Introduction to Petroleum Refining and Petrochemical Processes

Chapter 1: Formation and Exploitation of Petroleum and Natural Gas

- Definition and origin of petroleum
- Reservoirs and characteristics of crude oils
- Extraction techniques

Chapter 2: Petroleum Refining Schemes

- Nomenclature and characteristics of petroleum products
- Main process schemes for production
- Environmental constraints and evolution of refining

Chapter 3: Petrochemical Manufacturing Schemes

- Diversity of petrochemical industry products
- Main manufacturing pathways in petrochemistry
- Examples of processes (PVC, Ammonia)

Chapter 1: Formation and Exploitation of Petroleum and Natural Gas

1. Definition

The term petroleum comes from the Latin **Pétra-Oléum**, which literally means "**rock oil**".
It is flammable oil that varies in color from **yellow to black**. It consists of a wide variety of hydrocarbons found in the Earth's sedimentary layers.

- Petroleum refers to a liquid composed mainly of:

✓ **Hydrocarbon molecules** (formed only of carbon and hydrogen).

✓ This petroleum also contains, in **variable proportions** (on average **15%**), **heavier** and more **complex molecules** (including oxygen, nitrogen, and sulfur) called resins or asphaltenes.

This petroleum was formed within **sedimentary** basins through the **transformation of organic matter**. One of the essential conditions for petroleum formation is the **accumulation of a significant amount of organic matter**, which must be **rapidly buried** to **limit bacterial degradation in the presence of oxygen**.

Some of its components can be:

✓ **Gaseous,**

✓ **Liquid,**

✓ **And sometimes solid** (Depending on **temperature and pressure**).

This explains the **variable consistency** of petroleum, which can be more or less viscous or liquid.

2. Origin of Petroleum

Many scientists have studied the **origin of petroleum**. Two main theories have emerged: **the mineral origin theory** and **the organic origin theory**. Today, the latter is considered the most plausible.

Petroleum and natural gas are believed to have formed from **organic matter**, whether **animal or plant-based**.

The transformation of organic matter into petroleum takes **tens of millions of years**, passing through an **intermediate substance called kerogen**.

Organic matter accumulated at the **bottom of seas, oceans, lakes, and deltas**, mixing with **mineral materials** (such as **clay particles or fine sands**), forming **sedimentary mud** and creating what is known as **"sapropel"**.

Over **geological time**, the **pressure** from accumulating sediments, combined with **temperature** and the **action of bacteria** in a **reducing environment** (i.e., in the absence of oxygen), gradually transformed this **sapropel into petroleum**.

3. Composition

Since petroleum is an **organic material**, its mass percentage of carbon and hydrogen is dominant. However, some **metallic or non-metallic** elements exist **in minor percentages**, such as **nitrogen, oxygen, sulfur, chlorine, calcium, sodium, potassium, silicon, phosphorus, nickel, iron**, etc.

The elemental composition of crude oils falls within the following ranges:

- **Carbon: 84-87%**
- **Hydrogen: 11-14%**
- **Nitrogen, sulfur, oxygen: 0-7%**

4. Formation of Oil Deposits

The part of the subsurface where oil is formed is called the **source rock**. Once formed, oil is subjected to several forces: the weight of sediments, geological forces, differences in density with the accompanying saltwater, etc. To reduce the effect of these forces, oil tends to move to other locations by following a path through the most permeable rocks or existing fractures within these rocks.

