Chapter II: Oil refining diagram

I. Introduction

Petroleum is a fossil fuel made up of a mixture of hydrogen and mostly carbon. The composition varies from field to field, but is roughly 83-87% carbon, 10-14% hydrogen and 0,6-6% sulfur, oxygen 0.05–2.0 % and nitrogen 1-2%

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

- Measurements of density, viscosity, etc., carried out on the various fractions obtained by distillation. These methods provide useful information for refining and upgrading petroleum products
- Liquid chromatography, gas chromatography, mass spectrometry, etc., on various dissolved fractions. They can be used to identify the various families of compounds present.

II. Crude oil classification: Oil can be quoted in three ways:

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
- **Medium oils with** a density between 0.824 and 0.875
- **Heavy oils** with densities ranging from 0.875 to 1
- **Extra-heavy oils** with a density greater than 1

B) Classification according to the K_{UOP} correction factor: This factor can measure the nature of kerosenes and take on the following values depending on the nature of the oil:

- K_{UOP}=10 for pure aromatics
- K_{UOP}=11 for pure naphthenes
- K_{UOP}=12 for iso-paraffins
- K_{UOP}=13 for n-paraffins

C) Classification chemical: It is the classification of crude according to the predominant hydrocarbon families.

- Paraffins
- Naphthenic
- Aromatics

III.Crude oil composition

Petroleum products are all different, depending on their origin and chemical composition.There are hundreds of crude oils in the world, depending on their geological location, such as Arabian Light (Middle Eastern benchmark crude), Brent (European benchmark crude) and West Texas Intermediate (WTI, American benchmark crude).

The hydrocarbons contained in petroleum are grouped into three families:

Paraffins (alKanes)

Naphtenes (cycloalkanes)

Aromatics

A-Chemical composition

A.1) Hydrocarbons

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

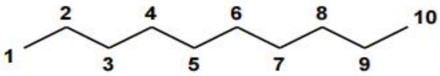
These are saturated hydrocarbons with the formula CnH2n+2 where n is the number of carbon in the hydrocarbon chain

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 pentadecane
…..........................
C20:C20H42 eicosane
C21:C21H44 heneicosane
C22:C22H46 doeicosane
…............................
C30:C30H62 triacontane
C40:C40H82 tetracontane
C50:C50H102 pentacontane

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

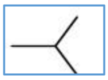
- ***Normal paraffins***: the carbon chain is a single straight chain.



le Decane

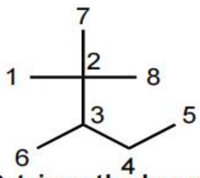
- ***Iso-paraffins*** :

The carbon chain is a branched chain (these are paraffins isomers, they are differentiated by the use of the prefix **iso**).

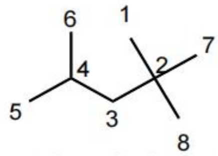
The first in the iso-paraffin series is iso-butane : 

For the nomenclature, we consider the longest straight chain and locate the positions of the branched chains by numbering the carbons of the main chain from left to right.

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



2,2,3 trimethylpentane

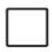


2,2,4 trimethylpentane

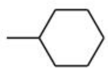
B. Naphtenes : *(Cycloalcanes) CnH2n*

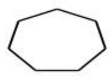
These are saturated cyclic hydrocarbons, and their names are those of kerosenes preceded by of the prefix cyclo, we find :


