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Course Handout :

Introduction to refining and
petrochemicals.

L2 Process Engineering



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Preface

This teaching document, entitled "Introduction to Refining and petrochemicals", is intended for second-year students preparing their Process Engineering degree. It is written for clarity and comprehension, in accordance with the official program established by ministerial decree of the Ministry of Higher Education and Scientific Research.

The aim of this handout is to provide process engineering students with the basic concepts concerning the origin of petroleum, its extraction, and the refining and petrochemical industries. It is divided into three chapters:

The first chapter covers the fundamentals of the origin of petroleum and natural gas, their composition and properties, as well as the classification of crude oils, deposits, petroleum characteristics, petroleum exploration and exploitation techniques such as drilling.

The second chapter describes the main oil refining processes, from the reception of crude oil, while examining environmental constraints and the evolution of this industry.

Finally, the third chapter outlines and explains some petrochemical manufacturing schemes and processes.

I would like to express my gratitude to the reviewers who have contributed to the improvement of this document, and hope that it will provide process engineering students with the essential information for a thorough understanding of the oil and gas industry sector.

The handout is aimed at L2 Process Engineering students. The programme for the "introduction to refining and petrochemicals» module of the HARMONISED ACADEMIC Licence course (2022) in French, is:

Chapitre 1: Formation et Exploitation du Pétrole et Gaz naturel

Définition et origine du pétrole, Gisements et caractéristiques des pétroles, Techniques d'exploitation

Chapitre 2: Schémas de raffinage du pétrole

Nomenclature et caractéristiques des produits pétroliers, Principaux schémas de procédés de fabrication, Contraintes environnementales et évolution du raffinage

Chapitre 3: Schémas de fabrication pétrochimique

Diversité des produits de l'industrie pétrochimique, Principales voies de fabrication en pétrochimie, Exemples de procédés (PVC, Ammoniac).

Chapter I: Production and exploitation of oil and natural gas.

I.1 Definition and origin of oil

I.1.1 Definition

The term "petroleum" derives from the combination of the Latin words "Petra" and "oleum", literally meaning "rock oil". It is a flammable natural oil, varying in hue from yellow to black, widely used as a source of energy in the form of fossil fuel. Petroleum is the result of a changing mixture of hydrocarbons combined with other elements, such as sulfur, nitrogen and oxygen. Some of its constituents can adopt gaseous, liquid or even solid states, depending on temperature and pressure, which explains its variable consistency, sometimes viscous, sometimes liquid. Generally speaking, petroleum is found in the earth's sedimentary layers, occupying the empty spaces of porous rocks commonly referred to as "reservoir rocks". Currently, a diversity of crude oil types exists, totaling over "400 varieties of crude in the world".

I.1.2 Origin of oil

Oil is formed in sedimentary basins through the transformation of organic matter of animal or plant origin. In particular, it results from the decomposition of marine organisms, mainly plankton, which accumulate at the bottom of oceans, lakes and deltas.

From a chronological approach, this process of transforming organic matter into oil takes place over several tens of millions of years, approximately between 20 and 350 million years. This transformation involves an intermediate substance known as "kerogen". The oil thus produced can then be trapped in specific geological formations, known as "reservoir rocks", forming the conventional oil deposits that are exploited today.

To sum up, the stages in the formation of oil can be summarized as follows:

I.1.2.1 Accumulation of organic matter in sediments

Organic matter comes from living organisms (plankton, plants, animals, etc.). Composed essentially of carbon, hydrogen, nitrogen and oxygen, it forms what is known as "biomass". This biomass is generally destroyed by bacteria, but a small proportion (less than 1%) settles to the bottom of aquatic environments, where it is partially preserved in an oxygen-poor environment. It then mixes with mineral matter (clay particles or fine sand), creating sedimentation sludge. These accumulate in successive layers over tens or even hundreds of meters.

I.1.2.2 kerogen formation

In the early stages of the sedimentation process, up to around 1,000 meters below the seabed, the organic matter present in sediment deposits is transformed by anaerobic bacteria, which thrive in oxygen-free environments. These micro-organisms decompose the oxygen and nitrogen present in

the organic matter, forming kerogen. This compound appears in solid form, dispersed in filaments throughout the sediment, and is mainly composed of carbon and hydrogen.

1.1.2.3 Maturation of kerogen into oil

Through their own mass and the accumulation of new deposits, sedimentary layers naturally sink into the earth's crust. At depths in excess of 1,000 metres below the seafloor, the mineral residues of sedimentation muds solidify to form a relatively impermeable rock, known as "bedrock", which acts as a trap for kerogen.

As it is deposited, the bedrock is subjected to increasingly high geothermal pressures and temperatures, rising by around 3°C every 100 meters. When the temperature exceeds 60°C, corresponding to a burial depth of around 1,500 to 2,000 meters, the kerogen undergoes thermal cracking, also known as "pyrolysis". This process eliminates the nitrogen and oxygen residues, leaving behind water, CO₂ and hydrocarbons, molecules made up exclusively of carbon and hydrogen. The result of this chemical transformation is crude oil, a mixture of liquid hydrocarbons. The transformation of kerogen also generates gaseous hydrocarbons, such as methane. The proportion of gas in the bedrock depends on the duration and temperature of the kerogen transformation process:

- Between 60°C and 120°C (2,000 and 3,000 meters below the surface), kerogen produces mainly oil, with a small amount of gas.
- Above 120°C (i.e. 3,000 meters), oil production from kerogen becomes negligible. The liquid hydrocarbons present in the bedrock are then transformed into gaseous molecules under the influence of temperature and pressure.
- Above 150°C (i.e. burial depths in excess of 4,000 meters), oil is no longer formed, and only gases are produced.

1.2 Formation of oil fields

The underground zone where oil is formed is known as the source rock. Once formed, oil is subject to various forces, such as the weight of sediments, geological forces and density variations with accompanying salt water. To minimize the impact of these forces, oil tends to migrate to other locations by following pathways through the most permeable rocks or cracks within them. This migration takes place from the source rock to the earth's surface, through sediments, due to the lower density of oil compared with water. The point at which this migration stops is called a "trap". An oil trap comprises a porous rock, also known as "store rock" or "reservoir rock", where the oil accumulates. Above this "store rock" is a layer sufficiently impermeable to prevent oil migration to the surface, known as the "cap rock" or "impermeable rock" (Figure I. 1).

Together, the source and reservoir rocks form what is known as an oil reservoir. Within this porous reservoir, gas accumulates on top of crude oil, which in turn lies on top of water due to the respective densities of these substances (natural gas being lighter than oil, itself lighter than water).

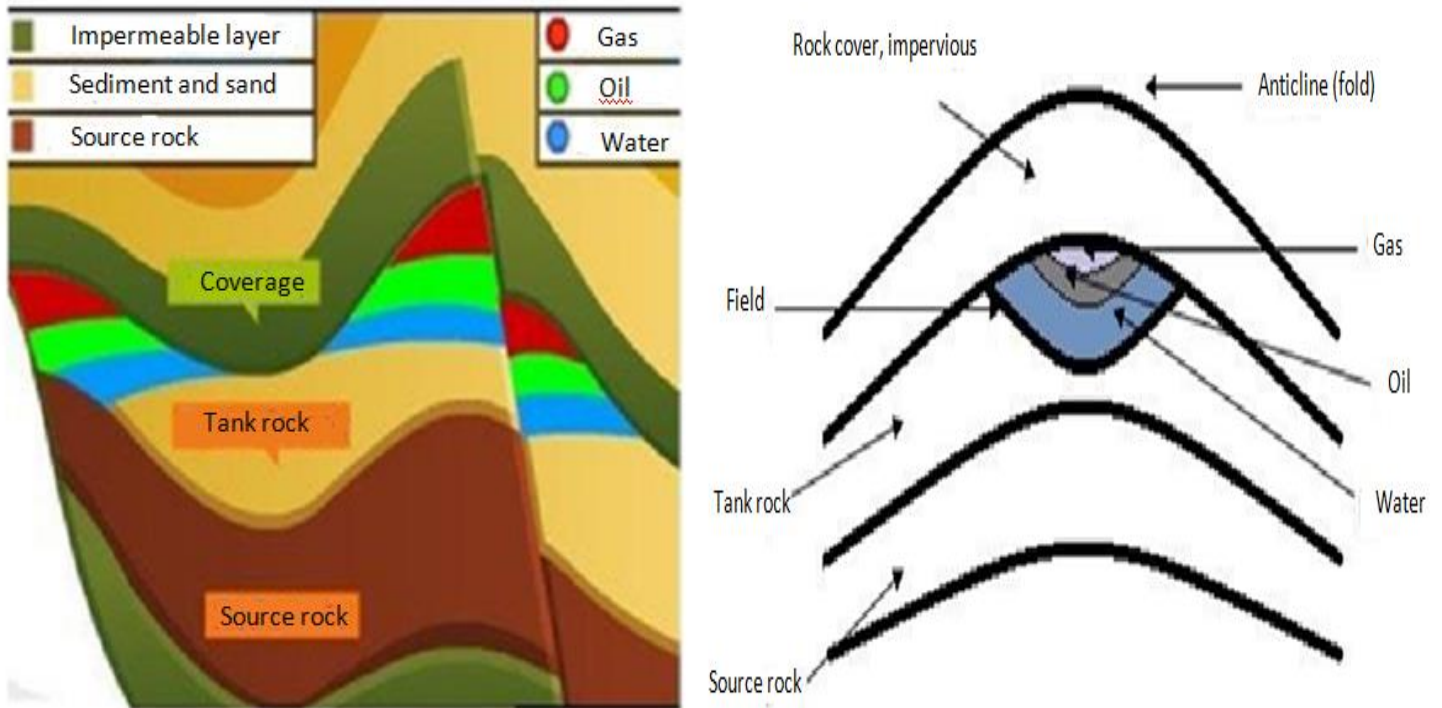


Figure I.1. Simplified diagram of an oil field

I.3 Oil classification

Every formation process is unique: an oil deposit contains a mixture of hydrocarbons that characterizes it according to the geological history of the area in which it developed.

Geographical origin is therefore one of the criteria used to classify oil (Persian Gulf, North Sea, Venezuela, Nigeria, etc.).

However, there are other criteria for making comparisons between different sites.

The most important of these are measurements of crude oil viscosity and sulfur content.

Each oilfield formation process is unique, characterized by a mixture of hydrocarbons that reflects the geological history of the region in which it evolved. Geographical origin thus becomes a major criterion for oil classification, with distinctions such as Persian Gulf, North Sea, Venezuela, Nigeria.....

However, to enable comparisons between different sites, other criteria are also taken into consideration. Among these, measurements of crude oil viscosity and sulfur content play a crucial role.

A) Based on viscosity, four types of deposits are identified (light, medium, heavy or extra-heavy, and bitumen). The more viscous the crude oil, the "heavier" it is:

- Light oil deposits, such as those in the Sahara, have a viscosity close to that of diesel fuel.
- Medium oil fields, such as those in the Middle East, have a viscosity intermediate between light and heavy oil.
- Heavy or extra-heavy oil deposits, like those in South America, have a crude oil that hardly flows at ambient temperature.
- Bitumen deposits, mainly located in Canada, are characterized by crude oil that is highly viscous, even solid at ambient temperature. This property is of crucial importance in assessing the profitability of operations, as low-viscosity or light oil is easier to extract and process than heavy oil.

B) Sulfur content distinguishes crude oil into two categories: sweet (low sulfur content) or sour (high sulfur content). Sweet oil deposits are found mainly in Africa, while sour oil deposits are found mainly in North America.

I.4 Oil fields and exploitation

I.4.1 Searching for fields

In search of new discoveries, geologists and geophysicists work to identify geological structures likely to host oil deposits. Geologists analyze soil and rock samples, while geophysicists examine the earth's crust at depth, in the areas where oil deposits are thought to lie. They reconstruct the image of deposits and deformations of geological layers, providing crucial information for locating areas where oil could be "trapped".

I.4.2 Characteristics of fields

For a field to be exploitable, a number of conditions must be met:

- The presence of a porous, fissured rock, such as limestone or sandstone, which facilitates the accumulation of oil.
- The presence of an impermeable rock, capable of stopping the upwelling of oil and gas, which are less dense than water. This impermeable rock acts as a trap, creating an environment where oil can accumulate.

I.4.3 Petroleum prospecting

Petroleum prospecting is the intensive study of petroleum geology. This activity begins with the creation of maps using aerial photos. Petroleum prospecting comprises two distinct branches:

- The geological study, or geological prospecting proper, focuses on the formation of deposits and other characteristics of rocks as reservoirs or covers.
- The study of internal structures comes under the heading of geophysical prospecting, involving teams scouring the terrain to be prospected (explored) and drawing up structural maps.

1.4.4 Prospecting methods (for oil exploitation)

a) Geological prospecting

All rocks that could constitute an oil field are considered to be sedimentary, although there are no direct methods for searching for hydrocarbon deposits in sedimentary terrain. However, indirect methods can be used to identify the potential presence of "traps", without being able to guarantee in advance whether these traps actually contain oil.

b) Geophysical prospecting

This method is based on the variation of certain geophysical parameters of the terrain caused by the presence of hydrocarbons, providing qualitative results. Among the techniques used in this type of prospecting are the following:

- The gravimetric method: based on the measurement of variations in the gravity field caused by the presence of an oil deposit, as the presence of rocks containing hydrocarbons increases the gravity field.
- The magnetic method: measures variations in the vertical component of the earth's magnetic field caused by the presence of an oil deposit.
- Electrical method: based on variations in the resistivity of sedimentary terrain when crossed by electrical currents, in the absence and presence of an oil deposit.
- The seismic method: the most commonly used, it involves the controlled explosion of a light explosive charge in a shallow well. The sound waves resulting from the explosion propagate through the surrounding sedimentary terrain, and in-depth analysis of the various sound waves collected allows us to conclude whether or not a hydrocarbon reservoir is present.