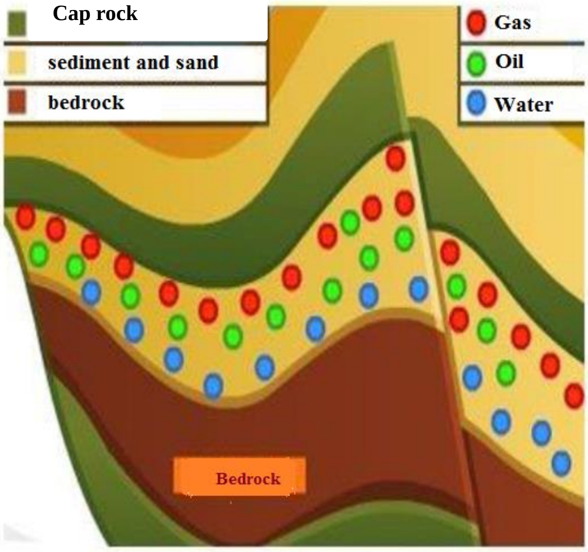
This migration occurs from the source rock toward the Earth's surface, passing through sediments due to the fact that oil has a lower density than water. The place where oil migration stops is called a **trap**.

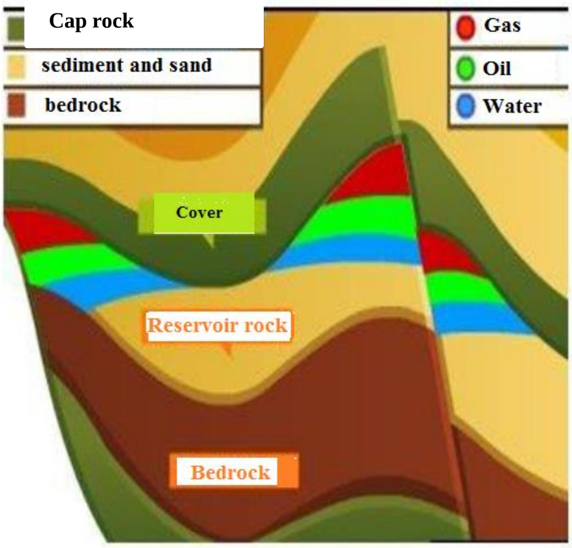
A trap consists of:

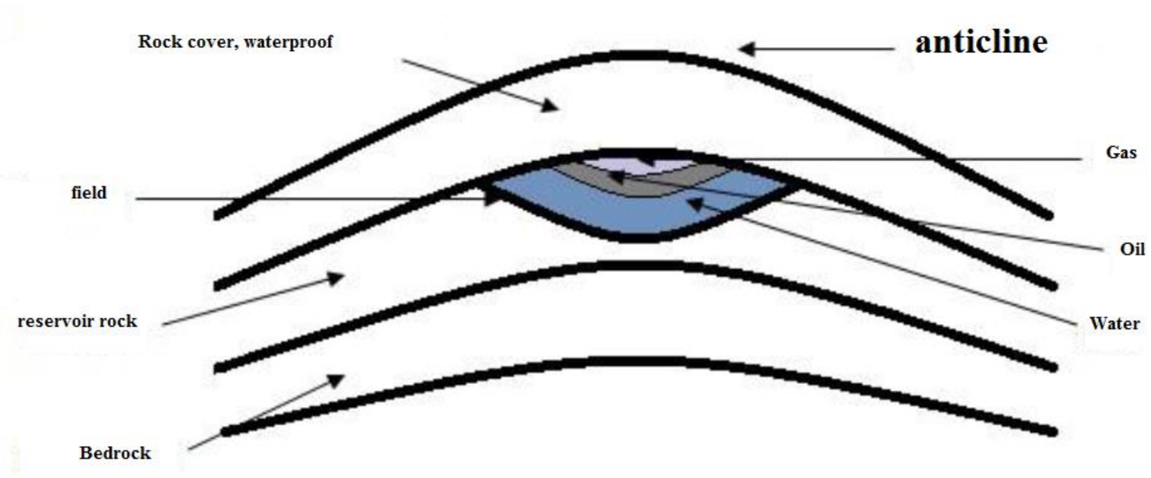
- A **porous rock** in which oil accumulates, known as the **"reservoir rock"**.
- Above this **reservoir rock**, there is a sufficiently **impermeable layer** that prevents the oil from migrating to the surface. This is called the **"cap rock"** or **"seal rock"**, such as a layer of salt, for example.

The combination of **source rocks** and **reservoir rocks** forms what is known as an **oil deposit**.

