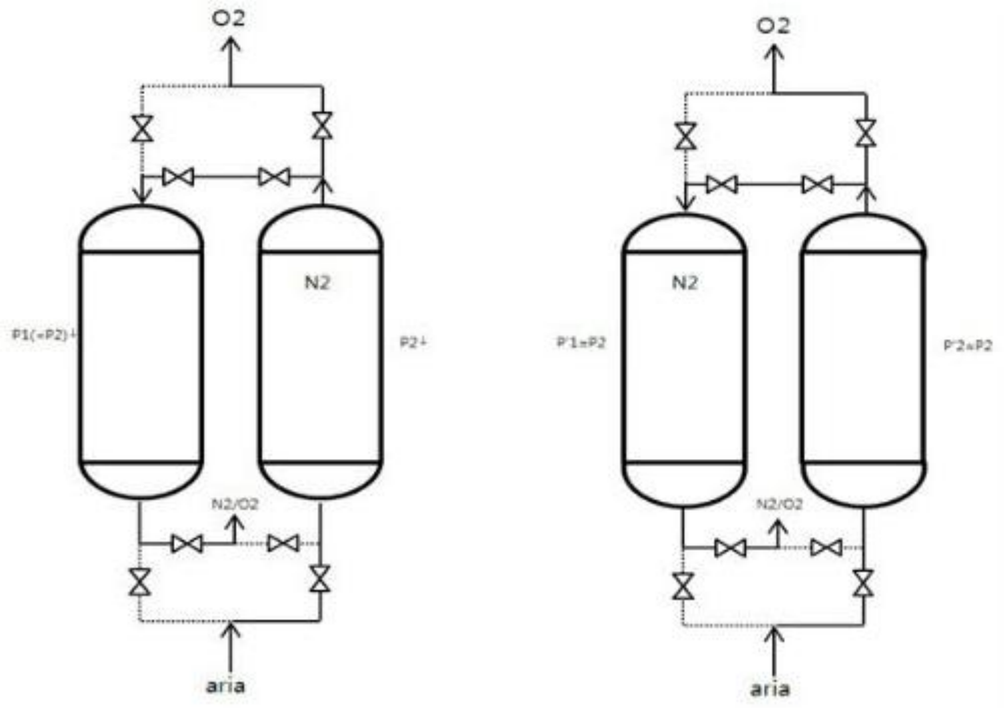

Fig. VII.2 Pressure Swing Adsorption method

VII.1. 3. Membrane separation

Uses semi-permeable membranes to separate gases based on their molecular size or solubility.

- **Principle**: Membranes allow some gases to pass through more quickly than others. For example, small molecules like hydrogen or helium pass through the membrane more easily than larger molecules like methane or nitrogen (Fig. VII.3).
- **Steps**:
    - The gas mixture is passed under pressure through a membrane.
    - The molecules that pass through the membrane faster are recovered first.
- **Applications**: Hydrogen separation, oxygen enrichment of air, biogas production.

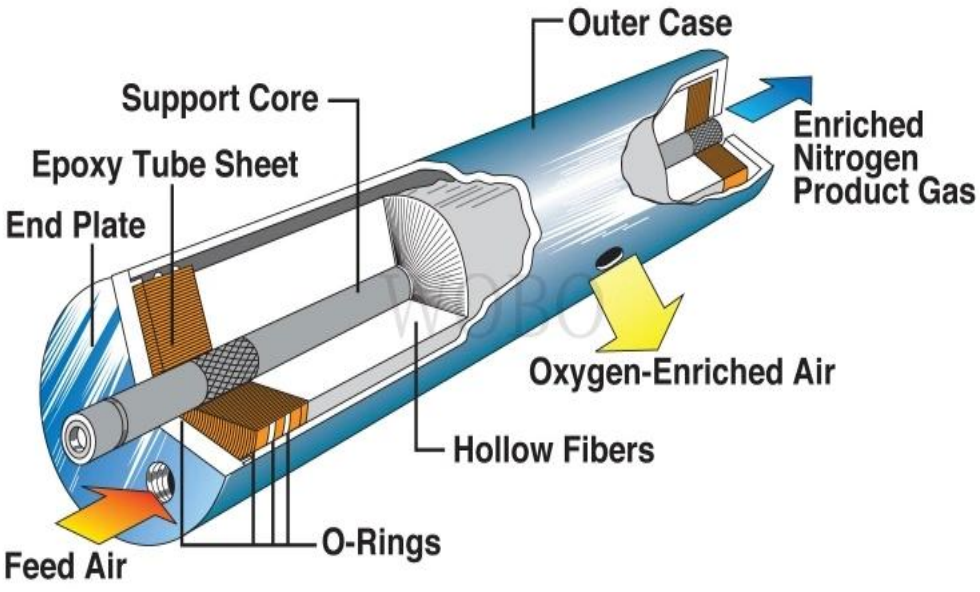

Fig. VII.3 Membrane separation

VII.1.4. Chemical absorption separation

Uses chemical reagents to specifically capture certain gases (Fig. VII.4).