1.4.5 Onshore drilling methods

To exploit fields rationally, all geological and physical methods are used to obtain information on the physical and mechanical properties of rocks. This makes it possible to reconstruct the characteristics of a deposit and estimate the corresponding reserves. Often, the necessary information is not available until several years after the wells intended to exploit the deposit have been drilled. Economic investments are therefore always subject to risk, and mathematical models are now used to simulate the profitability of a deposit. Well drilling accounts for 80% of investments in this exploration phase.

I.4.5.1 The Drilling

When potential oil structures have been identified, whether by geological or geophysical prospecting, the next step in oil development is drilling.

Drilling involves digging a hole, also known as a "well", in the earth. This operation involves driving a string of rods into the subsoil while injecting a special mud. The function of this mud is to bring rock fragments and gas samples to the surface. Usually, several drillings are required to more precisely delimit the potential field.

At present, the most commonly used process is rotary. A cutting instrument called a drill bit is used to drill the well, rotating at the bottom of the well.

Well drilling is carried out using a drill bit (Figure I.2), also known as a tricone, a tool specially designed for the oil industry. It takes the form of a single cone made of very hard special steel, or of three cones nested together. Originally, the lower surface of these cones was encrusted with diamond dust, enabling the most resistant rocks to be broken during drilling. During the drilling process, these cones rotate, breaking the rocks they pass through, and progressively sink into the subsoil.

I.4.5.2 Drilling rig

- The drilling rig consists of a metal tower called a derrick (Figure I.3), used to insert hollow rods screwed end-to-end vertically into the ground. The derrick is around 45 m high, enabling the drill rods to be manoeuvred and stored.

At the end of these rods, the drill bit head - made of very hard steel - attacks the rock.

The bit is pressed down and rotated at a maximum speed of 200 rpm.

The weight of the tool is ensured by the mass of the drill pipes, to which it is possible to add very thick pipes called drill collars.

The rock debris produced during drilling is brought to the surface by drilling slurry, a mixture of water and clay. This mud is injected through the drill bit orifice.

The mud is screened at the surface. The debris is collected by geologists and analyzed, while the mud is returned to the circuit. The slurry also serves to:

- Keep debris in suspension after traffic has stopped;
- Maintain the borehole walls by exerting lateral pressure;
- Retain fluids contained in the rock under pressure, thus preventing fluids from entering the shaft;
- They also cool the drilling tool.

Rotary drilling rigs fall into three distinct categories:

- Light rigs, suitable for depths below 1500 meters;

- Medium rigs, designed for depths ranging from 1,500 to 3,000 meters;
- Heavy-duty rigs, designed for depths in excess of 3,000 meters.

Drilling Slurry: as the drill is progressed, the resulting cuttings are transported to the surface by a continuous flow of slurry introduced simultaneously with the drill bit. This mud is made from water, special clays (bentonites) and various chemicals.

In addition to its primary role of evacuating cuttings, drilling mud has other secondary roles:

- It holds the well walls in place by depositing a thin layer of clay.
- The hydrostatic pressure it exerts keeps the pressurized fluids encountered in the various layers in place.
- It cools the drill bit and lubricates its various components to reduce the rate of wear.
- When the ground to be drilled doesn't contain water, the mud can be replaced by compressed air at 40 bar. This improves advance speeds and reduces bit fatigue.

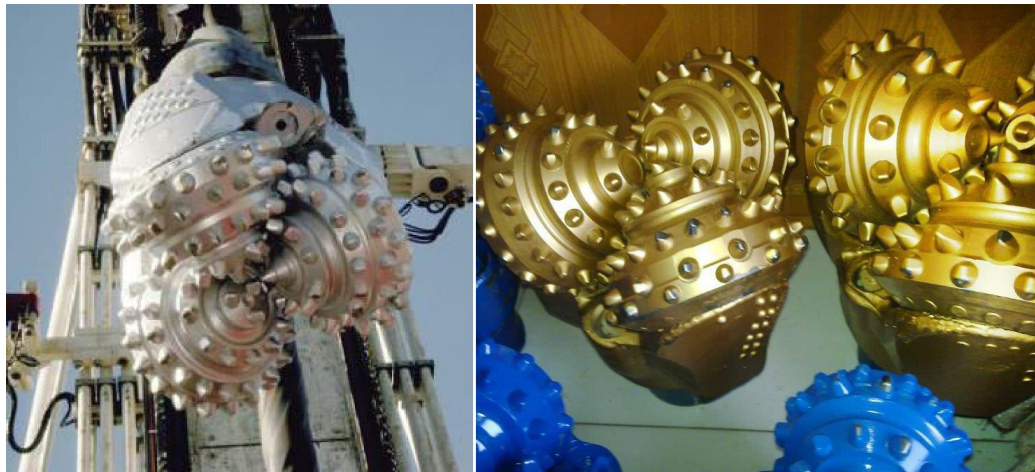


Figure I.2. Drill bits.

1.4.5.3 Start-up of an oil production field

After drilling into a reservoir and reaching the reservoir rock where large quantities of oil have accumulated, a series of pipes are installed to convey the oil to the surface.

There are two cases to consider:

- The pressure in the reservoir is sufficient for the oil to rise to the surface and flow at a sufficient rate. This is known as a controlled blowout.
- The pressure is too low for the oil to reach the surface with a suitable flow rate, in which case the mechanical pumping process is used. This consists of sending a pressurized gas to increase the pressure in the reservoir, allowing the oil to rise to the surface.

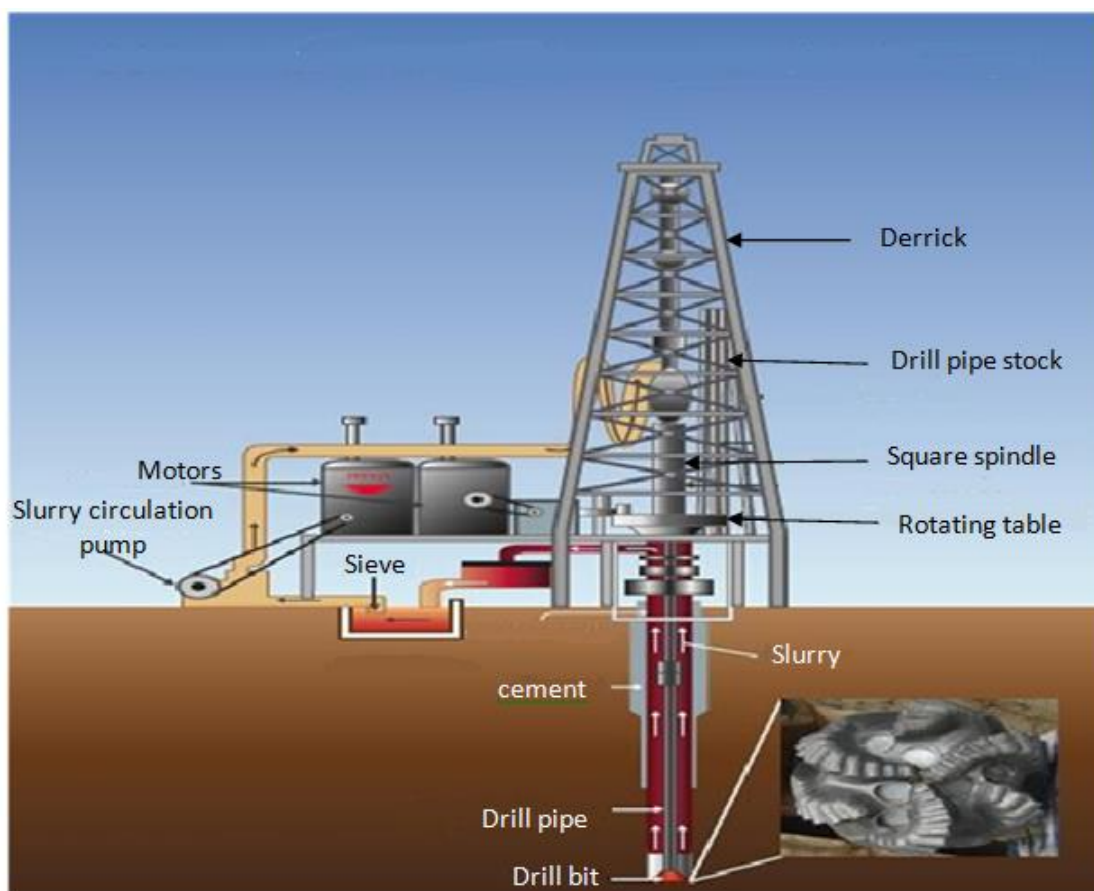


Figure I.3. Schematic diagram of a drilling rig

Chapter II: Oil refining schematic

II.1 Introduction

– The petrochemical industry is directly linked to hydrocarbons, either crude oil or natural gas. It lies at the interface between the oil refining industry, the natural gas industry and organic chemistry. Its aim is two fold:

- To offer synthetic products that can be substituted for natural commodity products.
- To offer synthetic products with original properties that complement natural products, known as "specialty products".

Petrochemical products are grouped into different categories used in everyday life: plastics, fibers, elastomers, detergents, solvents and fertilizers. These products can be divided into two groups:

- Products used for their chemical properties, such as fertilizers, detergents and solvents.
- Products used for their mechanical properties, such as plastics, elastomers and fibers.

All these products are obtained by reacting "base" molecules obtained from oil, gas or coal, using organic chemistry reactions.

Basic molecules must be:

- Reactive, enabling rapid and selective reactions, leading to high productivity while limiting the formation of by-products.
- Abundant, as they must lead to high-tonnage, low-cost products if they are to be economically competitive.

There are three main families of basic molecules, which make up the three branches of the petrochemical industry:

- Olefins (chemical double bonds);
- Aromatics (benzene, toluene, xylenes);
- Acetylenics (triple chemical bonds).

These molecules must be obtained with a high degree of purity, which requires the installation of numerous purification units.

NB: The basic molecules are produced by the main unit of the petrochemical plant: the steam cracker, but also come from the refinery. Olefins are found in the light cuts from catalytic cracking, and aromatics in the effluent from catalytic reforming.

II.2 Classification of crude oil

Petroleum, a fossil fuel, consists mainly of a mixture of hydrogen and carbon. Although its composition can vary from one deposit to another, it generally comprises around 80% carbon, 11% hydrogen, and between 1% and 2% sulfur, oxygen and nitrogen.

Various methods are used to determine the composition of crude oils:

- Density, viscosity and other measurements on the various fractions obtained by distillation. These techniques provide valuable information for the refining process and oil production.
- Liquid chromatography, gas chromatography and mass spectrometry, among others, on the various fractions dissolved. They enable us to identify the different families of compounds present in oil.

Oil can be quoted by three methods:

A) Industrial classification: Crude oils are generally classified according to density into 4 main categories:

- Light oils with a density of less than 0.828 ($d_4^{15} < 0.825$);
- Medium oils with a density between 0.824 and 0.875 ($0.825 < d_4^{15} < 0.875$);
- Heavy oils with a density ranging from 0.875 to 1 ($0.875 < d_4^{15} < 1.000$);
- Extra-heavy oils with a density greater than 1 ($d_4^{15} > 1.000$).

B) Classification using the KUOP correction factor :

This factor can measure the nature of the paraffines and take on the following values depending on the nature of the oil:

- KUOP=10 for pure aromatics;
- KUOP=11 for pure naphthenes;
- KUOP=12 for hydrocarbons with equivalent chain and ring weights.
- KUOP=13 for paraffins.

C) Chemical classification: This is the classification of crude oil according to the predominant families of hydrocarbons:

- Paraffins ;
- Naphthenic;
- Aromatics;

II.3 Composition of crude oil

Petroleum products are all different, depending on their origin and chemical composition. They are mainly made up of hydrocarbon molecules, i.e. molecules composed solely of hydrogen and carbon. These hydrocarbons are essentially linear chains of varying lengths, or cyclic naphthenic or aromatic chains. Different types of oil vary in density, fluidity, sulfur content and hydrocarbon classes. There are hundreds of crude oils in the world, depending on their geological location, such as Arabian Light (Middle Eastern benchmark crude), Brent (European reference crude) and West Texas Intermediate (WTI, American reference crude).

The hydrocarbons contained in petroleum are grouped into three families:

Paraffins (Alkanes)

Naphthenes (Cycloalkanes)

Aromatics

A) Chemical composition

A.1) The hydrocarbons

a. Paraffins (Alkanes) C_nH_{2n+2}

These are saturated hydrocarbons with the formula C_nH_{2n+2} , where n is the number of carbon atoms in the hydrocarbon chain.

Alkane nomenclature: C1 : CH₄ Methane C2 : C₂H₆ Ethane C3 : C₃H₈ Propane

C4 : C₄H₁₀ Butane C5 : C₅H₁₂ Pentane C6 : C₆H₁₄ Hexane C7 : C₇H₁₆ Heptane

C8 : C₈H₁₈ Octane C9 : C₉H₂₀ Nonane

C10 : C₁₀H₂₂ Decane

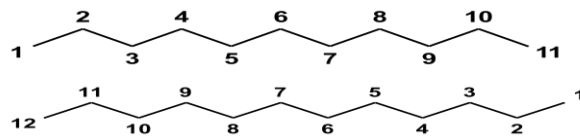
C11 : C₁₁H₂₄ undecane

C12 : C₁₂H₂₆ dodecane

C13 : C₁₃H₂₈ Tridecane C14 : C₁₄H₃₀ Tetradecane C15 : C₁₅H₃₂ Hexadecane.....

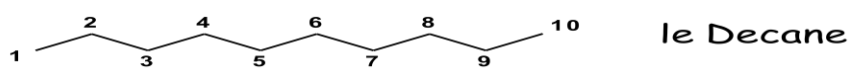
C20 : C₂₀H₄₂ Cosane C21 : C₂₁H₄₄ Henicosane C22 : C₂₂H₄₆ Docosane

C30 : C₃₀H₆₂ Triacontane C40 : C₄₀H₈₂ Tetracontane C50 : C₅₀H₁₀₂ Pentacontane



There are two types of Paraffins: alkanes (normal) and alkanes (isomeric).