cyclopropane

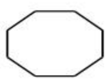

cyclobutane


cyclopentane

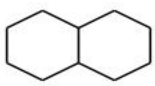

methylcyclohexane

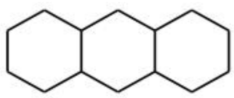

cycloheptane


cyclohexane


cyclooctane

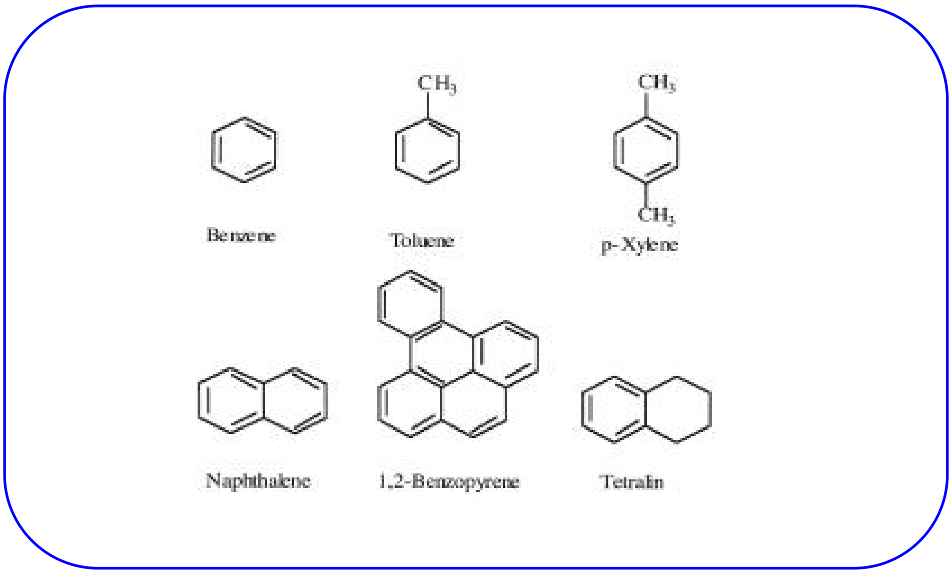
There are also naphthenes formed by the juxtaposition of two (or more) rings of six carbon atoms:


decaline
decahydronaphthalene


tetradecahydroanthracene

C. Aromatics:(Benzenes)*CnH2n-6*

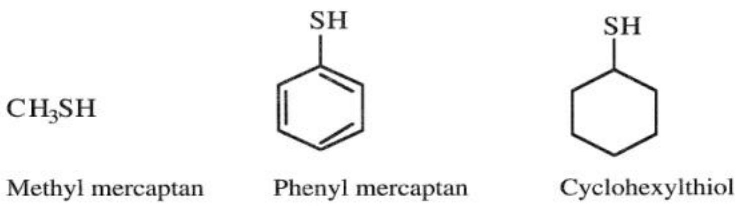
These are unsaturated cyclic structures with three double bonds in each ring.



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

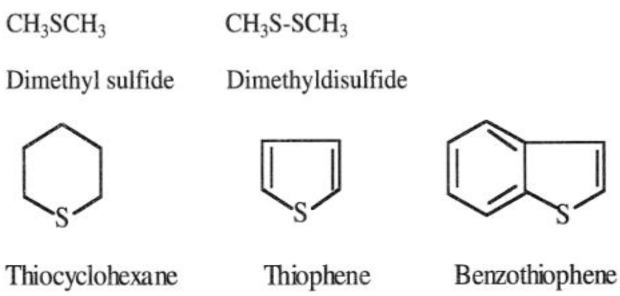
Sulfur compounds are present in crude oil in the form of organic sulfur compounds. Hydrogen sulfide **H_2 S** is the only non-organic compound present in crude oil. The presence of sulfur compounds in crude oil is harmful because of their corrosive properties. Organic sulphur compounds are generally classified into two groups

<u>Acidic compounds R-SH</u>: are thiols (mercaptans):



Thiols are corrosive compounds with a strong odour.

<u>Non-acidic compounds:</u> These include thiophenes, sulfides and disulfides.



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

A.3 Other compounds :

a. Oxygenated compounds: 0.05 to 1.5% by mass
b. Nitrogen compounds: 0.1 to 2% by mass
c. Metals: 0.005 to 0.015% by mass (including 75% of Nickel and Vanadium).
find Sodium, Calcium, Magnesium, Aluminium and Iron.

II.4 OIL DERIVATIVES

Under the effect of heat, the components of oil separate. The heavier components remain at the base, while the lighter ones rise (gas, petrol).