Within this porous reservoir, **natural gas accumulates above crude oil**, which, in turn, is found above water due to the respective densities of these substances (natural gas is lighter than oil, which is itself lighter than water).







Simplified diagram of an oil field

5. Classification of oil

At the discovery of an oil reservoir, the oil undergoes a series of analyses, allowing its classification. The classification of oil is of utmost importance because it helps us understand the appropriate treatment methods, the types of products to be obtained, and their quality. There are three main types of classification:

5. 1. Industrial Classification

According to this classification, we can distinguish:

- **Light Crude Oil**: If $\rho_{15}^{15} < 0.828$
- **Medium Crude Oil**: If $0.828 < \rho_{15}^{15} < 0.8840$.
- **Heavy Crude Oil**: If $\rho_{15}^{15} > 0.884$

General Rule:

- A **light crude oil** contains a relatively large quantity of **light fractions** (**gasoline, kerosene, light gas-oil**) and **paraffin**. It has **low sulfur content** and few **gums**. The **octane rating** of the gasoline is **low**, but the **lubricating oils** obtained are of **high quality** (high viscosity index).
- **Heavy oils** are **aromatic oils** that contain **little gasoline** but have a **high octane rating**, as well as **high gum content**. This type of oil can produce a high yield of coke

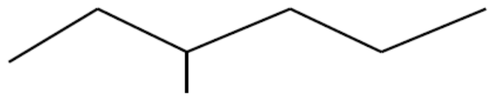
and good-quality bitumen. This classification, which only takes into account the density at 15°C **(ρ_{15}),** remains incomplete.

5.2. Chemical Classification

5.2.1. Classification of Crude Oils (P.O.N.A)

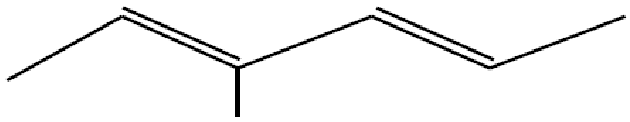
Crude oils are classified into four categories based on the content and nature of the hydrocarbons they contain:

1. **Paraffinic (P)**: These are saturated alkanes with the general formula $\mathbf{C_nH_{2n+2}}$
    - If the number of carbon atoms **($1 \leq n \leq 4$)**, these hydrocarbons are in a gaseous state: CH_4, C_2H_6, C_3H_8, C_4H_{10}.
    - If the number of carbon atoms (**$5 \leq n \leq 16$**), these hydrocarbons are in a liquid state: C_5H_{12} … $C_{16}H_{34}$.
    - If the number of carbon atoms (**n** > **16**), these hydrocarbons are in a solid state.



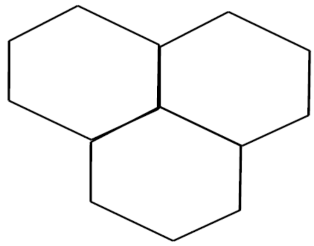
Paraffine

2. **Olefins (O)**: These are unsaturated alkenes (with a double bond) with the general formula $\mathbf{C_nH_{2n}}$. They are found in the products of petroleum distillation or in products obtained through cracking.



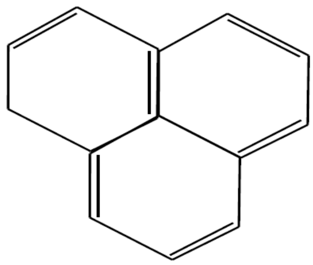
Olefines

3. **Naphthenic (N)**: These are saturated polycyclic or monocyclic compounds found in the light fraction (naphthenes) or in the heavy fraction (branched and polycyclic naphthenes).



Naphtenes

4. **Aromatic (A)**: These are unsaturated cyclic hydrocarbons (monocyclic or polycyclic). They make up 5 to 15% of the gasoline fraction and 15 to 35% of the kerosene fraction. They are also found in oils and asphalts.