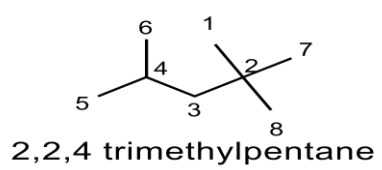
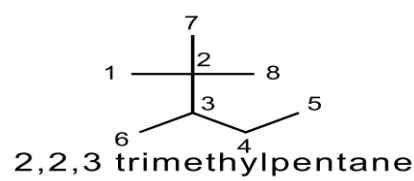
- **Normal paraffins:** the carbon chain is a single straight chain.



- **Iso-paraffins :** The carbon chain is branched (these are isomers of normal Paraffins, differentiated by the prefix **iso**).

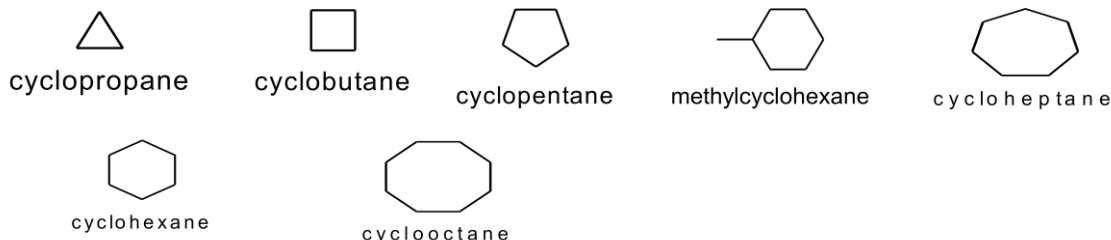
- The first in the iso-paraffin series is iso-butane :
- For nomenclature purposes, we consider the longest straight chain and identify the positions of the branched chains by numbering the carbons of the main chain from left to right.

Example: below are two isomers of isooctane (08 carbons), which has a total of 18 isomers.

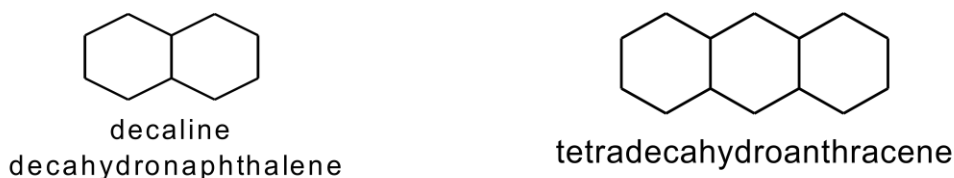


b. Naphthenes: (Cycloalkanes) C_nH_{2n}

They are saturated cyclic hydrocarbons, and their names are those of alkanes preceded by the prefix cyclo:

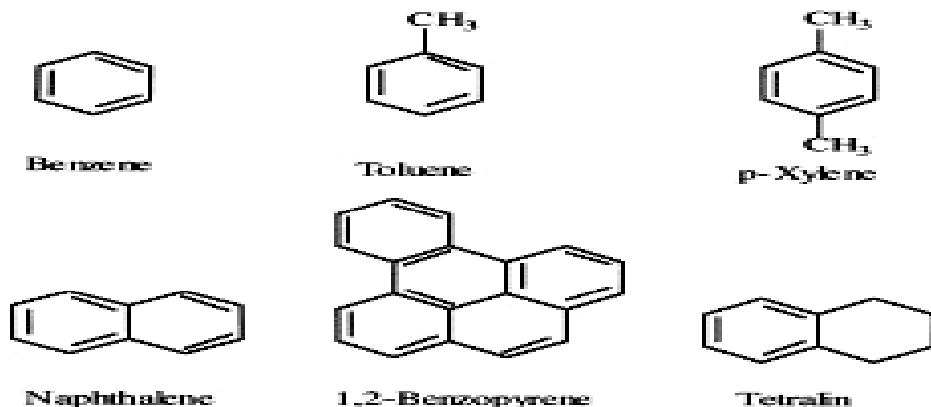


There are also naphthenes formed by the association of two (or more) rings of six carbon atoms:



c. Aromatics: (Benzenes) C_nH_{2n-6}

These are unsaturated cyclic structures with three double liaisons in each ring.

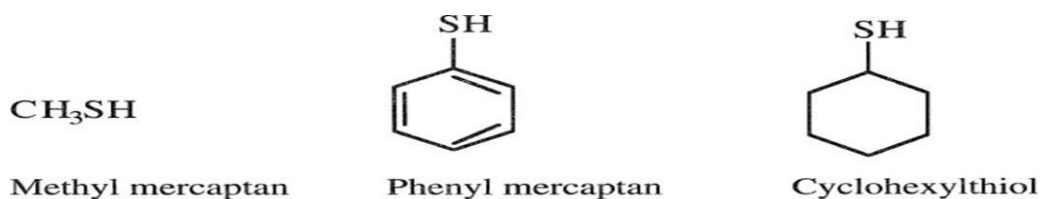


A.2) Sulfur compounds: (0.05% to 6% by mass)

Sulfur compounds are present in crude oil in the form of organic sulfur compounds. Hydrogen sulfide H_2S is the only non-organic compound present in crude oil. The presence of sulfur compounds in crude oil is harmful because of their corrosive properties.

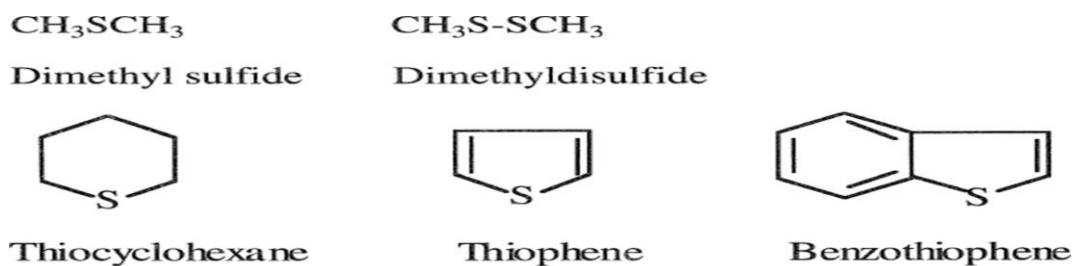
Organic sulfur compounds are generally classified into two groups: acidic and non-acidic compounds.

- **Acidic compounds R-SH:** are thiols (mercaptans):



Thiols are corrosive compounds with a intense odour.

- **Non-acidic compounds:** These include thiophenes, sulfides and disulfides.



Non-acidic compounds are non-corrosive and low-odour.

A.3) Other compounds:

- Oxygenated compounds: 0.05 to 1.5% by mass
- Nitrogen compounds: 0.1 to 2% by mass
- Metals: 0.005 to 0.015% by mass including (75% Nickel and Vanadium), Sodium, Calcium, Magnesium, Aluminum and Iron.

II.4 Reference crudes

– More than 130 types of crude oil are marketed the world over, out of a total of 400 known crude types. Their price is determined by differential from reference crudes of known standard quality. These reference crudes are :

– **WTI (*West Texas Intermediate*):** (40 °API et 0.3 % S)

This type of crude is used as a reference in North America. It is light, unsulfured crude. It is the WTI price that is usually quoted in articles.

– **Brent :** (38 °API et 0.3 % S)

– Brent is a type of crude oil (light, unsulfured) produced from fields in the North Sea. According to the International Petroleum Exchange, where the price of Brent is quoted, this price is used to set the price of two-thirds of the crude oils sold in the world.

– **Dubai Light:** (32 °API et 2 % S)

A crude (light sulfur) in the Persian Gulf, Dubai light is used as a reference to fix the selling price

of other crudes in the region destined for Asia, the Middle East and Asia.

NB: Algerian crude is referred to as "sahara blend", a mixture of crudes from several fields in the Hassi Messaoud region.

Density between 43 and 47 °API, a light crude.

Sulfur content 0.1% "low sulfur content".

II.5 Petroleum Refining

Petroleum refining refers to all treatments and transformations designed to extract the maximum number of products with high commercial value from petroleum. Depending on the objective, these processes are generally combined in a refinery.

The refinery is the place where oil is processed to extract commercially viable fractions.

There are simple and complex refineries. Simple refineries consist of just a few processing units, while complex refineries have many more.

II.5.1 Crude oil pretreatment

Crude oil often contains:

- Water, inorganic salts, suspended solids and traces of water-soluble metals.
- On arrival at the refinery, crude oil is stored in large tanks. Crude oils are stored and separated according to their sulfur content.

The first step in the refining process is to remove these contaminants by desalting, to reduce corrosion and fouling of installations, and to prevent poisoning of catalysts in production units. Three typical crude oil desalting methods are used: Chemical desalting, electrostatic separation and filtration are three typical crude oil desalting methods.

- In chemical desalting, water and surfactants are added to the crude oil, heated to dissolve or bind salts and other impurities to the water, and the mixture is then stored in a tank for the aqueous phase to settle.
- In electrostatic desalting, high-voltage electrostatic charges are applied to concentrate the suspended droplets in the lower part of the settling tank.
- A third, less common process involves filtering hot crude oil through diatomaceous earth.

In chemical and electrostatic desalting, the raw material is heated to a temperature of between 66°C and 177°C, to reduce viscosity and surface tension and thus facilitate mixing and water separation. The pH of the water is then adjusted using a base or acid.

The waste water and the contaminants it contains are collected at the bottom of the settling tank and conveyed to the waste water treatment unit. Desalted crude oil is recovered from the upper part of the settling tank and sent to an atmospheric distillation tower (fractionation tower).

II.5.2 Description of the electrostatic crude desalination method

The crude oil enters the bottom of a horizontal tank fitted with two flat electrodes, which are energized with a very high voltage electric current (20-33 kV AC). The crude, which contains water and salts, is mixed with fresh demineralized water via a mixing valve in the lower part of the tank to dissolve the salts in the aqueous phase. The optimum temperature for solubilizing the salts in the aqueous phase is 120°C-130°C, so the crude must be preheated to this temperature before it enters the desalter (figure II.1).

The crude-water-salt mixture moves to the top of the tank as an emulsion, where it comes into contact with the flat electrodes. The water droplets are ionized by the electric charge and coalesce to form large water droplets which then fall by gravity to the bottom of the tank. Electrical desalination can reduce salt content by 90% to 98%.

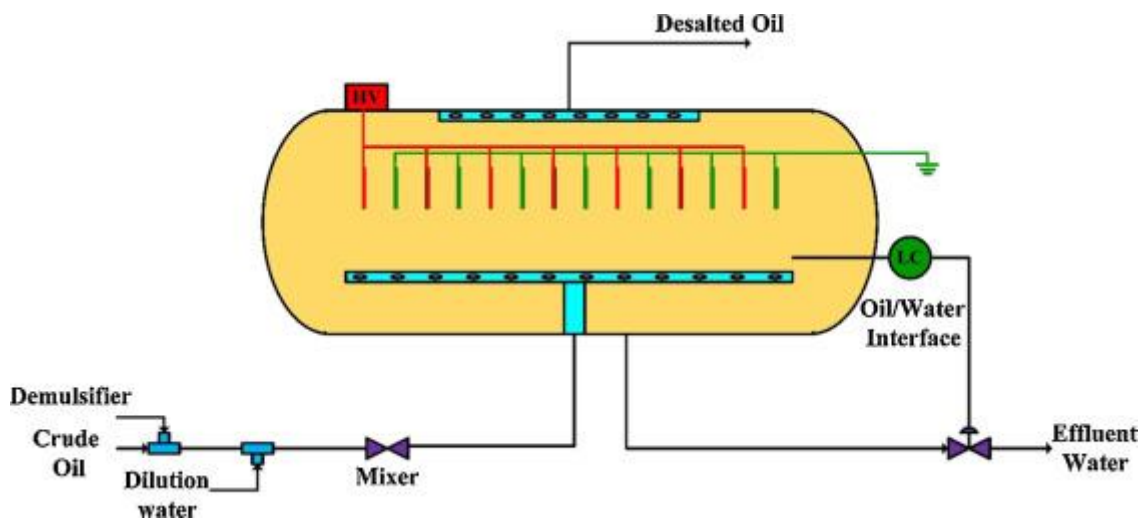


Figure II.1. Crude oil desalination process.

II.6 Main manufacturing process diagrams

II.6.1 Definition and categories

Oil refining is an industrial process that transforms crude oil into various finished products such as gasoline, heavy fuel oil and naphtha. Crude oil is a heterogeneous mixture of various hydrocarbons (molecules made up of carbon and hydrogen atoms), unusable as it is. Its components must be separated to obtain the final products that can be directly exploited. In general, there are two main types:

- Energy products, such as gasoline, diesel or fuel oil;
- Non-energy products, such as lubricants, bitumen and naphtha used in petrochemicals.

Today, refining is no longer limited to separating different hydrocarbons. Plant-based chemical processes are also used to optimize the final products. The various petroleum cuts can thus be

transformed, improved and blended to obtain commercial products that meet environmental standards.

II.6.2 Three refining steps

Crude oil processing is an essential operation. In a refinery, crude oil is transformed into finished products following rigorous processes involving three main types of operation: separation, conversion and upgrading.

II.6.2.1 Separation processes

The first step is to separate the molecules by atmospheric distillation (i.e. at normal atmospheric pressure), according to their molecular weight.

This process involves heating the oil to 350/400°C to evaporate it. Heating takes place at the base of a 60-meter-high distillation tower, also known as a topping tower. Crude oil vapors rise up the tower, while the heavier molecules or heavy residues, remain at the base without evaporating. As the vapors rise, the molecules condense one after the other into liquids, until the gases alone reach the top of the tower, where the temperature is only 150°C. At different levels of the tower are trays for collecting these increasingly lighter liquids. Each tray corresponds to a distillation fraction, also known as a petroleum cut, from bitumen (highly viscous hydrocarbons) to gas (Figure II.2 and II.6).

The heavy residues from this distillation still contain many medium-density products. They are subjected to a second distillation in another column, which recovers more medium products (heavy fuel oils and diesel).

