Chapter N °2:
Petroleum Refining Schemes

Chapter 2: Petroleum Refining Schemes

- Nomenclature and characteristics of petroleum products

- Main process schemes for production

- Environmental constraints and evolution of refining

1. Introduction

Petroleum is a fossil fuel composed of a mixture of hydrogen and primarily carbon. The composition varies from one field to another, but it generally contains about **80%** carbon, **11%** hydrogen, and **1%** to **2%** sulfur, oxygen, and nitrogen.

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

- Density, viscosity, etc., measurements carried out on the various fractions obtained by distillation. These methods provide useful insights for refining and upgrading petroleum.
- Liquid chromatography, gas chromatography, mass spectrometry, etc., on various dissolved fractions. These allow the identification of different families of compounds present.

2. Refining Principle

Petroleum may be considered "**black gold**" but in its **crude form**, it is not very useful. It must first undergo numerous transformations to become usable. This is the role of the **refinery**. Oil refining is an **industrial process** that transforms crude oil into various finished products such as gasoline, heavy fuel oil, or naphtha.

Crude oil is a **heterogeneous mixture** of various hydrocarbons (molecules composed of carbon and hydrogen atoms) and is unusable in its raw state. There are several types of crude oil, distinguished in part by their viscosity and sulfur content. Its components must be separated to obtain directly exploitable final products.

A refinery must be designed to process a wide range of crude oils. Some refineries are adapted to a specific crude oil when the estimated resource of that particular crude is sufficiently significant.

3. Petroleum Derivatives

- Under the effect of heat, petroleum components separate. The heaviest components remain at the bottom, while the lighter ones rise (gases, gasoline).
- The main products used as fuels and combustibles include liquefied petroleum gases, gasoline, kerosene, jet fuels, diesel fuels, fuel oil, and refining residues.

3. 1. Natural Gas

- Natural gas is a **fossil fuel** composed of a mixture of **hydrocarbons**, naturally present in **porous rocks** in gaseous form or **dissolved in petroleum** within reservoir rocks at the reservoir pressure.
- There are several types of natural gas, distinguished by their origin, composition, and the type of reservoirs in which they are found.
- Gas is primarily composed of methane (over 90%) and also contains other hydrocarbons such as ethane, propane, and butane in very low concentrations (around 1 to 4%).
- It also contains sulfur compounds, nitrogen, carbon dioxide, other mineral compounds, and small quantities of helium (He), mercury (Hg), and argon (Ar).
- Natural gas is the second most important energy source for electricity production, after coal.

3. 2. Liquefied Gases

- These consist of a mixture of **paraffinic** and **olefinic** hydrocarbons such as methane, ethane, propane, and butane. They are used as fuel and are stored and handled in liquid form under pressure.
- Their **boiling point** ranges between approximately **–74°C** and **+38°C**. They are colorless, and their vapors are denser than air and extremely flammable.
- Their main qualities, in terms of safety and occupational health, are their low vapor pressure and low contaminant content.
- They have a wide range of uses, including domestic heating, energy for household use (stoves, ovens, bakeries, catering), and as a clean fuel for certain vehicles.

3. 3. Gasoline

A. Automotive Gasoline

- **Automotive gasoline** is a mixture of **hydrocarbon** fractions, mainly composed of **light hydrocarbons** with a relatively **low boiling point**. It is the most important refining product.
- Gasoline has a **boiling point** between **ambient temperature** and approximately **204°C**, with a flash point below **–40°C**.
- It’s most important characteristics are the octane rating, volatility, and vapor pressure.

- For optimal use, it must not contain heavy hydrocarbons that could harm engine performance. It should also be free from sulfur compounds or acidic products that could corrode engines and fuel tanks.
- Additives are used to improve gasoline properties and protect the engine against oxidation and rust formation.

B. Aviation Gasoline

- Aviation gasoline is a high-octane fuel specially formulated to ensure good performance at high altitudes.

3. 4. Special Gasolines

- Due to their specific characteristics, they are used as solvents and raw materials in the production of adhesives, rubber, inks, tires, pharmaceuticals, etc.

3. 5. White Spirit

- A category of hydrocarbons used as a solvent in the preparation of paints, varnishes, and cleaning products.

3. 6. Kerosene

- A petroleum fraction historically used in oil lamps until the advent of electric bulbs. Today, it is used in the preparation of household and agricultural insecticides.

3. 7. Kerosene Fuels

- Kerosene fuels are mixtures of **paraffins** 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.
- Kerosene fuels are used for lighting and heating, as solvents, and as components of diesel fuels.

3. 8. Diesel Fuel

- Used as fuel primarily for diesel engines.