Aromates

5.3. Technological Classification

a- This classification is based on the **sulfur content** in the crude oil and its derived fractions:

- **Class 1**: Low sulfur crude oil: **S ≤ 0.5 %**
- **Class 2**: Sulfurous crude oil: **0.5 % < S ≤ 2 %**
- **Class 3**: Highly sulfurous crude oil: **S > 2%.**

Classes	sulfur content %			
	On oil	**Oil** $PI \div 200$	**Jet fuel** $120 \div 240$	**Diesel fuel** $240 \div 360$
Class 1	≤ 0.5	≤ 0.15	≤ 0.1	≤ 0.2
Class 2	$0.5 \div 0.2$	**0.15**	≤ 0.25	≤ 1.0
Class 3	> 2	> 0.15	> 0.25	> 1.0

b. Potential Content of Light Products (PF ≤ 350 °C)

This classification distinguishes three types of crude oil based on the potential content of light products (i.e., products that distill below **350 °C**):

- **Type 1**: Light product content ≥ 45%
- **Type 2**: Light product content between 30% and 45%
- **Type 3**: Light product content ≤ 30%.

c. Base Oil Content and Quality

This classification is based on the **content of base oils** and **residual oils**, as well as their quality, determined by properties like **viscosity index**. The oils are classified into groups and further divided into subgroups based on these characteristics.

- **Groups**: These are based on the proportion of base oils and residual oils in the crude.
- **Subgroups**: These depend on the **viscosity index**, which is a measure of how the oil's viscosity changes with temperature. A higher viscosity index indicates better performance over a wider range of temperatures.

Typically:

- **Group I**: Contains less than 90% base oils, with a viscosity index of 80-90.
- **Group II**: Contains 90% or more base oils, with a viscosity index of 85-100.
- **Group III**: Contains 90% or more base oils, with a viscosity index greater than 100. These oils are often considered "synthetic" or high-performance oils.
- **Group IV**: Fully synthetic oils, with a very high viscosity index.
- **Group V**: Any oil that doesn't fit into the previous categories, including esters, phosphate esters, and others.

The subgroups further refine the quality based on the **viscosity index**, defining whether the oil is suitable for higher or lower temperature applications.

6. Temperature and Temperature Scales

Certain properties characterizing petroleum and/or petroleum fractions are given or expressed as a function of temperature, such as density, **TVR,** $\mathbf{K_{U.O.P}}$, etc. These temperatures are generally expressed in Anglo-Saxon scales, which have mathematical relationships with the international scales, as we will see below.

6.1. Celsius Scale (Centigrade)

The Celsius scale is the most commonly used daily scale, expressed in degrees Celsius (°C). This scale has its origin at 0°C, the freezing point of distilled water, and its upper limit at 100°C, the boiling point of distilled water under atmospheric pressure.

$$\mathbf{T\ (°C) \in [-273.15, +\infty]}$$

6.2. Absolute Scale (Kelvin)

Kelvin chose an absolute scale (positive or zero) based on the Celsius scale to avoid the negative sign in low temperatures, which does not align with the ideal gas law, which is strictly absolute. This scale is most commonly used in thermodynamics.

$$\mathbf{T(K) = t\ (°C) + 273.15}$$

6.3. Fahrenheit Scale

The Fahrenheit scale is used by Anglo-Saxon countries instead of the Celsius scale. It is commonly used in the petroleum industry to express certain quantities that are related to temperature.