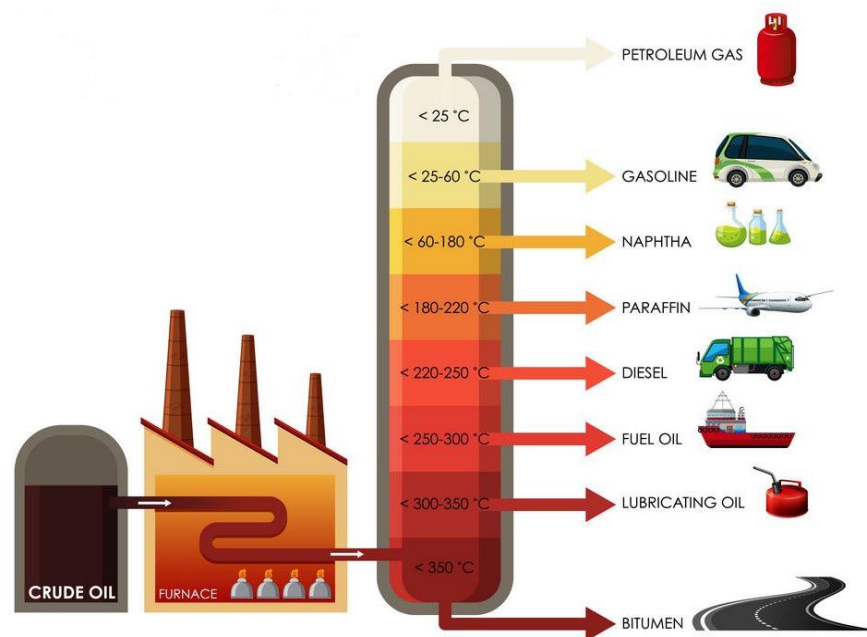


Figure II .2. Fractional distillation crude oil

II.6.2.1.1 Types of initial petroleum distillation plant

There are three types of atmospheric distillation. The choice of these types depends on two factors:

- The nature of the crude oil to be processed.
- The products to be obtained.

1/ Atmospheric distillation unit with a single column

This type of process is used to treat crude oil with a low content of light, low-sulfur fractions, in order to avoid costly corrosion of the main column.

Advantages :

- Simple design.
- Low temperatures can be used (between 330 and 380°C). For oil rectification, vaporization of the heavy fractions takes place in the presence of the light fractions.
- This process is compact (i.e. doesn't take up a lot of surface area).

Disadvantages :

- Plant capacity is small.
- This unit does not process light oil, which contains a lot of gasoline, because of the increased pressure in the column, which requires thicker walls and increases the cost price.
- It is difficult to keep the fractionating column regime constant (pressure, temperature, etc.) if the gasoline and water content of the oil varies.
- This unit is designed to process heavy oil.

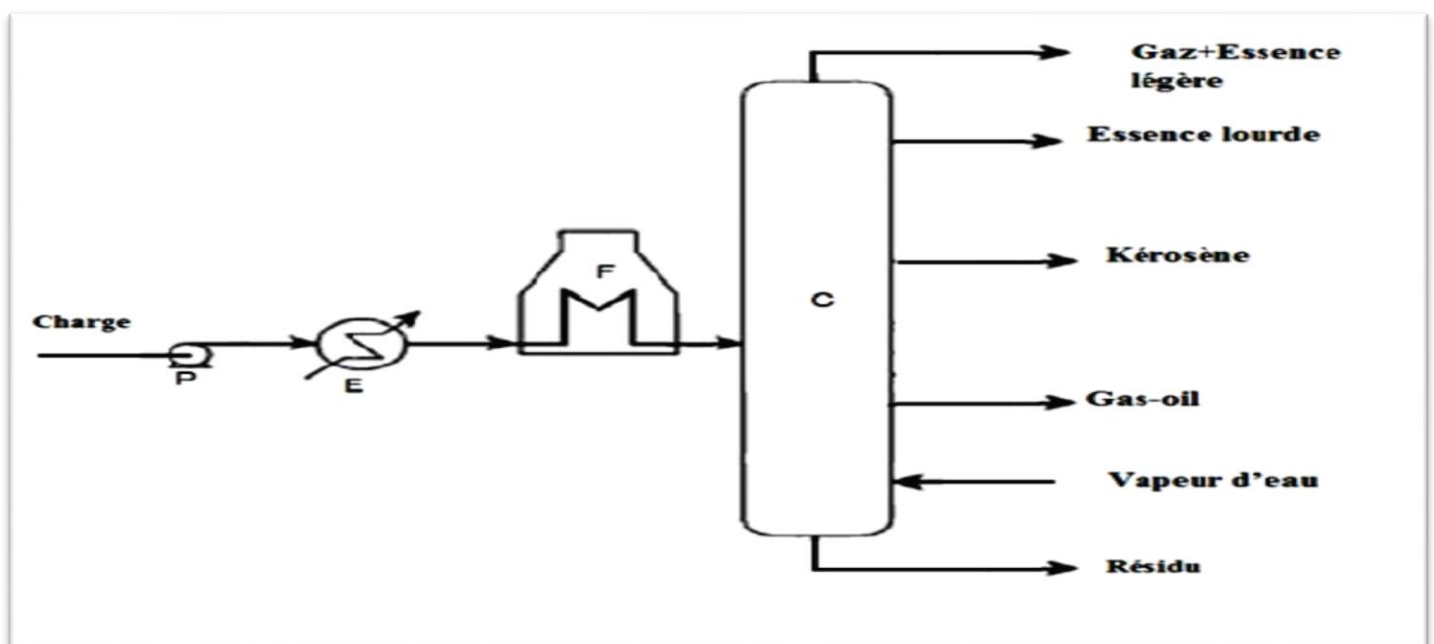


Figure II.3. Atmospheric distillation plant with a single column.

2/ Atmospheric distillation unit with Flash balloon

This type of process processes unstabilized, sulphurous crude oil.

Advantages :

- The design is simple and can process different oils with good fractionation quality.
- Oil that no longer contains light fractions (flashed) does not cause pressure build-up in the furnace and in the atmospheric column.
- The elimination of light fractions (in the distillation column) reduces the furnace's output, because the flow rate of topped crude is lower than that of crude oil.
- Plant capacity is high.
- Possibility of processing unstabilized crude oils with high sulfur content.

Disadvantages :

- High temperature at furnace outlet required to evaporate heavy fractions in the second column.
- Energy consumption is 40% higher than with the single-column design.
- An additional column is required, as well as two additional pumps for charging the furnace and for cold reflux.
- Plant complexity.

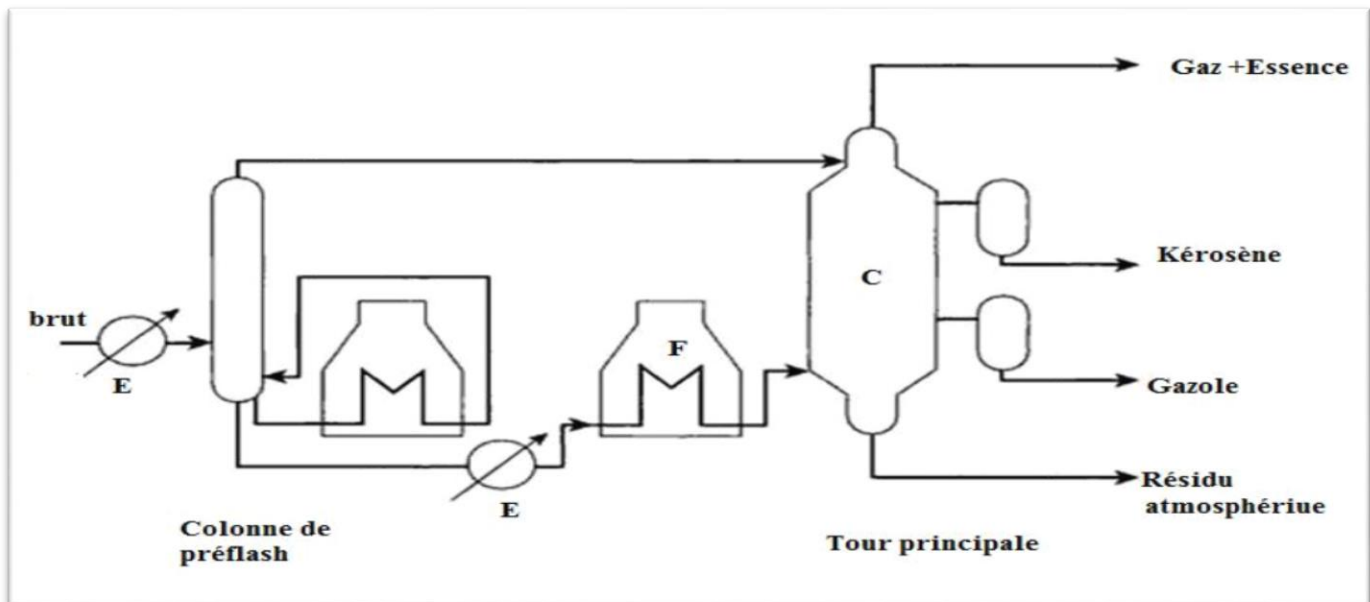


Figure II.4. Atmospheric distillation plant with flash balloon.

3/ Atmospheric distillation unit with pre-distillation

This installation processes a charge containing a large quantity of light fractions.

Advantages:

- High unit capacity.
- Possibility of processing light oils (but only if the gas content does not exceed 1.5%).

- Pre-evaporation of light petroleum gas reduces furnace capacity.
- Absence of exaggerated pressure in the furnace-pump system.

Disadvantages:

- If light fraction content varies, column operation is bad.
- Complexity and impossibility of distilling crude oil rich in sulfur compounds.

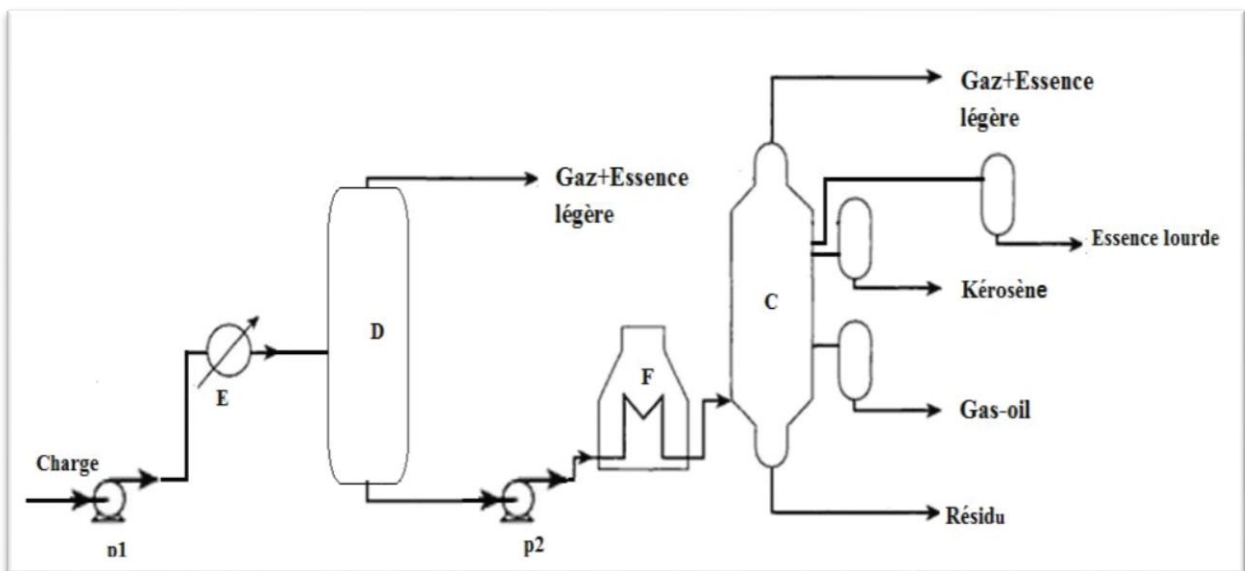


Figure II.5. Atmospheric distillation plant with pre-distillation.

II.6.2.1.2 Vacuum distillation

The heavy residue from atmospheric distillation is heated again to around 400°C and then sent to a distillation column similar to the previous one, but at reduced pressure. The vacuum is provided by a system of pumps.

This technique is the application of the physical law according to which the boiling point, and therefore the condensation point, of a substance depends on the pressure.

If the pressure drops, so does the boiling point.

Vacuum distillation therefore makes it possible to make cuts at lower temperatures. Vacuum distillation will produce heavy diesel and distillate cuts.