3. 9. Domestic Fuel

- A type of diesel fuel intended for domestic heating, agricultural tractors, and public works machinery.

3. 10. Marine Diesel Fuel

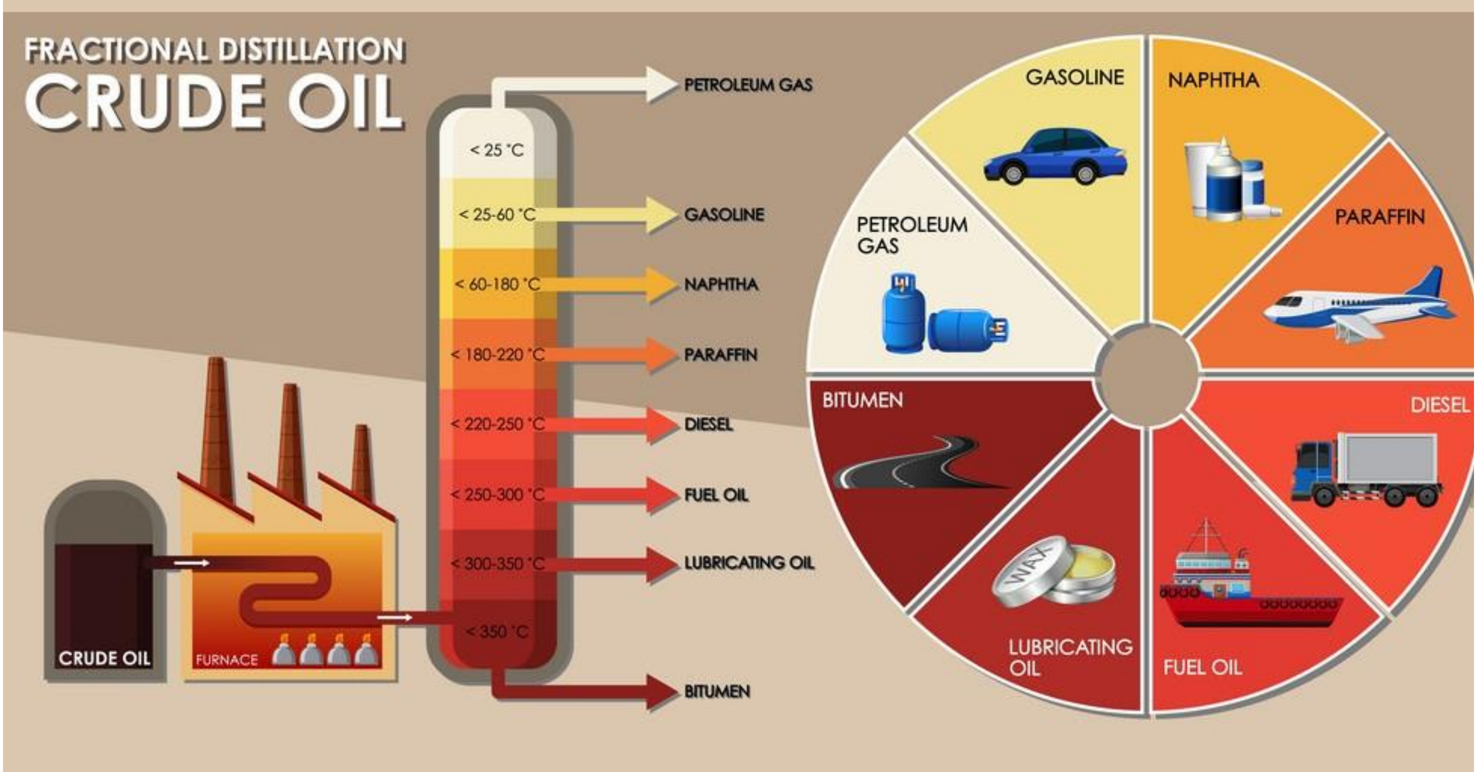
- A type of diesel fuel intended for fishing boats equipped with diesel engines.

3. 11. Oils and Greases

- Mainly composed of heavy hydrocarbons, they have high viscosity and are used for lubricating and greasing engines.

Different types include:

- **Motor Oils**: Designed for vehicle engines.
- **Industrial Oils**: Intended for engines other than vehicle engines, such as steam turbines, gas turbines, compressors, etc.
- **Lubricating Greases**: Prepared from soap gel dispersions in oil.
- **Paraffin's and Waxes**: Denser and more compact than greases, obtained as a residue during crude oil distillation. They are used in candle manufacturing, polishes, skincare creams, etc.