The main products used as fuels are liquefied petroleum gases, gasoline, kerosene, jet fuels, diesel fuels, fuel oil and refinery residues.

1. Natural gas

- Natural gas is a fossil fuel made up of a mixture of hydrocarbons naturally present in porous rock in gaseous form, or dissolved in oil in reservoir rock at reservoir pressure.

-There are several forms of natural gas, distinguished by their origin, composition and the type of reservoir in which they are found.

- gas is still mainly composed of methane (over 90%), but also contains other hydrocarbons such as ethane, propane and butane at very low levels, of the order of 1 to 4%.

it also contains sulfur compounds, nitrogen, CO_2, other mineral compounds and small quantities of helium (He), mercury (Hg) and argon (Ar).

Natural gas is the second most important energy source for power generation, after coal.

2. Liquefied gases

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°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 (stoves, ovens, baking, catering) and as a clean fuel for certain vehicles.

3. Gasoline

A. Automotive gasoline: is a mixture of hydrocarbon fractions consisting mainly of light to heavy hydrocarbons. It is the most important refining product.

Gasoline has a boiling point between room temperature and around 204°C. The most important characteristics of gasoline are octane number.

For their proper use, it is essential that they contain no hydrocarbons which are harmful to engine performance.

They must not contain sulphur compounds or acidic products likely to corrode engines and tanks.

Additives are used to improve gasoline properties and protect the engine against oxidation and rust formation.

B. Aviation gasoline: is a high-octane product specially formulated to ensure good high-altitude performance

4. Special gasoline

Thanks to their specific characteristics, they are used as solvents and raw materials in the manufacture of glues, rubber, inks, tires, pharmaceutical products, ...

5. White-spirit

This is a class of hydrocarbons used as a solvent in the preparation of paints, and cleaning products.

6. Lamp oil

It's a petroleum fraction used for a very long time in kerosene lamps, until the advent of electric light bulbs. Since then, it has been used in the preparation of insecticides for domestic and agricultural use.

7. kerosenes

Kerosenes are mixtures of kerosenes and naphthenes, generally containing less than 20% hydrocarbons.

They have a flash point above 38°C and a boiling point between 160°C and 288°C.

Kerosenes are used for lighting and heating, as solvents and as constituents of diesel fuels.

8. Diesel

Used as a fuel, mainly for diesel engines.

9. Heating oil

It's a diesel fuel, but intended for domestic heating, farm tractors and public works equipment.

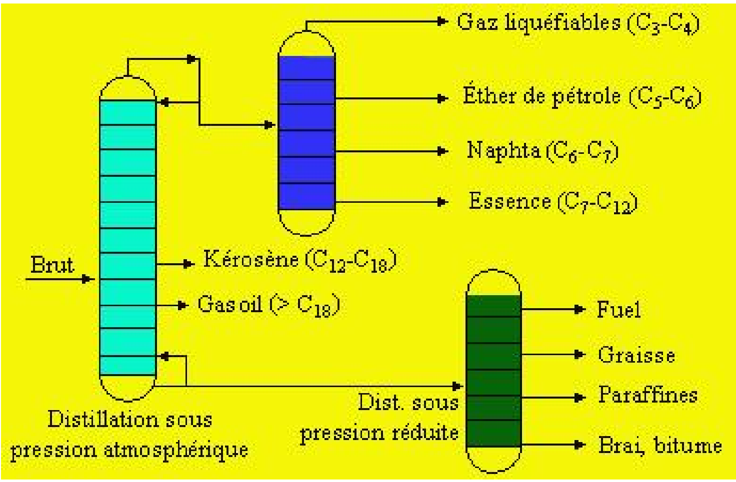
10. Light marine diesel

This is a diesel fuel designed for diesel-powered fishing boats.