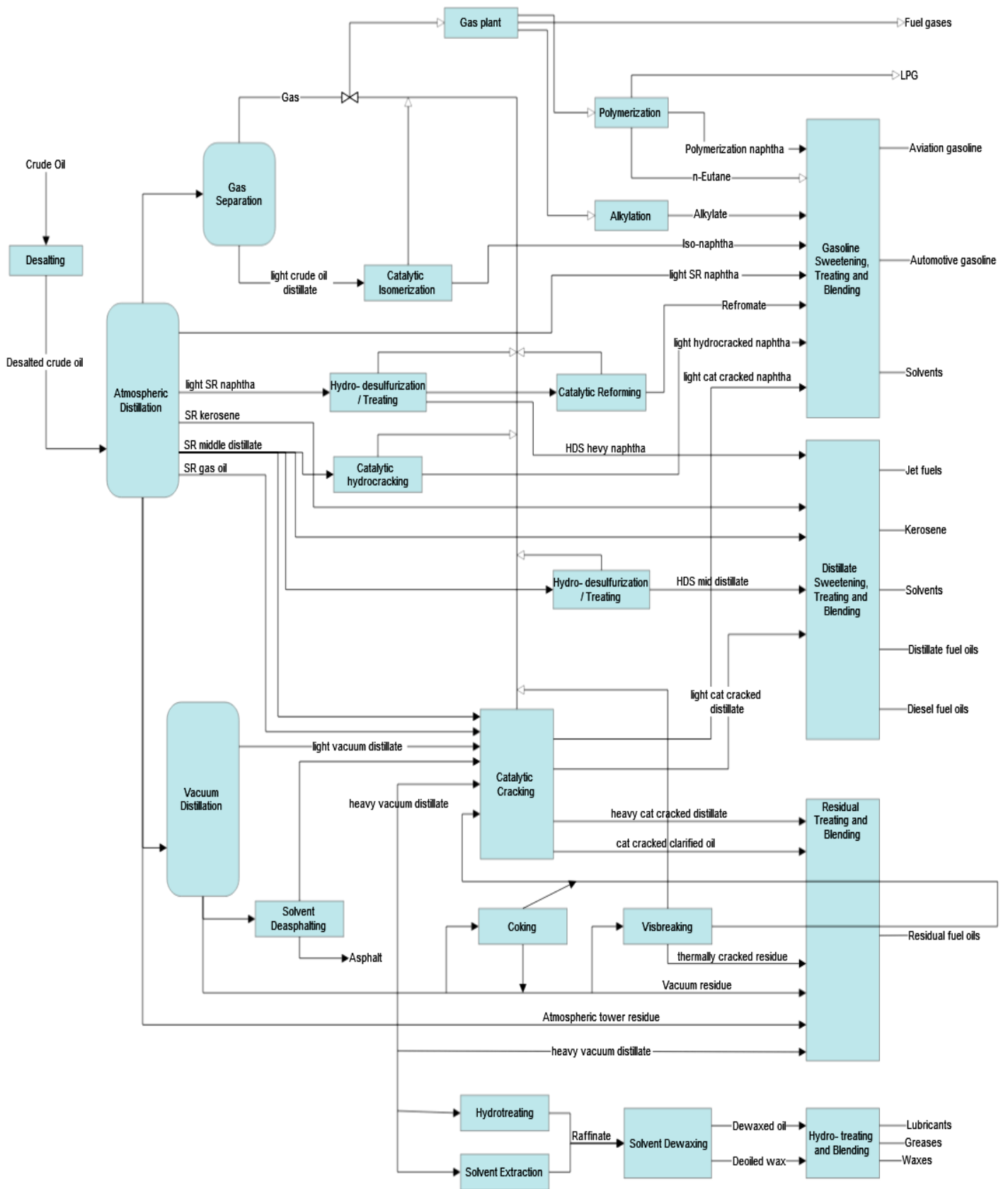


Figure II.6. petroleum refining process

II.6.2.2 Conversion processes

II.6.2.2.1 Catalytic cracking

After separation operations, the proportion of heavy hydrocarbons is still too high. To meet the demand for lighter products, these heavy molecules are "broken" into two or more lighter molecules.

This conversion process, applied at 500°C, is also known as catalytic cracking, as it involves a catalyst (Figure II.7). In this way, 75% of the heavy products subjected to conversion are transformed into gas, gasoline and diesel. Other processes improve this result by adding hydrogen (hydrocracking) or using carbon extraction methods (deep conversion). The more advanced the conversion, the more costly and energy-intensive it is. The refiners' constant aim is to strike a balance between the degree and cost of conversion.

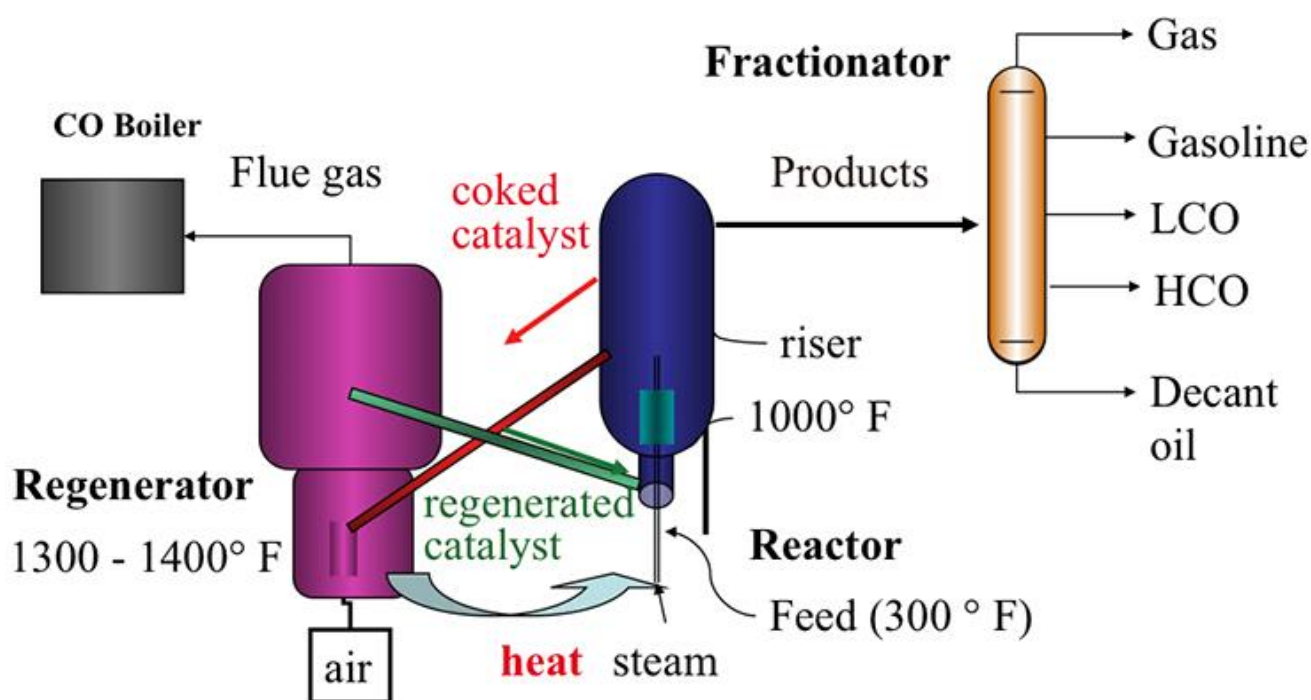


Figure II.7. Catalytic cracking process

II.6.2.2.2 Catalytic reforming

Catalytic reforming (Figure II.8) has been a gasoline refining process since its origins in the USA in 1939, but it also plays a significant role in the supply of aromatic hydrocarbons to the petrochemical industry, the steam cracking of petroleum cuts being the second main route for the production of benzene, toluene and xylenes. Catalytic reforming is a refining method for converting naphthenic molecules into high-octane aromatic molecules used as the basis for

automotive fuels. Originally, the aim of catalytic reforming was essentially to convert low-octane petroleum cuts (40 to 60), commonly known as naphthas, into high-octane fuel bases (90 to 100). Since this improvement in octane was essentially due to a sharp increase in the aromatic content, the process was considered for use in the production of aromatics. In this case, a selected gasoline cut was processed under specific conditions, with a view to producing hydrocarbons specifically for the chemical industry.

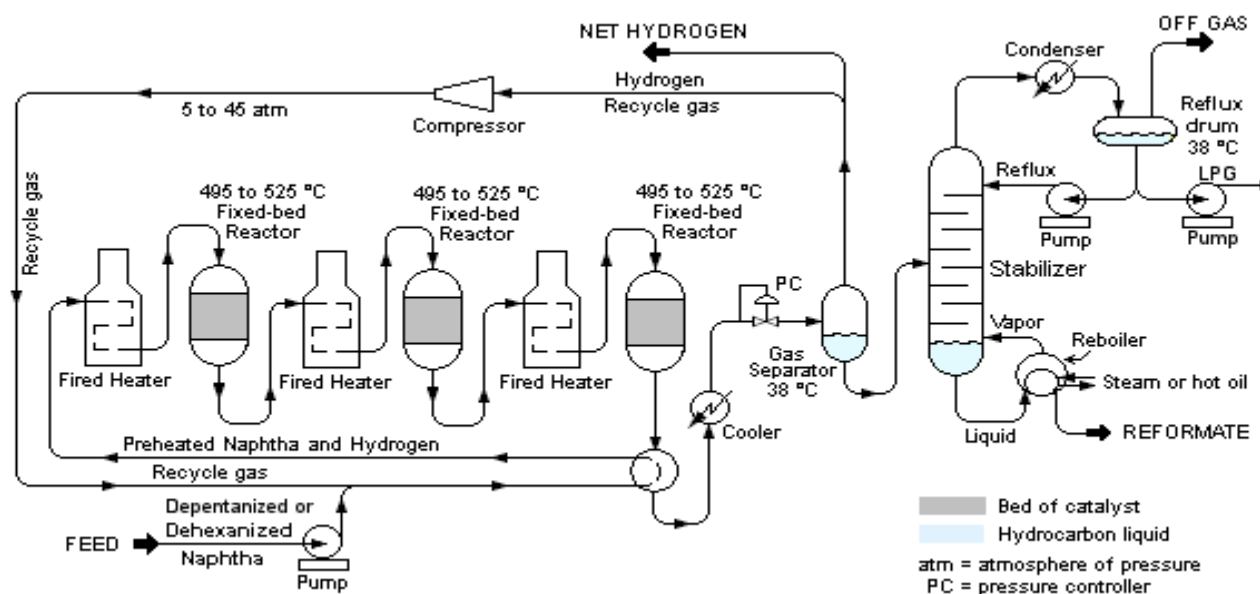


Figure II.8. Catalytic reforming process.

II.6.2.3 Improvement processes

They involve greatly reducing or eliminating corrosive or environmentally harmful molecules, particularly sulfur. European Union (EU) standards on sulfur emissions are strict: since January 1, 2009, gasoline and diesel containing more than 10 ppm (10 mg/kg) of sulfur must not be used in Europe. These measures are designed to improve ambient air quality by optimizing the efficiency of catalytic exhaust treatment technologies. Diesel fuel is desulfurized at 370°C, under a pressure of 60 bars and in the presence of hydrogen, which extracts most of the organic sulfur in the form of hydrogen sulfide (H₂S). The latter is then processed to produce sulfur, a substance used in industry. Kerosene, butane and propane gases are washed with sodium hydroxide. This treatment, known as sweetening, rids these products of the mercaptans (thiols) they contain.

II.6.2.4 Petroleum products

Generally there are different types of usable petroleum by-products from the refining industry. In addition, most of the petroleum products derived from refining are used as a source of energy, i.e. as fuels.

II.6.2.4.1 Gasoline

Gasoline is a flammable liquid produced by the distillation of petroleum, used as a fuel in internal combustion engines. It is a fuel for spark-ignition engines (gasoline engines). It is a mixture of hydrocarbon fractions consisting mainly of light hydrocarbons with relatively low boiling points. It is the most important refining product. Gasoline has a boiling point between room temperature and around 204°C, and a flash point below -40°C. The most important characteristics of gasoline are octane number, volatility and vapor pressure. For their proper use, it is essential that they contain no heavy hydrocarbons, which are harmful to engine performance. They must not contain sulfur compounds or acidic products likely to corrode engines and tanks. Additives are used to improve the properties of gasoline and protect the engine against oxidation and corrosion.

The chemical composition of gasoline is generally as follows:

- 20% to 30% alkanes, saturated hydrocarbons with the formula C_nH_{2n+2} ;
- 5% cycloalkanes, saturated cyclic hydrocarbons;
- 30% to 45% alkenes, unsaturated hydrocarbons;
- 30% to 45% aromatic hydrocarbons, from the benzene family, etc.

Flash point: is the temperature at which a liquid produces sufficient vapors to ignite momentarily in the presence of a conventional heat energy source.

Octane number: measures the ability of a fuel not to ignite spontaneously (without a flash) when mixed and compressed in an internal-combustion engine cylinder:

- The octane rating scale takes as its reference 100 (%) the resistance of iso-octane to self-ignition.
- So a high-octane gasoline (98) will be more resistant to auto-ignition than a lower-octane gasoline (95).

There are two octane ratings:

- Research Octane Number (RON) characterizes a fuel's behavior at low revs or during acceleration;
- Motor Octane Number (MON) evaluates a fuel's resistance to knocking at high engine speeds.

For many years, a certain quantity of tetramethyl lead $Pb(CH_3)_4$ or, better still, tetraethyl lead $Pb(C_2H_5)_4$ was added to gasoline to reduce the tendency of gasolines containing a high percentage of heptane to detonate. This was a way of artificially increasing octane number (1 g-l⁻¹ of PTE gave a 10-point gain) and promoting engine lubrication, but it also led to the release of large quantities of lead into the environment, a metal of known toxicity.

II.6.2.4.2 Gazole

Diesel is a fuel for compression-ignition (diesel) engines. Physically, it is a light fuel oil and, legally, a fuel derived from petroleum refining. It is generally used as fuel for diesel engines. The cetane number assesses a fuel's ability to ignite on a scale from 0 to 100, and is particularly important for diesel engines, where the fuel must self-ignite under the effect of compression. A fuel with a high cetane number is characterized by its ease of auto-ignition. The cetane number is to the diesel engine what the octane number is to the gasoline engine. However, they describe radically opposed fuel qualities, adapted to the type of engine. While the former describes a self-ignition capacity sought by the diesel engine, the latter describes a detonation resistance capacity sought by the gasoline engine.

A fuel is said to have a cetane number of x , when it has the same auto-ignition power as a mixture consisting of $x\%$ by volume of n -cetane and $(100-x)\%$ α -methyl-naphthalene. Cetane number for heating oil: 40 and cetane number for diesel: 51.

II.6.2.4.3 Kerosene

Kerosene is the most widely used jet fuel. It is used for civil and military jets, turboprop aircraft and helicopters powered by turbine engines. It boils at between 150°C and 250°C and, like diesel, belongs to the category of medium-density distillates. Kerosene is lighter than diesel, but heavier than gasoline. Because of its extreme conditions of use at high altitudes (low temperatures and air pressure), it has to meet particularly stringent quality requirements. Kerosene is generally a mixture of hydrocarbons containing alkanes ($\text{C}_n\text{H}_{2n+2}$) with chemical formulas ranging from $\text{C}_{10}\text{H}_{22}$ to $\text{C}_{14}\text{H}_{30}$.

II.6.2.4.4 GPL

They are a mixture of paraffinic and olefinic hydrocarbons such as methane, ethane, propane and butane. They are used as fuel and are stored and handled as pressurized liquids. They have boiling points ranging from -74°C to $+38^{\circ}\text{C}$. They are colorless and their vapors are denser than air and extremely flammable. Their main qualities, from an occupational health and safety point of view, are their low vapor pressure and low contaminant content. They are used in a wide variety of applications, including home heating, as a source of energy for domestic use (cooking rings, furnaces, baking, restaurants) and as a clean fuel for certain vehicles.