4. Refinery Structure

4.1. Simple Refinery

The first refineries were made up of only **one unit**: **atmospheric distillation**. This practice is no longer economically viable, and the simplest refineries now also include **ancillary units** for **desulfurization** and reforming, as well as **vacuum distillation**. A refinery consisting only of these units is referred to as a "**hydroskimming refinery**". These are virtually **nonexistent today**.

Modern refineries also include, in **addition to the aforementioned units**, conversion units (**cracking**) that allow for the transformation of **heavier petroleum fractions**, whose price is increasingly less attractive and which can only be used in specific industrial installations, into lighter fractions that can constitute ordinary fuels (diesel, kerosene, or gasoline).

Simple Refinery Scheme

4.2. Complex Refinery

Complex refineries can therefore have, in addition to the units mentioned above, other units, and the most common of which include:

- Catalytic cracking (fluid catalytic cracking, FCC);
- Viscosity reduction (vis breaking);
- Isomerization;
- Polymerization;
- Steam cracking;

- Bitumen blowing;
- Coking.

In this case, we refer to it as **deep conversion**. These techniques are increasingly used due to market evolution: available crude oils tend to become heavier, while demand is shifting towards the "top of the barrel." The market for heavy fuel oils is shrinking (partly because they are often replaced by natural gas), while consumption of automotive fuels continues to grow.

Complex Refinery scheme

5. Separation Processes: Analysis of Crude Oil and Petroleum Fractions

5.1. Distillation (T.B.P)

This is a fractional distillation process aimed at determining the content of gasoline, kerosene, diesel, and lubricating fractions (oil, grease) in crude oil. The curve resulting from this distillation, **T = f (% Volume of distillate)**, is called the **True Boiling Point (T.B.P) curve**. This curve is used in calculations for treatment and distillation columns and their planning. The distillation (T.B.P) is used in laboratories with an apparatus (LPRN-1); this column is equivalent to a 10-theoretical-tray packed column and has a reflux ratio of 5. At the beginning of the T.B.P distillation, the dissolved gases that do not condense are collected and analyzed by chromatography.

The atmospheric distillation is carried out up to **400°C**, recording the initial and final temperatures for each fraction. Beyond **400°C**, a vacuum distillation of the atmospheric residue is performed at lower pressures (**5-100 mmHg**). If the vacuum residue is still significant **(≥30%)**, another vacuum distillation is performed between 3 to 5 mmHg in another apparatus equivalent to 2 theoretical trays, and the volume of the remaining residue is measured.

The representative curve, **Temperature = f (% Total Distillate)**, resulting from this distillation, is called the **Distillation (T.B.P) curve**. This curve allows you to know the percentage of important fractions (gasoline, kerosene, and diesel) in crude oil.