11. Oils and greases

They are mainly composed of heavy hydrocarbons and are highly viscous. They are used for engine lubrication and greasing. A distinction is made between

- Motor oils: for vehicle engines.
- Industrial oils: for engines other than those used in vehicles, such as machines and steam turbines, gas turbines, compressors, etc.
- Lubricating greases: prepared by dispersing soap gels in oil.
- paraffins and waxes: they have a denser and more compact structure than fats, obtained as a residue during the distillation of crude oil, used to make candles, shoe polish, etc.



Hydrocarbons	Applications
Liquefied gases	Domestic and industrial gas Motor fuel gas Lighting gas Ammonia Synthetic fertilizers Alcohols Solvents and acetone Plasticizers Resins and fibers for plastics and textiles Paints and varnishes
Raw materials for the chemical industry	Rubber products
Diesel	Cracking charge Heating oil and diesel fuel Fuel for metallurgy Absorption oil for benzene and gasoline extraction
Technical oils	Textile oils Medicinal oils and cosmetics White oil for the food industry
Lubricating oils	Transformer and spindle oil Engine oils Machine and compressor oils Turbine and hydraulic oils Transmission oils Insulating oils for machines and cables Oils for axles, gears and steam engines Metalworking, cutting and grinding oils Cooling and rustproofing oils Heat exchanger oils Greases and lubricants Printing ink oils
Residual fuel oil	Boiler oil and process oil
Bitumen	Road bitumen Roofing materials Asphalt lubricants Foundation insulation and protection Waterproof paper products

II.5 Oil Refining

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

The **refinery is** where oil is processed to extract marketable fractions.

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

Simple refineries

Complex refineries

II.6 Crude oil pretreatment

Crude oil often contains :

-water, inorganic salts, suspended solids and traces of soluble metals in water.

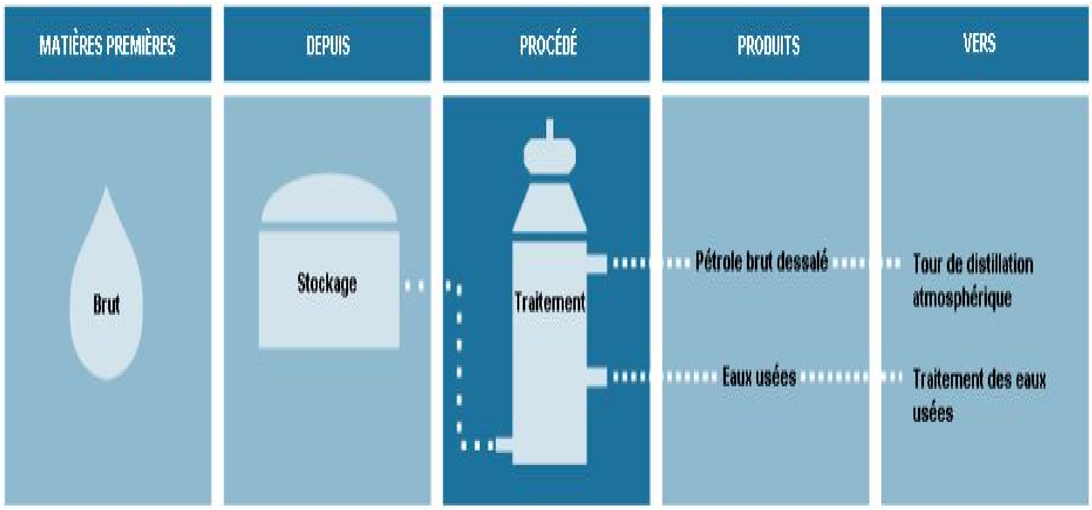
-On arrival at the refinery, crude oil is stored in large tanks. The crude oils are stored and separated according to their sulfur content.

The first step in refining is to remove these contaminants by desalting in order to reduce them:

-corrosion and fouling of plants, prevent poisoning of catalysts in production units.

Three typical crude oil desalting methods are used:

-Chemical desalting, electrostatic separation and filtration are just three of the methods available of crude oil desalting processes.



Source: d'après Occupational Safety and Health Administration (OSHA), 1996.

Desalting process (pre-treatment)

- 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 kept in a tank for the aqueous phase to settle.