II.6.2.4.5 Fuel oil

Fuel oil is a petroleum-derived fuel used in boilers. It is classified as a fossil fuel and is involved in air pollution. Fuel oil is derived from petroleum refining, and its characteristics are similar to those of diesel fuel. It is derived from the middle cuts of petroleum from which kerosene, diesel and

domestic heating oil are produced.

II.6.2.4.6 JP-5

JP-5 (Jet Propellant n°5), is a jet fuel with a high flashpoint (above 60°C) developed in 1952 for military use, particularly as fuel for aircraft carriers where the risk of fire is high. It is a yellow liquid, based on kerosene. The freezing point of JP-5 is -46°C.

II.6.2.4.7 Asphalt

Asphalt is essentially made up of heavy hydrocarbons. Only around 30% of the world's crude oils are suitable for the production of asphalt. To be used, asphalt is separated from crude oil by distillation in refineries. It is the heaviest petroleum product. Asphalt is liquefiable when hot, and adheres to the surfaces to which it is applied. It possesses a number of physico-chemical qualities that have been used by man since prehistoric times. In everyday language, it is often confused with pitch, coal tar or road asphalt, of which it is only one component.

II.6.2.4.8 Lubricant oil

Are oils derived from crude oil. Lubricating oil is obtained by distilling and refining crude oil. Its properties depend to a large extent on the quality and consistency of the crude oil from which it is refined, as well as on the refining process itself. The oils used in car engines are not the only lubricants. There are many different types, such as metalworking fluids, transformer oils, gearbox oils and hydraulic oils. Fluid oils and solid and semi-solid greases are also used for lubrication.

II.6.2.4.9 Paraffins

A white, solid substance derived from petroleum, used in candle-making and to waterproof paper. Kerosenes, of which there are several types, are alkanes, i.e. straight-chain saturated hydrocarbon molecules with a non-cyclic chain, and have the gross formula C_nH_{2n+2} , where n is between 18 and 32, and molar mass between 275 and 600 g/mol. A distinction is made between kerosenes made from linear alkanes (n-alkanes) and those made from branched alkanes (iso-alkanes):

- Liquid or fluid paraffines (paraffinum perliquidum), ($n = 8$ to 19) with a viscosity of 25 to 80 mPa.s;
- Oily or pasty paraffines (paraffinum subliquidum), with a viscosity of 110 to 230 mPa.s;
- Solid paraffines (paraffinum solidum), waxes ($n = 20$ to 40) with a solidification temperature between 50 and 62°C.

II.6.2.4.10 Goudron

Goudrons are brown to black, highly viscous or even solid coal derivatives (tar pitch). They are by-products of the distillation of coal during the manufacture of coke, or of its gasification into coal gas. In common parlance, they are often confused with oil-based asphalt.

II.7 Environmental constraints and refining evolution

Oil has a major impact on the environment, in two main ways:

- It contributes to carbon dioxide (CO₂) emissions: increased anthropogenic CO₂ emissions are generally considered to be one of the main causes of global climate change;
- It also contributes to urban air pollution, lake pollution, the destruction of biodiversity and the depletion of various ecosystems;

The exploitation of oil resources also affects landscapes, agricultural systems and tourism. In short, the exploitation and use of oil affects human health and activity on multiple levels. The use of energy in general and oil in particular, makes a major contribution to global economic development, with positive consequences for human health and well-being.

But energy and oil also contribute to forms of pollution that lead to health problems, environmental destruction and, through global warming, potentially serious consequences for development across much, if not all, of the planet. The environmental consequences are considerable throughout the oil development process. At every stage in the oil production process (exploration, extraction, transport, refining,), all natural environments (air, water, soil) are affected in very different ways and to very different degrees.

II.7.1 Advantages of oil

The advantages of oil are as follows:

- It is available on almost every continent;
- It is easy and inexpensive to transport by ship;
- The chemistry of oil is very rich. It can be used to produce gases such as methane, propane and butane, fuels such as gasoline, kerosene, diesel and fuel oil, and aromatic compounds;
- This is the most concentrated form of liquid energy currently available.

II.7.2 Disadvantages of oil

The disadvantages of petrol are as follows:

- The search for new oil fields is becoming increasingly difficult and expensive;
- Its transport is the source of numerous pollutants, in particular "oil slicks";
- As with coal, its combustion produces carbon dioxide, which is released into the atmosphere, contributing to the greenhouse effect.

II.7.3 Impact of fuel consumption

Vehicle fuels, one of the main products derived from petroleum, emit numerous atmospheric pollutants. These pollutants include

- Volatile organic compounds (such as Benzene and Toluene, some of which are toxic);
- Nitrogen oxides, which lead to acid rain and ground-level ozone.

II.7.4 The main components of urban air pollution

- Sulfur dioxide, one of the main causes of acid rain, particles that can cause respiratory ailments;
- Extracted from gasoline;
- Plumb;
- Fine particles from diesel combustion;
- Carbon dioxide, the main greenhouse gas resulting from the use of gases and fuels for transport, electricity generation, heating, etc...

II.7.5 Impact on nature

II.7.5.1 Air pollution

Several stages in the oil production process release toxic materials into the air and/or greenhouse gases. For example, refining releases sulfur oxides, nitrogen oxides, volatile organic compounds, carbon monoxide, benzene and other greenhouse gases. Of course, transportation also plays an important role in this pollution.

II.7.5.2 Soil pollution

When a multinational decides to launch production, it builds one or more pits (or "pools") in the wild, where it discharges toxic compounds into the environment. Once production is complete, she leaves the waste behind and digs elsewhere. The materials left behind penetrate the soil, polluting it before reaching the underground water system.

II.7.5.3 Water pollution

As mentioned above, the extraction of asphalt sands requires a lot of water and the use of solvents, which are discharged into pits. These wastes sink to the water table. Animals and humans use the water for drinking and eating (fish).

Illegal degassing, i.e. cleaning out the bunkers of empty oil tankers to prevent explosions, is the primary source of water pollution. In general, ships (often oil tankers) do this at sea to avoid paying the cost of cleaning (€0.15 per m³). Continuous discharges are more devastating than occasional oil pollution.

II.7.6 Health impacts

The consequences for health are significant:

- Cancers (air and water);
- Cardiac attacks (air and water);

- Nervous system problems (benzene);
- Eye troubles ;
- Anemia (benzene);
- Leukemia (benzene);
- Fœtus problems (benzene) ;
- Health problems caused by arsenic, lead and mercury;
- Respiratory problems, asthma (air).

II.7.7 Catastrophes

Risks associated with the oil industry include:

- Gas explosion;
- Hydrocarbon fires;
- Tanker accident;
- Oil spills;
- Illegal degassing;
- Oil pipeline leaks and ruptures.

Chapter III : Petrochemical manufacturing processes

III.1 Petrochemical production plans

The petrochemical industry presents a larger variety of products. Here are some of the most frequently used synthetic products:

- **Polyethylene:** used to manufacture a wide range of objects such as basins, bottles, pots, etc.
- **Polystyrene:** for insulation and packaging.
- **Polyamides:** such as nylon, the first synthetic textile. It owes its popularity to its steel-like strength (50,000 folds before breaking), high elasticity and hydrophobic (water-repellent) properties.
- **Polyacrylics:** where orlon (or crylon in France) is used to weave knitwear and clothing against the cold. It's a warm, woolly, bulky fabric.
- **Polyvinyls:** these are non-flammable, insulating fibers. They are used in the manufacture of upholstery fabrics (e.g. PVC).
- **Polysters:** mainly tergal. These fabrics are wrinkle-resistant, dimensionally stable and shrink-proof. They are widely used in clothing fabrics.
- **Detergents:** synthetic detergents are another major petrochemical invention. These detergents can replace conventional cleaning products such as soap, bleach and acids. Their wetting power reinforces the moistening action of water, optimizing cleaning. On the other hand, synthetic detergents retain their properties, whereas soap, in hard water, forms insoluble products. These detergents are used to clean dishes, walls, windows, washing powder, etc.
- **Synthetic fibers.**
- **Plasticizers.**
- **Elastomers.**
- **Adhesives.**
- **Nylon.**
- **Pharmaceuticals.**
- **Cosmetics.**
- **Fertilizers.**

III.2 Main petrochemical manufacturing processes

Generally there are two main types of petrochemical process:

III.2.1 Steam cracking (Vapocracking)

This type of process produces olefins. By definition, olefins are unsaturated carbides, i.e. they have a single double bond between two carbon atoms. Steam cracking is a petrochemical process by which saturated hydrocarbons are broken down into smaller, often unsaturated molecules. It is therefore the main source for the production of alkenes (ethylene, propylene etc...), which are

important intermediates in the manufacture of a range of products. The starting products are often naphtha (a transparent liquid produced by the distillation of petroleum), but can also be ethane (a hydrocarbon of the alkane family with the crude formula C_2H_6). They are mixed in steam and brought to around $800^\circ C$ as they pass through pipes heated by furnaces, for a time of less than a second. These reaction products are then quenched to obtain the desired mixture of alkenes.

For example, the following diagrams (figure III.1 and figure III.2) show all the ethylene and propylene derivatives obtained by vapocracking.

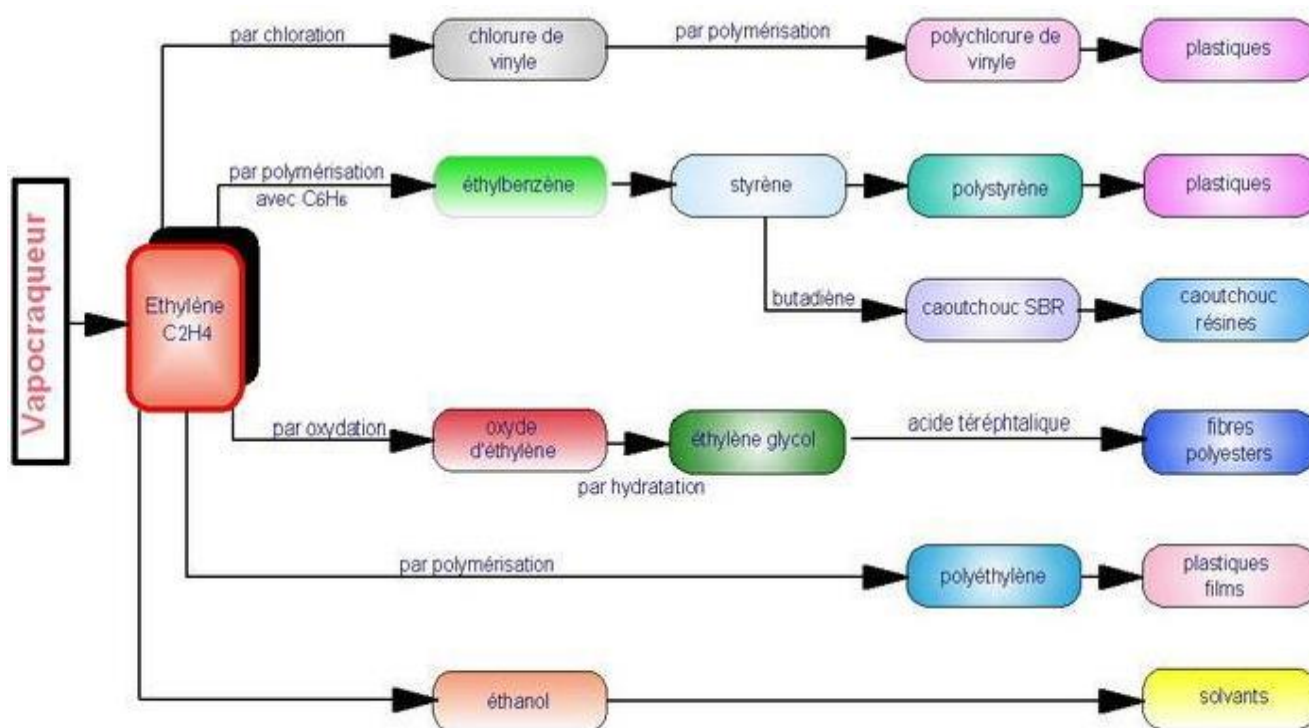


Figure III.1. Ethylene conversion

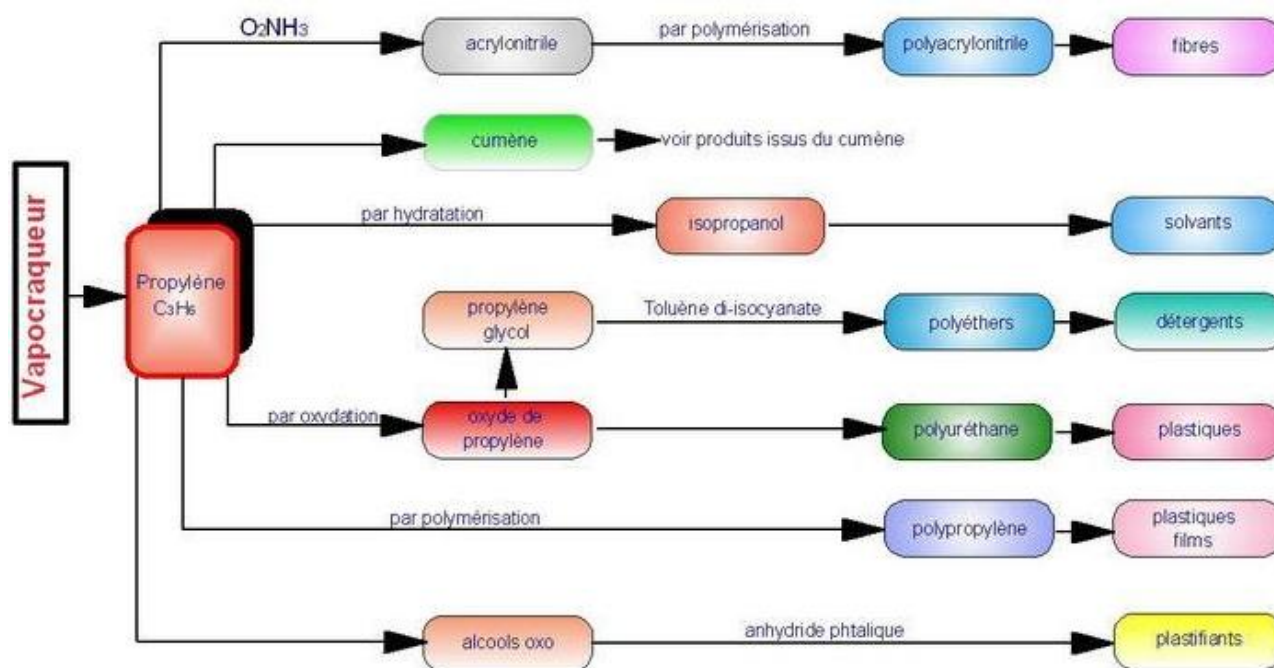


Figure III.2. Propylene conversion

III.2.2 Extraction processes

In this type, aromatics are extracted. In general, aromatic hydrocarbons yield solvents, gums, resins and products used in the manufacture of synthetic rubber, plastics, polyester fibers, paints and varnishes.