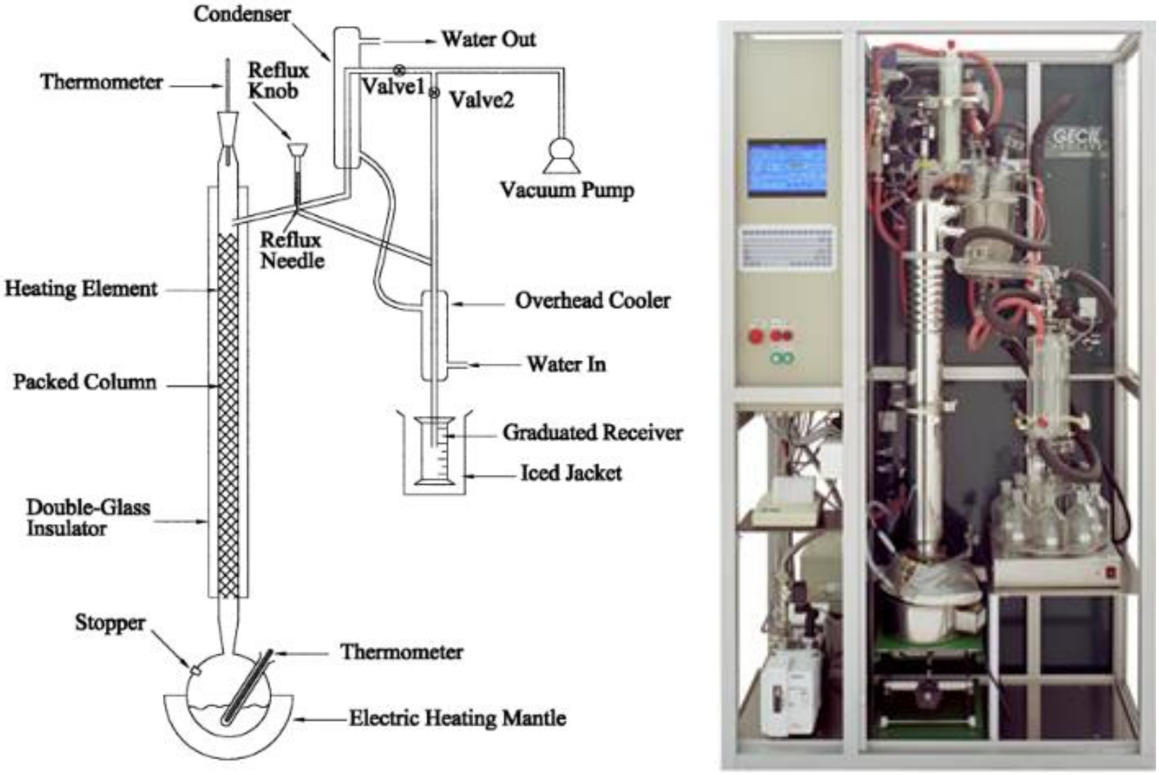


Figure. Schematic of the TBP distillation apparatus.

5.2. Distillation (A.S.T.M)

The **A.S.T.M distillation** (**A**merican **S**ociety of **T**esting **M**aterials) is used for petroleum fractions (**gasoline, kerosene, diesel, fuel**). The apparatus consists of a **100 ml** flask heated by a Bunsen burner or electric resistance. The vapors of the fraction are condensed by a mixture of water and ice and collected in a graduated cylinder.

At the beginning, the **temperature** of the **first drop** of condensate is recorded, marking the initial point of distillation. Then, temperatures are noted when **5%, 10%, 20%,** …, **90%**, and **95%** of the product are distilled. Finally, the **maximum temperature recorded** before it decreases is called the **final point of distillation**. The volume of the remaining residue in the flask is measured.

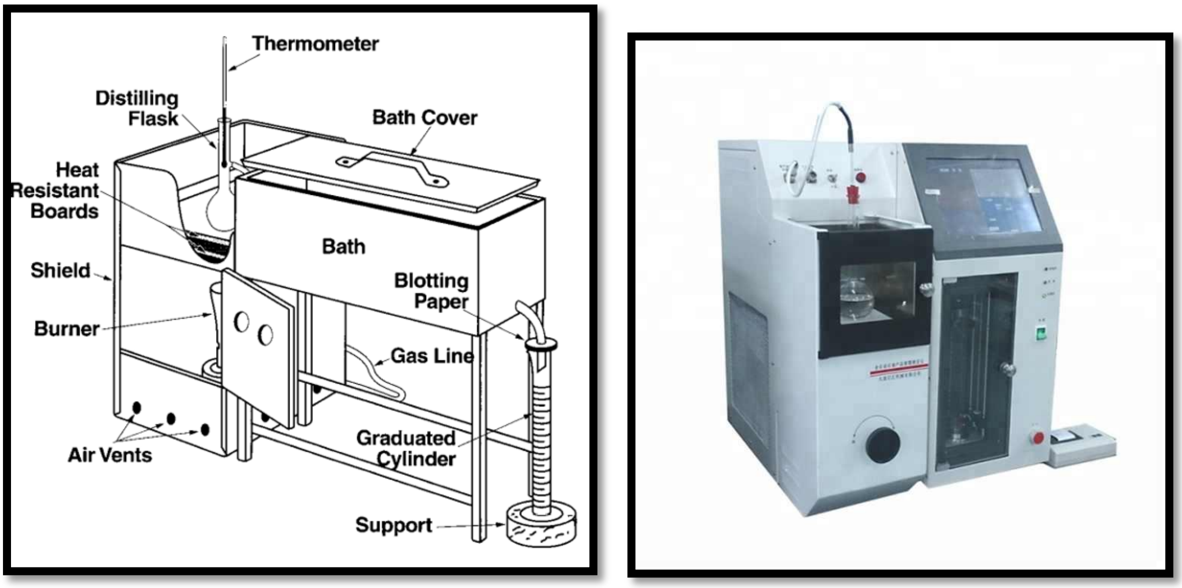
The material balance will be:

% Distillate + % Residue + % Loss = 100%, or simply:

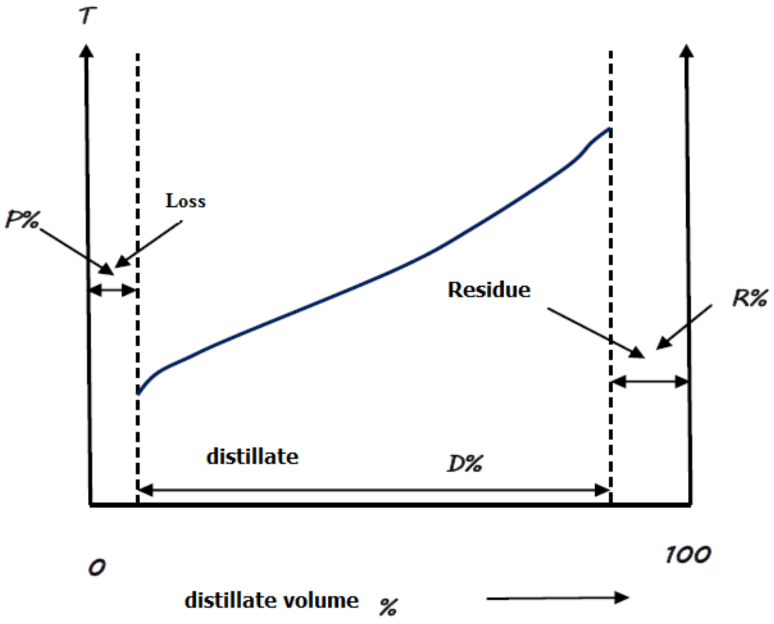
D % + R % + P % = 100%

By knowing the distillate and residue percentages, we can calculate the percentage of losses, which correspond to the very light fractions that are not condensed. This percentage (**P %**) is placed at the beginning of the **axis** of distilled percentages, making all the distillate percentages higher by (**P %**).

The curve **Temperature = f (% Total Distillate)** resulting from this distillation is called the **Distillation (A.S.T.M) curve**. The difference between the final and initial temperatures helps compare the qualities of the distilled products.



Distillation (A.S.T.M)



Curve Distillation (A.S.T.M)

5.3. Calorific Power

The calorific power is the **amount of heat** in **joules** or **calories** released during the complete combustion of **one cubic meter**, **one kilogram**, or **one mole** of fuel (oil, gasoline, kerosene, diesel, gas…) usually at **15 °C** and under atmospheric pressure. The unit of calorific power is therefore: **(J/m^3), (J/kg), or (J/mol)**.

In other words, the calorific power represents the **enthalpy of combustion** per unit **volume**, **mass**, or **mole** of fuel at a temperature of **15°C**.

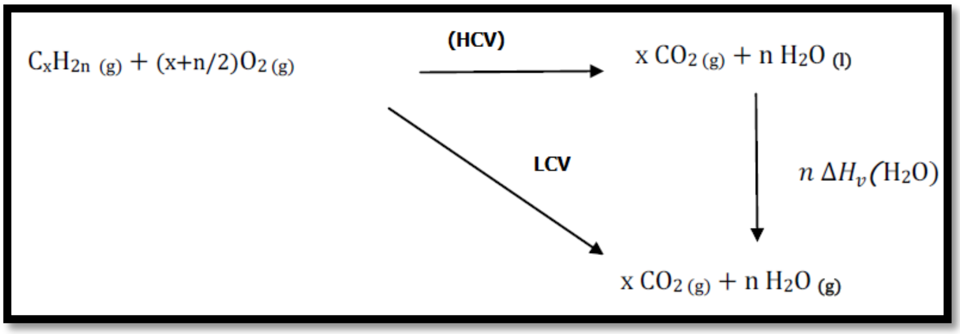
5.3.1. Higher Calorific Power (H.C.V)

It is the **calorific power** of the **fuel** measured or calculated when the **water** released from combustion in **liquid form**.

5.3.2. Lower Calorific Power (L.C.V)

It is the **calorific power** of the **fuel** measured or calculated when the **water** released from combustion in **vapor form**.

To find the **relation** between the (**H.C.V**) and (**L.C.V**), we analyze the example of the combustion reaction of a **gaseous hydrocarbon**, assuming that combustion releases **(n) moles** of **water**:



Since both the (**H.C.V**) and (**L.C.V**) are **heats released**, it is obvious that:

(H.C.V) < 0 and **(L.C.V) < 0**.

On the other hand, we have: $\Delta H_x > 0$, then according to the reaction scheme above, we get:

$$(LCV) = (HCV) + \frac{n(\Delta H_v)_{(H_2O)}}{M}$$

n: Number of moles of H_2O produced per mole of fuel.
M: Molar mass of the fuel (g/mol)
$\Delta H_{(v)(H_2O)}$: Enthalpy of condensation of water

We can rewrite the previous equation using the enthalpy of condensation of water instead of its vaporization enthalpy, thus:
$\Delta H_{vap} = -\Delta H_{cond}$, leading to the following.