-In **electrostatic desalting**, high-voltage electrostatic charges are applied to concentrate 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, thus facilitating mixing and water separation;

- Adjusting the pH of the water with a base or acid

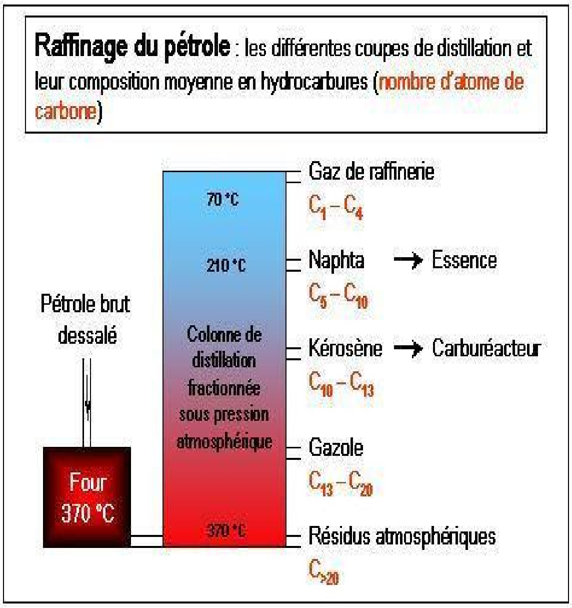
-Waste water and the contaminants it contains are collected from the lower part of the settling tank and sent to the wastewater treatment unit. Desalted crude oil is recovered from the upper part of the settling tank and sent to an atmospheric distillation tower (fractionation tower).

II.7 Crude oil separation processes

The first step in the refining process is to fractionate the oil. in atmospheric and vacuum distillation towers.

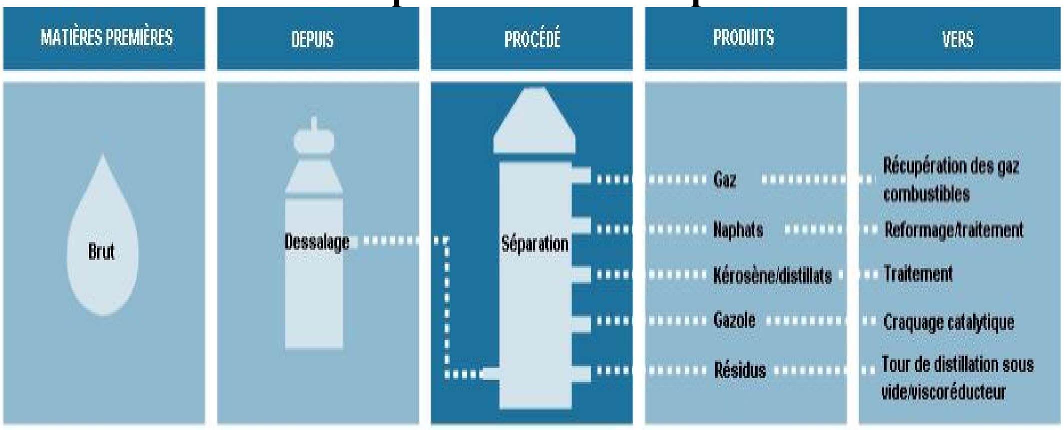
Distillation is the process of separating the different components of a liquid mixture according to their boiling temperature.
Petroleum distillation is the fundamental operation which, using a process based on the boiling points of the various products, enables the separation of large groups of hydrocarbons known as "**cuts**" or "**fractions**".
Crude oil is distilled in two complementary stages. A first, atmospheric distillation separates gases, gasolines and naphtha (light cuts), kerosene and diesel (medium cuts) and heavy cuts.
The residues from the heavy cuts then undergo vacuum distillation to separate certain medium products.