In general, the extraction process uses a solvent, dimethyl sulfoxide, added to a certain percentage of water. The aromatics are then re-extracted from their association with this solvent using butane, which is non-aromatic and is easily separated from the aromatics by distillation. These two aromatics extractions are fed into liquid-filled columns, known as extractors, which are fitted with a rotating shaft carrying stirring turbines. This is how benzene is isolated.

Extraction and re-extraction of aromatics are carried out in liquid-filled columns, called extractors, fitted with a rotating shaft carrying stirring turbines. This is how benzene, toluene and xylenes are isolated.

All aromatics, once extracted and purified, serve as raw materials for further hydrogenation or oxidation reactions to produce plasticizers, solvents, fibers, insecticides and many other products. The following diagrams show how benzene, cumene, toluene and xylenes are transformed. Benzene transformations can lead to products as shown below (figure III. 3).

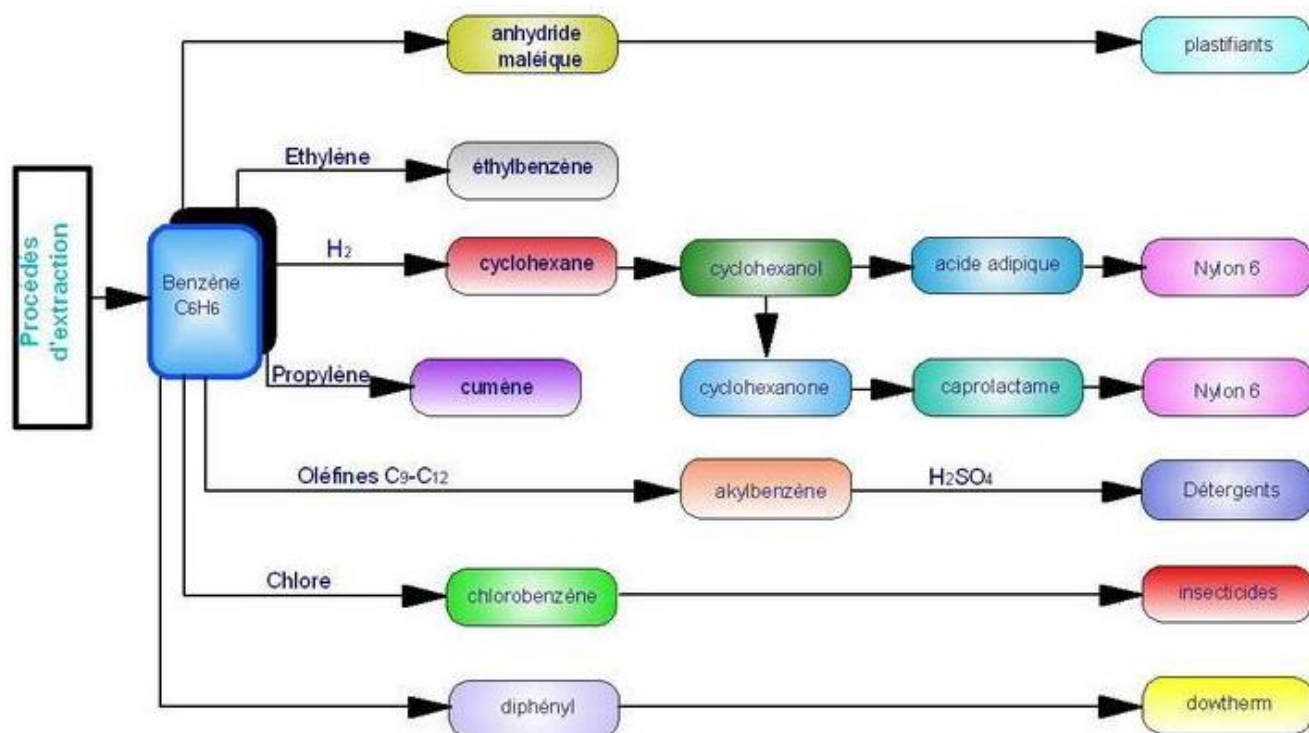


Figure III.3. Benzene conversion

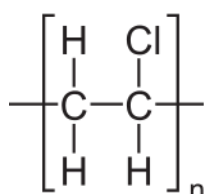
III.3 Examples of processes

III.3.1 Industrial PVC production

III.3.1.1 Definition of PVC (polyvinyl chloride)

PVC is a plastic material made from salt and petroleum derivatives. As the main component is chlorine, the manufacture of a certain quantity of PVC requires less petroleum than many other polymers.

PVC is a thermoplastic material: it melts when heated to a certain temperature and solidifies when cooled.



Structure of poly (vinyl chloride)

It was discovered in 1835 by a French physicist, Victor Regnault. The first European patent was filed in 1914 by the German Friedrich Klatté, and industrial production of PVC began in 1935. PVC resin (Fig. III.4) is made from two raw materials: 57% sea salt (NaCl) and 43% petroleum. It

is the only plastic made from more than 50% mineral raw materials.

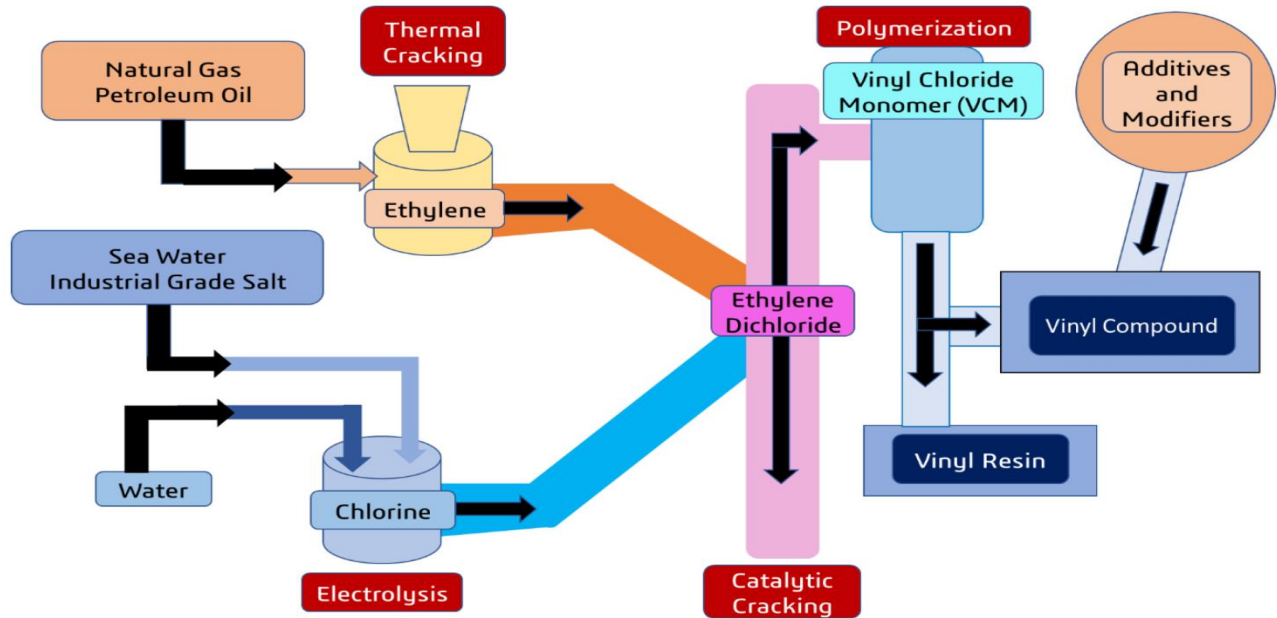


Figure III.4. Schematic of PVC resin production

III.3.1.2 PVC characteristics

- Solidity: mechanical resistance and lightness
- Longevity: over 30 years for windows, and over 60 for pipes
- Easy maintenance: sponge or mop
- Fire resistance: flame-retardant
- Insulation: thermal, acoustic, electrical
- Economy: excellent value for money
- Creativity: unlimited
- Recyclability: 100%
- Hygiene: high sanitary quality.

III.3.1.3 PVC types

In industry, there are four types of PVC:

- **Rigid PVC**, mainly used in the construction industry for pipes and windows;
- **Expanded PVC**, better known as Forex, mainly used to make signs;
- **Flexible PVC**, used to manufacture certain floor coverings
- **PVC films** such as stretch film or adhesive films used in advertising.

III.3.1.4 Techniques for transforming to finished products

After addition of additives, PVC is available in various forms: granules, powder or liquid paste.

- **Extrusion:** compounds in pellet or powder form are passed through a heated sheath to produce a continuous stream of tubes, profiles (windows, closures, electrical panels, etc.) or cladding sheets, which have to be cut to size.
- **Extrusion** blow-molding: air is blown into a mold to press the material against the walls. This process can be used to manufacture hollow bodies, drums, bottles, greenhouse film, etc.
- **Injection:** the granules are melted, then mixed and pushed by a screw into a mold. The result is fittings, drawers, electrical boxes and switches...
- **Calendering:** passing between heated rollers, the material is stretched to produce floor and wall coverings, tablecloths, packaging, waterproof films...
- **Thermoforming:** PVC sheets are heated and applied to a mold. The result is panels for kitchen furniture, trays, helmets, etc.
- **Coating:** a liquid PVC paste called Plastisol is poured onto a substrate to produce coated fabrics for leather goods, floor and wall coverings...
- **Fluidization:** PVC powders are applied by dipping in a fluidized bed. They are used, for example, to coat wire mesh and metal tubes.

III.3.1.5 Main applications

- Construction: pipes, profiles (doors and windows), cables, floor coverings, roof coatings, pipes
- Packaging: food, pharmaceutical and cosmetic products
- Consumer durables: shoes, credit cards, clothing, toys
- Automobile sector: each car contains around 10 to 16kg of PVC (covering parts, dashboards, door panels)
- Medical sector: blood bags, catheters, small tubes and pipes, surgical gloves, inhalation masks, sterile packaging.

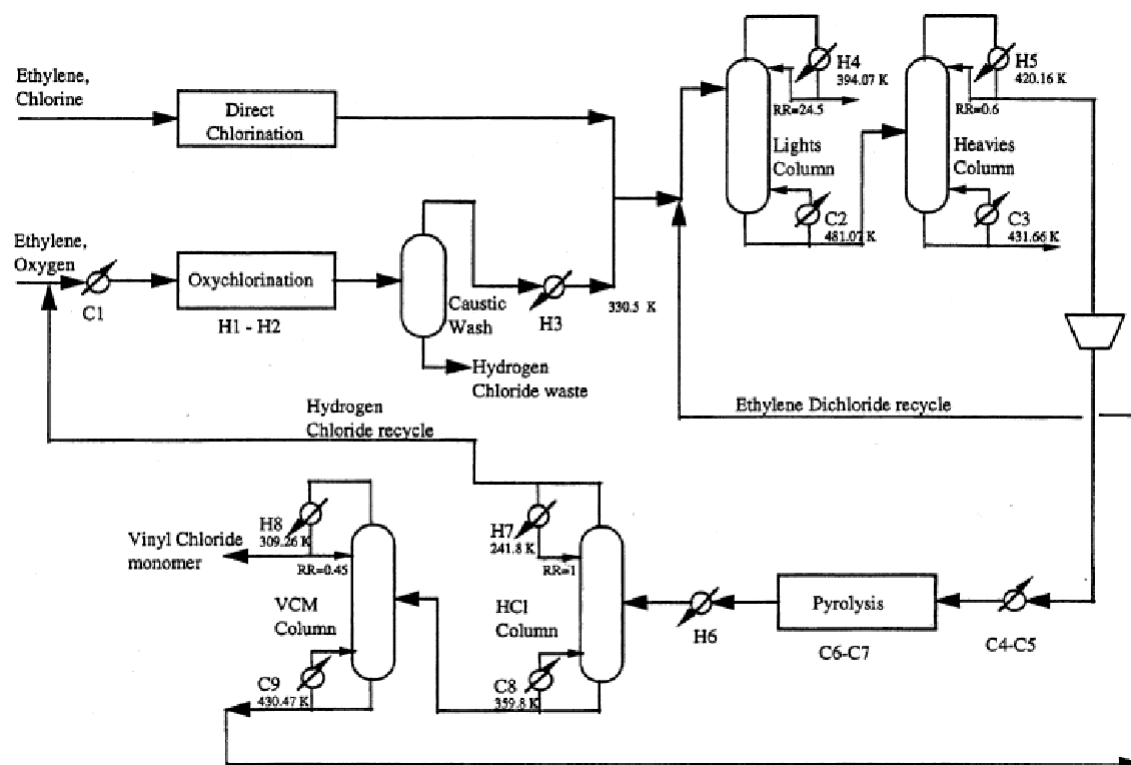


Figure III.5. Polyvinyl chloride process plant

III.3.1.6 Health and safety

Under normal conditions of use, a PVC object does not release any products from its formula.

Certain plasticizers used in its composition may present a health risk.

PVC allows the use of chlorine released during the manufacture of products such as soap and detergent. Today, it's one of the solutions for avoiding large-scale, dangerous storage of chlorine.

This polymer takes the form of a white powder. It is not classified as hazardous by European regulations. The approvals granted to PVC for food and medical applications are the best proof of this.