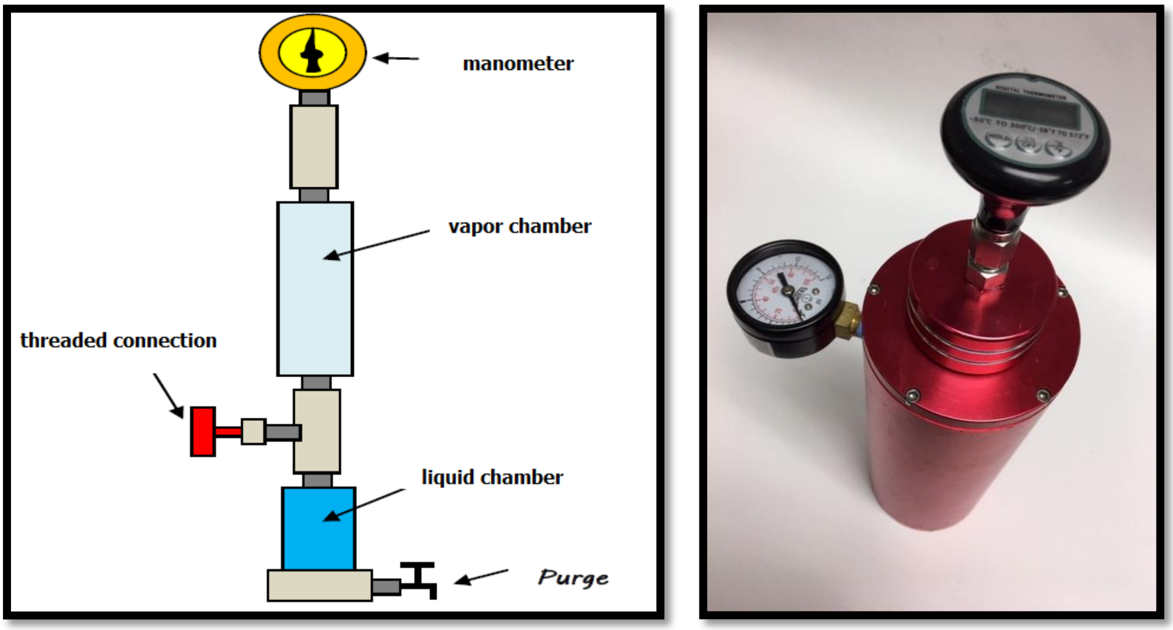
$$(HCV) = (LCV) + \frac{n(\Delta H_{cond})_{(H_2O)}}{M}$$

5.4. Reid Vapor Pressure (R.V.P)

The vapor pressure of a **pure hydrocarbon** measures the **tendency of molecules** to escape **from the liquid phase to form a vapor phase** in equilibrium with the liquid phase; the **vapor pressure** is a function of **temperature**.

The **Reid Vapor Pressure (R.V.P)** measures the content of **light fractions** in gasoline and characterizes its **volatility** and losses during transport and storage. It is **measured in bars** or **kg/cm². (1 bar = 0.981 kg/cm²).**

The (**R.V.P**) is the **pressure developed by gasoline** placed at **100°F** (**37.8°C**) in a closed apparatus called a **Reid Bomb**. The tank is filled with gasoline, and it is brought into contact with an **air chamber**. The mixture is agitated, and the Reid Bomb is placed in a water bath at 100°F. Once equilibrium is reached, the pressure indicated by the manometer is read; this value corresponds to the (R.V.P) of the trapped gasoline.