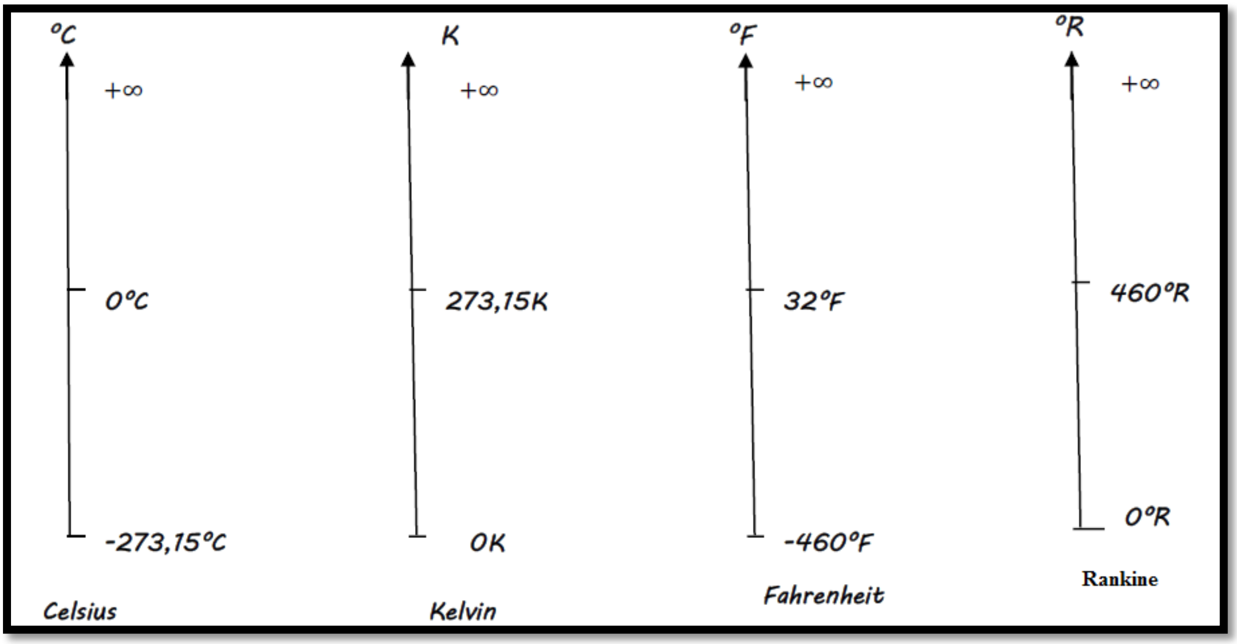
$$\mathbf{T\ (°F) = 1.8 \cdot t\ (°C) + 32}$$

$$\mathbf{T\ (°F) \in [-460, +\infty]}$$

6.4. Rankine Scale

The Rankine scale is an absolute scale used by Anglo-Saxon countries instead of the Kelvin scale. This scale is used to avoid negative signs in low temperatures expressed in Fahrenheit. It is used in certain equations or relationships that require a positive sign, such as the equation for determining the characteristic factor (KU.O.P) of petroleum.

$$\mathbf{T\ (°R) = T\ (°F) + 460}$$



7. Reservoirs and Oil Extraction

7.1. Search for Reservoirs

To find new reservoirs, geologists and geophysicists seek to identify geological structures that might contain oil. Geologists examine soil and rocks samples, while geophysicists explore the Earth's crust at presumed reservoir locations and reconstruct the image of deposits and deformations of geological layers to help geologists locate where oil might have been "trapped."

7.2. Characteristics of Reservoirs

For a reservoir to be exploitable, it must have the following characteristics:

- A **porous and fractured rock**, such as limestone or sandstone, which allows oil to accumulate.
- An **impermeable rock** that prevents the upward migration of oil and gas, which are less dense than water, creating a trap where oil accumulates.

7.3. Oil Prospecting

Oil prospecting involves studying petroleum geology. This prospecting begins with the creation of maps using aerial photographs. Petroleum prospecting is the set of techniques used to predict the location of oil reservoirs; it is divided into two branches:

- **Geological study**, or the actual geological prospecting, which focuses on the formation of oil reservoirs and other characteristics of rocks as reservoirs (or covers).

- **Study of internal structures**, which is geophysical prospecting conducted by teams that survey the terrain to be explored and create structural maps.

7.4. Methods of Oil Prospecting (Oil Exploration)

7.4.1. Geological Prospecting

It is accepted that all rocks capable of forming an oil reservoir are sedimentary. However, there are no direct methods for searching for hydrocarbon deposits in sedimentary terrain. Instead, there are indirect methods that help detect the possible presence of "traps" without being able to determine in advance whether these traps contain oil or not.