Plastification and toxic risk

Plasticizers are often added to PVC (to form plastisols, for example) to improve certain characteristics (flexibility, elongation at break, resistance to cold and impact, etc.) or to facilitate processing.

Among the plasticizers used, certain phthalates are harmful. Over time, they can migrate and deposit on the surface of flexible PVC objects. For this reason, a European directive restricts their use in toys.

Other plasticizers are authorized, from the adipate family or even vegetable oils (e.g. soybean oil). For many years, they have been used in the manufacture of food-grade stretch film.

However, some hydrophobic plasticizers migrate into the food when they come into contact with food fats. Other alternatives are being developed to eventually replace PVC in food films.

III.3.2 ammonia synthesis

Ammonia is one of the most important synthetic chemicals, mainly used in the fabrication of fertilizers, explosives and polymers. This article describes the various stages in the industrial process of ammonia synthesis. The principle involves reacting nitrogen from the air with dihydrogen. This process requires the use of a feedstock, mainly natural gas, coal or naphtha. This article also describes the physico-chemical properties of ammonia, and provides information on toxicity, the dangers associated with its use, and precautions for use and storage.

Ammonia (NH₃) is a chemical compound composed of one atom of nitrogen (N) and three atoms of hydrogen (H), existing in a liquid or gaseous state. The industrial production of ammonia is divided into two main stages: dihydrogen production and ammonia synthesis. Dihydrogen is obtained by reforming methane (or other heavier hydrocarbons such as coal and naphtha) with steam. Ammonia is then synthesized by catalytic reaction between nitrogen from the air and dihydrogen from natural gas/hydrocarbons and steam. This industrial ammonia synthesis process is known as Haber-Bosch. The technology for ammonia production is well established, with few significant modifications to the original synthesis process (Haber-Bosch). However, improvements have been made on the energy front, in particular to reduce CO₂ production or to introduce alternative energy sources (i.e. non-CO₂-generating process, alternative dihydrogen production by photo and electrocatalytic means).

Ammonia is mainly used in the production of fertilizers, explosives and polymers. In the agricultural sector, ammonia is the main component of nitrogen fertilizers, and around 80% of the world's ammonia production is used in the soil fertilizer industry. Ammonia is one of the world's most important synthetic chemicals, second only to sulfuric acid. Worldwide production is estimated at 140 million tonnes per year. Global ammonia production is dominated by China, with 32% of total world production. Other major producers are India (9%), the United States (7%) and Russia (7%).

III.3.2.1 Industrial production

III.3.2.1.1 Process principle

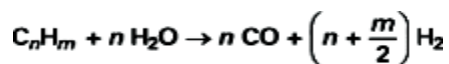
In the presence of a catalyst, dihydrogen from hydrocarbons and water reacts with nitrogen from the air. Dihydrogen is produced mainly by steam reforming of hydrocarbons, followed by steam conversion of the carbon monoxide produced.

The dihydrogen is purified of all accompanying oxygen compounds, before being

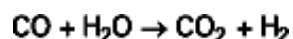
introduced into the catalytic reactor for ammonia synthesis.

The main reactions implemented are as follows:

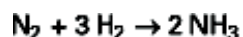
Reforming hydrocarbons (endothermic)



CO conversion (exothermic)



Synthesis (exothermic)



III.3.2.1.2 Primary materials

Natural gas is the essential source of dihydrogen for ammonia synthesis. Around 90% of ammonia production is currently based on natural gas, mainly for economic reasons: raw material, investment and operating costs.

Natural gas has completely supplanted naphtha as a raw material for the ammonia industry. Heavy fuel oils, which are relatively abundant and inexpensive, are used, but on a smaller scale, as their use in oxygen partial oxidation processes leads to costly installations that are not easy to operate. Similarly, ammonia production from coal remains marginal, with the exception of China, where coal is still the most commonly used primary material.

III.3.2.1.3 Process characteristics

Based on the principle of hydrocarbon reforming, a number of relatively similar ammonia production processes have been developed.

The distinctive features of these processes lie in the arrangement of the various sections of the production unit and in certain original technologies; the reactions implemented are always the same. The quest for energy savings is the most outstanding feature of modern ammonia production processes.

The unit processes involved in ammonia production are patented or the know-how of specialized companies.

The development of processes to reduce energy consumption has resulted in two major trends:

- considerable reduction in synthesis pressures (8 to 11 MPa instead of 20 to 30 MPa), resulting in the use of much larger volumes of catalysts;
- the search for optimum hydrocarbon consumption in synthesis gas preparation:

- by reducing primary reforming output, to operate with excess air in the afterburner and rectify the $H_2 + N_2$ mixture prior to introduction into the syngas loop (C.F. Braun process), thus reducing reformer furnace heating gas consumption,
- or by maximizing the various synthesis gas production reactions and maximizing heat recovery (Topsoe process), which optimizes process gas consumption,
- or by using the recovered heat to partially steam reform the hydrocarbon.

Other processes have been used on a smaller scale, mainly for syngas production:

- **Partial oxidation** with oxygen:

- **heavy fuels** (Texaco or Shell processes);
- **natural gas** (SBA and Topsoe processes);

- **Coal gasification**: there are ammonia units operating by coal gasification using the Koppers-Totzek and Linde and Lurgi processes;

- Steam reforming;

- electrolysis.

III.3.2.1.4 Industrial implementation

Ammonia production equipment is largely made of **ordinary steel**.

Refractory steels with a high Ni-Cr content are used for the reforming furnace tubes.

Alloyed Cr-Mo steels are used for medium- and high-temperature hydrogen-carrying parts.

Finally, **stainless steel** is used in equipment subject to corrosive conditions (presence of moist CO_2).

The low-temperature part of the synthesis loop is generally made of **carbon steel** resistant to cold embrittlement.

III.3.2.1.5 Installation description

A conventional plant for producing ammonia by reforming natural gas (Figure III.6) generally comprises the following stages:

- **final desulfurization** of the natural gas to remove the last traces of sulfur (< 0.1 ppm, i.e. 10^{-7} by mass) ;
- **primary reforming** at 3.8 MPa, possibly with pre-reforming ;
- **post-combustion** with air, into which synthetic nitrogen is introduced, followed by heat recovery and high-pressure steam generation or a reformer-exchanger;
- **conversion of CO** by steam, generally in two stages, at high temperature ($360^\circ C$) and

low temperature (220°C);

- **decarbonation** of syngas, where the CO₂ content is reduced to less than 0.1% by volume;
- **methanization**, which eliminates traces of oxygenated compounds;
- **gas compression**;

high-pressure ammonia synthesis loop (10 MPa), including :

- the catalytic synthesis reactor,
- a series of heat exchangers where the ammonia produced is condensed and separated in a liquid state,
- An ammonia refrigeration unit that supplies the cold required to condense and cool the ammonia produced.

The molar flow ratio of fresh gas to recycled gas at the synthesis compressor ranges from 1/3 to 1/4.

Ammonia plant operation is fully automated and digitally controlled.

The unit capacities involved are, in practice, 1,000 t of ammonia per day, or around 330 to 350 kt/year, and new plants are generally designed to go up to 2,200 tonnes of ammonia per day.

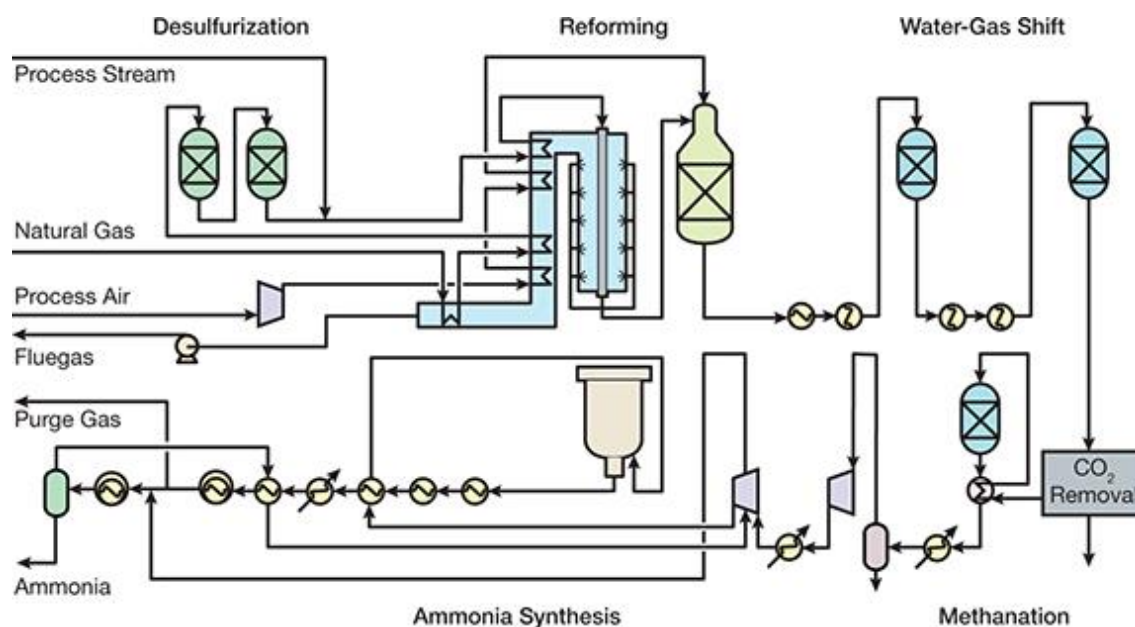


Figure III.6. Ammonia synthesis processes

III.3.2.1.6 Products obtained

Ammonia is produced in an anhydrous liquid state, generally at a temperature of -33°C, which enables it to be stored in tanks at atmospheric pressure.

The standard quality generally obtained contains:

- NH₃ 99.5% by mass, minimum;
- H₂O 0.5% by mass, maximum;
- incondensables 0.3% vol;
- oil 5 ppm (5×10^{-6} by mass).

A very significant **quantity of CO₂** is produced, of the order of 49 t/h in a 1000 t/d ammonia unit produce from natural gas. Such production is of great importance when urea production is associated with the ammonia unit. In other cases, the carbon dioxide is generally released into the atmosphere.

III.3.2.1.7 Type of effluent produced

An ammonia plant using natural gas reforming produces few effluents:

- Liquid effluents: steam condensates associated with syngas, which contain some ammonia, methanol and CO₂, and are generally treated by stripping and recycled to boiler water treatment (demineralized water production);
- Gaseous effluents: furnace fumes, sometimes CO₂, which are discharged into the atmosphere; there are practically no permanent noxious gaseous emissions.

III.3.2.2 Hygiene and safety

III.3.2.2.1 Pictograms and hazard statements

Pictograms and hazard warnings for ammonia are shown in figure III. 7. An irritant and caustic product, ammonia is highly irritating to the mucous membranes of the eyes, nose, throat and lungs. Levels of 5,000 ppm (i.e. 0.5% by mass) can be fatal within minutes, causing respiratory distress and asphyxiation. Eye irritation begins at 140 ppm (14×10^{-5} by mass).

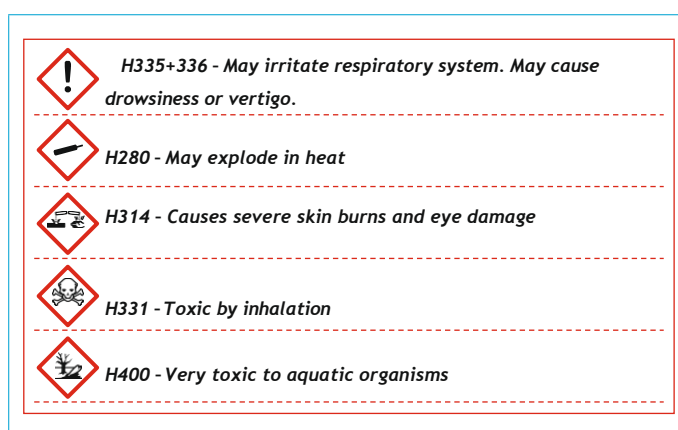


Figure III. 7. Pictograms and hazard warnings

III.3.2.2.2 Fire and explosion hazards

Ammonia forms explosive mixtures with air within the limits of 16 to 25% by volume.

Pure ammonia is a low-flammability gas, with an auto-ignition temperature of 651°C in the presence of iron.

Ammonia reacts violently on contact with certain products such as mercury, halogens, many oxides and peroxides, calcium, silver salts, etc., creating sources of fire and explosion.

In the event of fire, extinguish with carbon dioxide, powder or water spray.

III.3.2.2.3 Storage and handling

Ammonia storage and handling facilities are subject to the regulations governing classified installations.

In the presence of humidity, ammonia rapidly attacks copper, zinc, silver and their alloys.

Ordinary steel is generally used for ammonia storage, which takes place in special rooms, widely ventilated by high openings or chimneys.

III.3.2.2.4 Handling precautions

Personnel called upon to manipulate gaseous or dissolved ammonia must be instructed in the risks to which they are exposed. They should be provided with gloves, boots, aprons, impermeable and cotton clothing.

Handle and use compressed ammonia cylinders in accordance with the supplier's instructions. These cylinders must not be heated or subjected to impact.

In the event of ammonia leaks, use self-contained breathing apparatus and large quantities of water. Direct discharge of washing water into sewers or water sources must be avoided.

III.3.2.3 Environmental impact of ammonia

Ammonia emissions are mainly due to animal waste from livestock farming and fertilizer inputs for crop production. These entropic inputs of nitrogen lead to environmental problems such as acid rain, eutrophication of waterways and acidification of forest soils. In 2014, it was reported that 62% of rain acidification is due to ammonia emissions, 29% to nitrogen oxides and 8% to sulfur dioxide. Ammonia is also considered highly toxic to aquatic organisms, causing long-term adverse effects.

III.3.2.4 Main applications

Ammonia is the main source of plant-available nitrogen, and is therefore the essential building block of nitrogen fertilizers. It is the raw material for the production of nitric acid, ammonium nitrate and urea. Over 85% of ammonia production is destined for the fertilizer industry.

Another large fraction of production is used to manufacture nitrate derivatives (explosives).

Other uses include nitrogen derivatives for organic chemistry (amines, nitriles, etc.)

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