- **Principle**: Some gases chemically react with a solvent, while others remain inert. For example, carbon dioxide can be absorbed by alkaline solutions like sodium hydroxide.
- **Steps**:
    - The gas mixture passes through a liquid or solvent that reacts with a specific component.
    - The absorbed gas is then extracted from the solvent by regeneration, often through heating.
- **Applications**: CO_2 capture in power plants, natural gas purification.

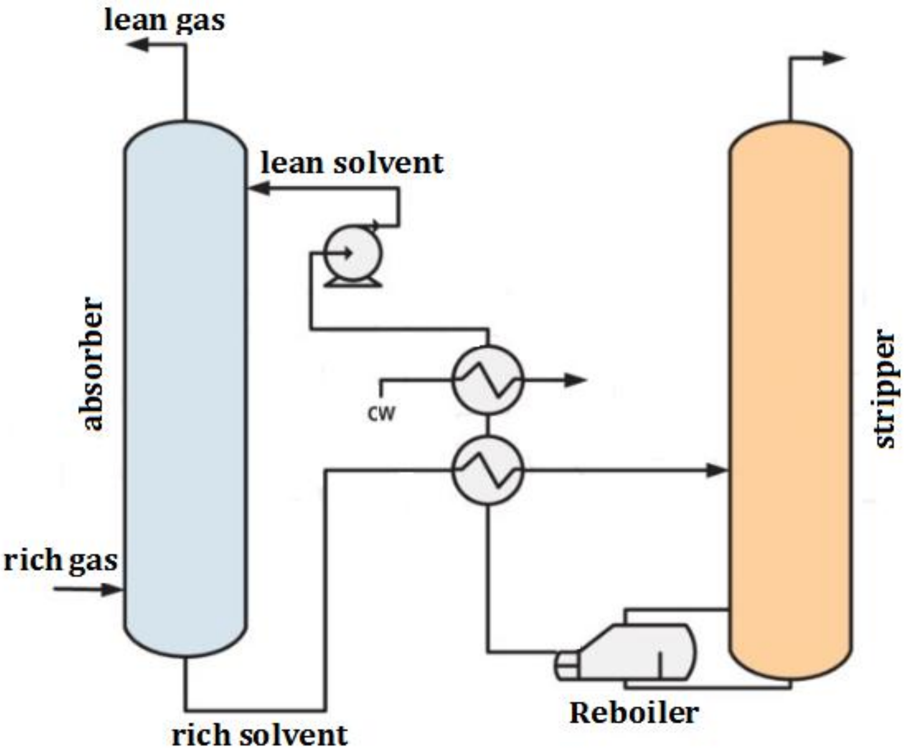

Fig VII.4 Chemical absorption separation

VII.1.5. Gaseous diffusion and centrifugation

- **Principle**: Mainly used for isotope separation. The gas enriched in one isotope passes through filters or undergoes centrifugal force, causing the separation of molecules based on their weight (Fig VII.5).
- **Applications**: Uranium enrichment for nuclear power plants.

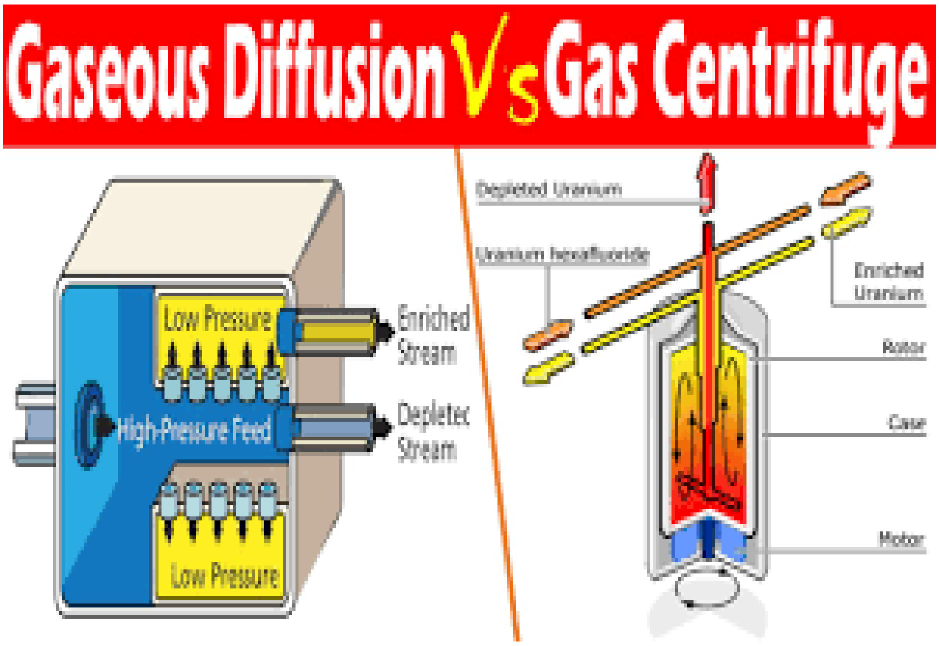

Fig. VII.6 Separation by Gaseous diffusion and centrifugation method

These methods are often combined in industry to obtain high-purity gases at optimized costs, depending on the complexity of the gas mixture to be treated.

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