7.4.2. Geophysical Prospecting

This method relies on variations in certain geophysical parameters of the terrain caused by the presence of hydrocarbons. However, this type of prospecting only provides qualitative results. Among the methods used for this prospecting, we can mention:

- **The gravimetric method**: Based on measuring variations in the gravitational field caused by the presence of an oil reservoir. In the ground, the presence of hydrocarbon-bearing rocks increases the gravitational field.
- **The magnetic method**: Measures variations in the vertical component of the Earth's magnetic field caused by the presence of an oil deposit.
- **The electrical method**: Based on variations in the resistivity of sedimentary terrains when traversed by electrical currents (in the absence and presence of an oil reservoir).
- **The seismic method**: This is the most commonly used method. A charge of a few kilograms of explosives is detonated in a shallow well. The resulting sound waves propagate through the surrounding sedimentary terrains. A proper study of the different sound waves recorded at various locations can determine the presence or absence of a hydrocarbon reservoir.

7.5. Land Drilling Methods

- For the efficient exploitation of oil reservoirs, all geological and physical methods are used to obtain information about the physical and mechanical properties of rocks. This helps in reconstructing the characteristics of a reservoir and estimating its reserves. Often, the necessary information is only available several years after drilling wells intended for reservoir exploitation. Economic investments are always at risk, which is why mathematical models are now widely used for simulations to predict the profitability of a reservoir. Drilling wells represents **80% of the total investment**.

8. Drilling

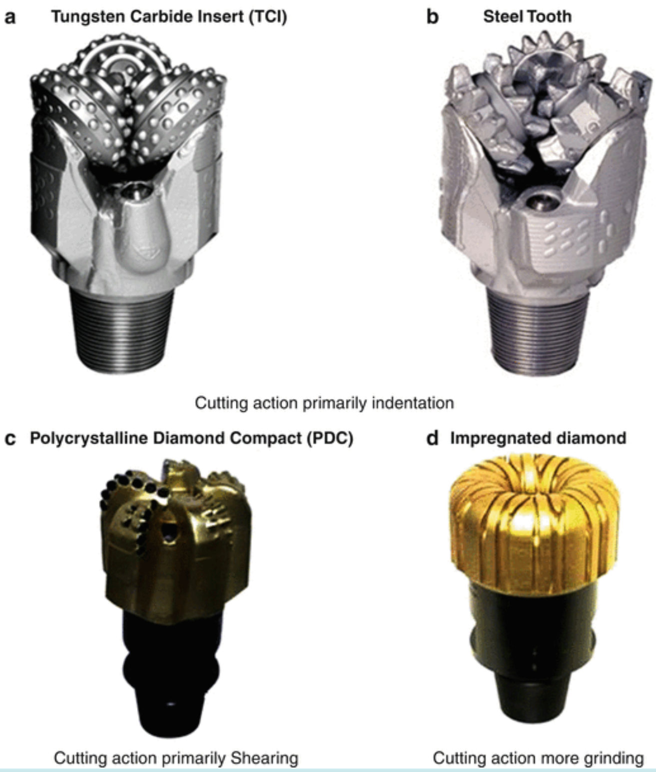
Once structures capable of containing oil have been identified—either through geological or geophysical prospecting—the next step in oil exploitation is **drilling**.