1. Atmospheric distillation :



The operation consists in separating the various components of a liquid mixture according to their evaporation temperature. The crude oil is injected into a large distillation tower, where it is heated to around 400°C. The different hydrocarbons contained in the crude oil are vaporized: first the light ones, then the medium ones, and finally some of the heavy ones. The temperature decreases as you move up the tower, allowing each type of hydrocarbon to liquefy and be recovered.
The lighter ones are collected at the top, and the remain at the bottom of the tower.

Atmospheric distillation process



Source: d'après Occupational Safety and Health Administration (OSHA), 1996.

Cut (nb of C)	Temperature evaporation	Product
C1 - C4	< 0 °C	Domestic gas Petrochemical raw materials
C5 - C6	20 - 60 °C	Petroleum ether
C6 - C7	60 - 100 °C	Light naphtha, white spirit, solvent
C6 - C11	60 - 200 °C	Gasoline fuel
C11 - C16	180 - 280 °C	Kerosene, diesel, heating oil
C18	350 °C	Heavy fuel oil, products for reduced-pressure distillation

2. Vacuum distillation :

The heavy residue from atmospheric distillation is reheated to around 400°C and then fed into a distillation column similar to the previous one, but at reduced pressure. Vacuum is provided by a pump system.

This technique applies the physical law according to which the boiling point is therefore condensation depends on pressure.

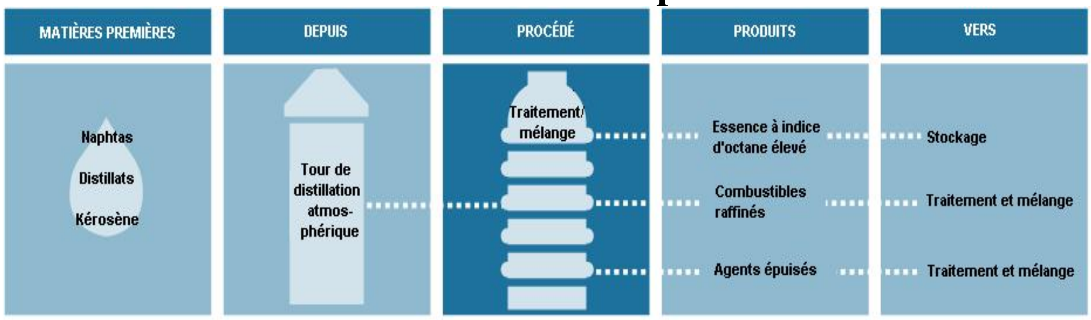
-If the pressure drops, so does the boiling point.

-Vacuum distillation therefore allows cuts to be made at lower temperatures.

too high a temperature would destroy the product)

Vacuum distillation will produce heavy diesel and distillate cuts.

Vacuum distillation process



Source: d'après Occupational Safety and Health Administration (OSHA), 1996.

II.8 Crude oil conversion processes

1. Cracking

In everyday life, demand is mainly for lightweight products, such as
fuels and heating oil (also known as HEL extra-light heating oil).

Demand for heavy heating oil, on the other hand, is falling year on year, particularly in Switzerland. This is why refineries are keen to increase production of lighter products. For this reason, many modern refineries are equipped with a cracking unit, a process that breaks down a complex organic molecule into smaller components, including alkanes, alkenes, aldehydes and ketones. Temperature and pressure conditions, as well as the nature of the catalyst, are decisive factors in cracking.

Three cracking processes characterize modern refineries: thermal cracking, Catalytic cracking and Hydrocracking.

- **Reforming:** Reforming i s a refining method for converting naphthenic molecules into highoctane aromatic molecules used as the basis for automotive fuels.

2. Thermal cracking process

Thermal cracking is the hydrocarbon transformation process that uses temperature as an activating agent. It involves heating the hydrocarbons (300 to 850°C) under high pressure. The rest of the equipment is used to separate the products obtained.

Thermal cracking essentially consists in breaking hydrocarbon molecules under the influence of temperature alone.

Thermal cracking reactions can be classified into two groups:

-**Primary reactions** that lead to the more or less complete disappearance of molecules subjected to the effects of temperature.