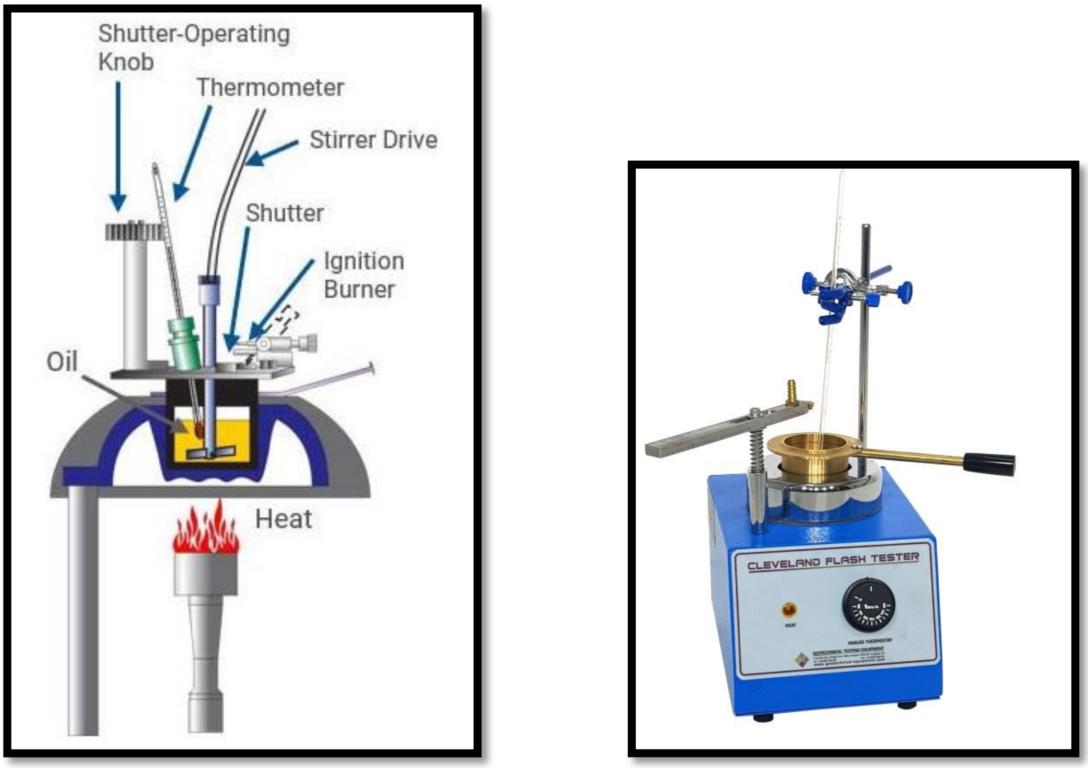
Reid bomb for measuring the (R.V.P) of gasolines

5.5. Flash Point

The flash point is an essential **characteristic** for **diesel** and **kerosene**. It is the **temperature** at which the **vapors** of the **petroleum product form a mixture** with **air** on the **surface** of the **liquid** that ignites in the presence of a flame **for a short time** and then extinguishes without the liquid catching fire.

The flash point characterizes the **content of light fractions** and the **fire hazard rate**.

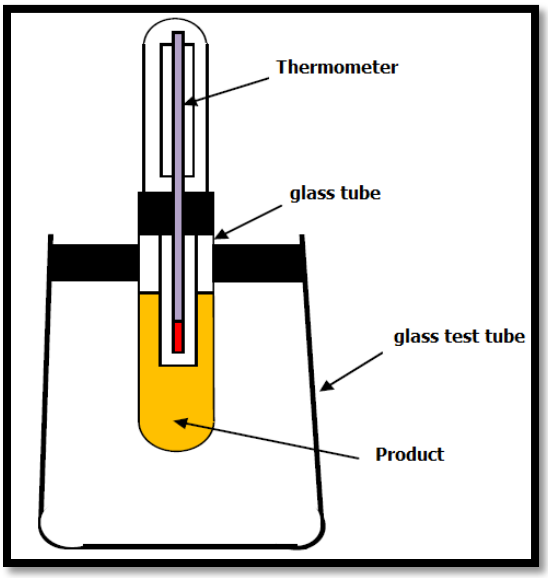
To increase the flash point of petroleum products, **light fractions are vaporized** (**extracted**) by **injecting water vapor** into the **column** in countercurrent (stripping with steam).



Flash point determination apparatus

5.6. Pour Point (Freezing Point)

The pour point of petroleum products (diesel, fuel oil, oil) is the lowest temperature (during cooling) at which the liquid product in the test tube no longer flows when it is inclined. This is an important criterion, especially when these products are used at low temperatures. The pour point increases with the paraffin content in the petroleum product.



5.7. Molecular Mass

Let (**n**) be the total number of chemical constituents of crude oil or its fraction. Let $\boldsymbol{x_i}$ and $\boldsymbol{M_i}$ represent the mole fraction and molecular mass of each constituent. The average molecular mass of crude oil or its fraction is given by the simple relation:

$$M_{\text{Mixture}} = \sum_{i=1}^{n} x_i M_i$$

And since the molar fraction (xi) is given by:

$$x_i = \frac{\frac{m_i}{M_i}}{\sum_{i=1}^{n} n_i}$$

$$M_{\text{Mixture}} = \frac{\sum_{i=1}^{n} \frac{m_i}{M_i} M_i}{\sum_{i=1}^{n} n_i} = \frac{\sum_{i=1}^{n} m_i}{\sum_{i=1}^{n} n_i}$$

5.8. Density of Crude Oil

The density is the **ratio** of the **crude oil's density** to that of distilled water at given temperatures.

$$\boldsymbol{D_4^{15} = \frac{\rho(crude\ oil\ at\ 15\ °C)}{\rho(Water\ at\ 4\ °C)}}$$

The **density** is expressed by the Anglo-Saxon term **Specific Gravity (SpGr 60/60)** measured by the **ratio** of the crude's density to that of water at the same temperature (**60°F**).