-**Secondary reactions** that partially or fully transform the products formed by primary reactions.

The composition of the final mixture depends on three parameters: **temperature**, **time** and **pressure**.
Given the complexity of reactions, it's impossible to define their exact mechanisms, even in the simplest cases.

Cracking conversion rate

It varies greatly from one oil cut to another and depends above all on several parameters:
-The nature of the raw material to be cracked
-Reaction temperature
-Cracking time
-Cracking pressure

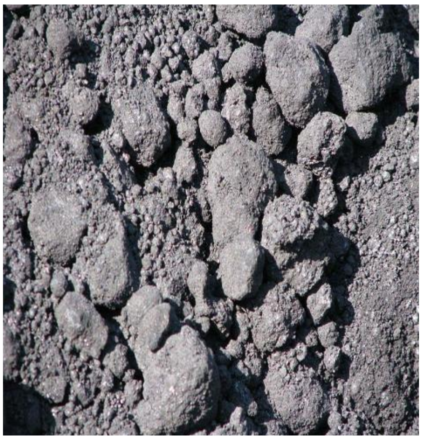
Cracking gasoline properties

Cracked gasolines have significantly higher octane ratings than straight gasolines, due to the fact that they contain a high proportion of branched and aromatic hydrocarbons, which improve octane ratings.

Thermal cracking applications

1) The manufacture of high-octane gasolines
2) The manufacture of light unsaturated hydrocarbons, which are the main raw materials for petrochemicals.
3) Coke production.

Petroleum **coke** comes in solid, black form, and consists mainly of carbon, with very little hydrogen and significant quantities of pollutants (sulfur, heavy metals...).
Depending on impurities, petroleum coke is used as a fuel or as a material for the manufacture of electrodes. For the manufacture of electrodes, petroleum coke is calcined to obtain a product composed of over 98% carbon. These electrodes are then used in the metallurgical industry, notably for aluminum and steel production.



3. Catalytic Cracking Process

It involves heating (450°C), at a pressure of a few bars and in the presence of a catalyst (aluminum silicates or zeolites), the heavy fractions from oil distillation to produce gasolines...

It provides better process control and is less energy-intensive.

Definition of a catalyst: In a chemical reaction, a catalyst is a substance which, without appearing in the final product and without undergoing any structural modification, accelerates the rate of the reaction.

Natural clays, silica-alumina and silica-magnesia were the first catalysts used in catalytic cracking. Synthetic catalysts (zeolites) are more efficient than conventional catalysts.

Influence of operating conditions

a) Temperature: at around 400-500°C, this accelerates the rate of reaction, but has less effect than in thermal cracking. As temperature rises, gasoline and coke yields decrease.

b) Pressure: increasing pressure favors conversion and gas production, while gasoline yield and octane number decrease, and coke production declines.

c) Catalysts: Research and development are focused on the development of increasingly efficient catalysts. The aim is always to achieve high activity and selectivity.

The different types of catalytic cracking.

1) Fixed-bed catalytic cracking :

was the first industrial process, completed in 1936. In this process, hydrocarbon vapors are heated to around 480°C and then passed through a mass of catalyst housed in a reactor. The resulting coke deposits on the catalyst and deactivates it, so the coke has to be burned off and the catalyst regenerated by injecting air or an inert gas.

Three reactors are used, working alternately in reaction and regeneration, with each reactor operating in a different mode.

operation being separated from the next by a purge of the gas produced in the previous operation.

For a reactor, the complete cycle takes 30 minutes, w i t h one third for the cracking phase itself, one third for catalyst regeneration and one third for purging.

Disadvantages of fixed-bed catalytic cracking:

- High operating costs.
- Alternating reaction-regeneration is a nuisance for the process.
- Possibility of corrosion of coolant bundles in catalytic beds if sulfur content of treated feedstock exceeds 0.2%.

These disadvantages were eventually to lead to the decline of fixed-bed units in favor of the more attractive moving-bed and fluidized-bed processes.

2) Moving-bed catalytic cracking.

The process was first put into operation in 1941, with the granular catalyst descending from a hopper in the upper part of the unit and passing by gravity through the reactor and regenerator, before being returned to the upper part by compressed air, from where it flows out again and the cycle begins again.

3) Fluid catalytic cracking

In this process the catalyst used is in powder form and circulates between the reactor and the regenerator.

Hot catalyst (590°C) from the regenerator is mixed with the feedstock, vaporizing it, and the mixture acts as a fluid feeding the reactor.

The coke formed as a result of cracking is burned by air injection.

III- Environmental impacts of oil production

1.Introduction

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

- It contributes to carbon dioxide (CO_2) emissions: increasing anthropogenic CO_2 emissions are generally considered to be one of the main causes of global warming.
- It also contributes to urban air pollution, lake pollution, the destruction of biodiversity and the impoverishment of various ecosystems.

The exploitation of oil resources also affects landscapes, farming systems and the environment tourism.

In short, the exploitation and use of oil affect human health and activity in many ways. 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 cause 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.

2.The advantages of oil

The advantages of oil are as follows:

- It's an energy that's available on just about every continent,
- It is easy and inexpensive to transport by boat,
- Petroleum chemistry is very rich. Petroleum produces gases such as methane, propane and butane, fuels such as gasoline, kerosene, diesel and heating oil, and aromatic compounds,
- It is the most concentrated form of liquid energy available today.

3.The disadvantages of oil

The disadvantages of oil are as follows:

- The search for a new oilfield is becoming increasingly difficult and costly,
- 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.

in the atmosphere, contributing to the greenhouse effect.

4.Impact of fuel use

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 tropospheric ozone.

5.The main components of urban air pollution

- Sulphur dioxide, one of the main causes of acid rain, particles that can cause respiratory ailments.
- extracted from gasoline.
- lead.
- fine particles from diesel combustion.
- Carbon dioxide is the main greenhouse gas resulting from the use of gases and fuels for transport, electricity generation, heating, etc

6.Impact on the health of indigenous people in certain regions of the world

Oil exploitation zones are expanding, sometimes covering land belonging to indigenous groups who are often forced to come into contact with diseases foreign to their region and with other social threats, which are often devastating to their traditional way of life.

-Thus, the introduction of infectious diseases, to which native communities have not developed immunity, is commonplace.

-Industrial activities can affect ecologically sensitive areas.

Impacts on nature

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.

2. Soil pollution

When a multinational decides to launch production, it builds one or more pits (or "pools") in the wild, where it discharges mounds of toxic products for humans and nature. Once production is complete, the company leaves the waste behind and digs elsewhere. The materials left behind penetrate the soil and pollute it before reaching the water table.

3. Water pollution

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

-illegal degassing, i.e. the action of cleaning the bunkers o f 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 clean-up costs (€0.15 per m3). Continuous discharges are more devastating than occasional oil spills.

Human impact.

1.Impoverishment of agriculture

It has been noted in several countries that oil production has a negative impact on farmland due to the large quantities of toxic waste discharged or leaking from wells, as well as on certain fruit trees due to air pollution.

2.Increased illness for local populations and overly long exposure periods

Whether it's water pollution from swimming pool waste, or air pollution from the burning of large quantities of oil, which in turn has repercussions on ecosystems, flora and fauna, humans remain a natural species and are therefore affected by all this pollution. The consequences for their health are considerable:

- Cancers (air and water)
- Heart attacks (air and water)
- Nervous system disorders (benzene)
- Impaired vision
- Anemia (benzene)
- Leukemia (benzene)
- Fetal problems (benzene)
- Nausea (cadmium)
- Chronic kidney and lung disorders (cadmium)
- Hypertension (cadmium)
- Diseases caused by arsenic, lead and mercury

- Respiratory problems, asthma (air)

3.Disasters

Risks associated with the oil industry include :

- Gas explosion
- Hydrocarbon fire
- Tanker truck accident
- Oil spills
- Illegal degassing
- Leaking or ruptured pipeline