$$\boldsymbol{Sp.Gr_{(60°/60°F)} = \frac{\rho(crude\ oil\ at\ 60\ °F)}{\rho(Water\ at\ 60\ °F)}}$$

Using the density measurements of water at different temperatures, we find the following relationships.

$$\boldsymbol{\rho_{(water\ at\ 20\ °C)} = 0.9982\ \rho_{(water\ at\ 4\ °c)}}$$

So we can conclude from the previous equations

$$\boldsymbol{D_4^{15} = 0.9982\ Sp.Gr_{(60°/60°F)}}$$

Measurement of Density by Pycnometers

To measure the density of crude oil and/or water in the laboratory, pycnometers, a water bath, and an analytical balance are used. First, weigh the empty pycnometer (with lid) thoroughly cleaned and dried, recording the mass as (m_0). Then fill it with distilled water and place it in a water bath at 20°C (as an example). After drying it externally, weigh it again (m_1). Next, repeat the same procedure with crude oil, recording the mass of the pycnometer filled with crude oil as (m_2).

The density of crude oil at 20°C relative to water at 20°C will be:

$$D_{20}^{20} = \frac{\rho_{(\text{crude oil at } 20°\text{C})}}{\rho_{(\text{water at } 20°\text{C})}} = \frac{m_2 - m_0}{m_1 - m_0}$$

Density in °(A.P.I)

Density is also expressed in degrees (**A.P.I**) using the relationship illustrated by the **American Petroleum Institute.**

$$°(A.P.I) = \frac{141.5}{\boldsymbol{Sp.Gr}_{(\mathbf{60°/60°F})}} - 131.5$$

With (**A.P.I**) : American Petroleum institute.

5.9. Characterization Factor (K.U.O.P)

Researchers Nelson, Watson, and Murphy from **U.O.P (United Oil Products)** proposed a simple formula to characterize different hydrocarbon families by calculating a **characterization factor (K.U.O.P)**. This factor helps classify crude oils based on the **P.O.N.A** criterion as mentioned in section (**5.8**).

$$K_{U.O.P} = \frac{\sqrt[3]{T\ °(R)}}{\boldsymbol{Sp.Gr}_{(\mathbf{60°/60°F})}}$$

T°(R): is the boiling point of the crude oil in **Rankine degrees**.

- **$K_{U.O.P}$ = 13**: The crude contains normal and **iso-paraffinic hydrocarbons**.
- **$K_{U.O.P}$ = 12**: The crude contains mixed hydrocarbons with equivalent **cyclic** and **chain structures.**

- **$K_{U.O.P}$ = 11**: The crude contains pure **naphthenic** or **lightly substituted aromatic hydrocarbons.**
- **$K_{U.O.P}$ = 10**: The crude contains pure **aromatic hydrocarbons**.

6. Evolution of Refining: Environmental and Economic Constraints

6.1. Environmental Challenges

Refineries emit pollutants and greenhouse gases. In response to stricter regulations, refiners make investments to reduce these emissions (e.g., the Esso refinery in Fos-sur-Mer, where nitrogen oxide emissions were significantly reduced). Additionally, refineries use large quantities of substances that are potentially harmful to humans and the environment. In France, they are classified according to the European Seveso directive, based on the quantities and types of dangerous products they use. This classification, calculated by a weighted sum of the quantities of products present at a site, determines the authorized threshold. Visual and noise pollution generated by the operation of a refinery is also taken into account.

6.2. Financial and Macroeconomic Challenges

In developed countries such as France, the refining sector occasionally faces economic difficulties, exacerbated by the mismatch between production capacities and consumption needs (high demand for diesel in Europe). New refineries are mostly being built in developing countries in Asia and Africa. In these regions, lower local costs compared to existing refineries, combined with significant logistical gains, help meet a rapidly growing domestic demand.

6.3. Major Players

Refining and petrochemical processes are primarily licensed by **Axens** (a subsidiary of **IFP Énergies Nouvelles**) and the American group **Honeywell UOP**.

6.4. Future

- Refining Processes Expected to Evolve

The oil refining sector faces several constraints that compel operators to adjust their production strategies. The quality requirements for finished products are becoming increasingly stringent.

The types of crude oil being processed are expanding, including heavier oils and unconventional oils (e.g., oil sands, shale oil).

Economic pressures are pushing for maximum value extraction from each barrel at a lower energy cost.

- Strict Regulations Forcing the Industry to Adapt Regularly

At the heart of environmental concerns, the refining industry is regularly required to adapt to standards set by institutions such as the **European Commission** or the **Environmental Protection Agency (EPA)**.