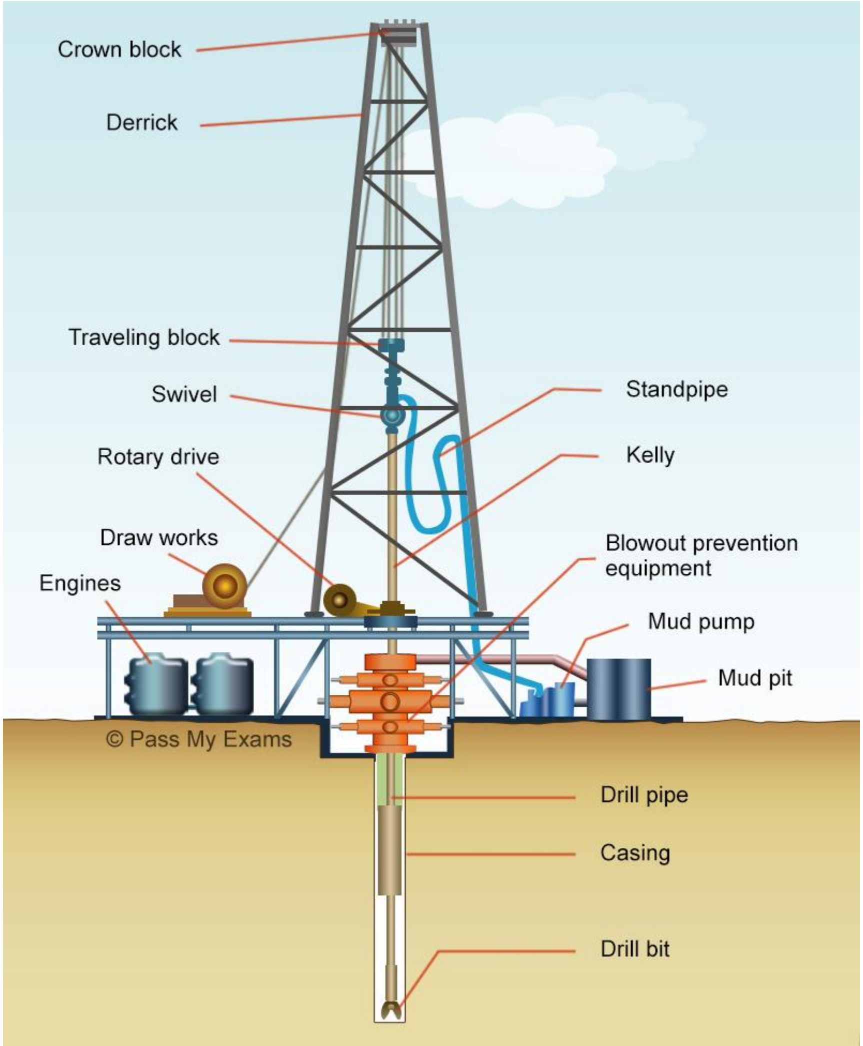
8.1. Definition of Drilling

- Drilling is the process of creating a hole (also called a "well") in the Earth's surface. It involves inserting a series of rods into the subsurface while injecting a special drilling mud. This mud helps bring rock fragments and gas samples to the surface. Multiple drill sites are required to better delineate a potential reservoir.
- Today, the most commonly used method is the **rotary drilling process**, which employs a **drill bit** (or **tricone bit**) that rotates at the bottom of the well to cut through the rock.

8.2. Drilling tools

Depending on its diameter, the tool can weigh from a few kilograms to several hundred kilograms. There are different types of drilling tools:





Scheme: Drilling for Crude Oil

9. Production or Extraction

Production refers to the extraction of hydrocarbons (oil, gas) from the reservoir to the surface. Several types of extraction methods can be distinguished.

9.1. Primary Extraction (Natural Production)

The pressure gradient between the reservoir rock and the top of the well is generally sufficient to transport oil to the surface through the production well. With this primary recovery technique, 15 to 20% of the hydrocarbons in place can be produced.

9.2. Secondary Extraction (Activated or Assisted Production)

The pressure in the reservoir gradually decreases with exploitation. This pressure drop can accelerate if there is no energy source, such as a gas cap. To improve the recovery rate, secondary recovery techniques can be employed. This allows for an additional 15 to 20% of hydrocarbons to be recovered, bringing the total recovery to about 30 to 35% of the hydrocarbons contained in the reservoir.

1. **Gas-lift Extraction** (Extraction par poussée de gaz)
   This method involves injecting gas into the well to lift the oil to the surface. The injected gas reduces the density of the oil, allowing it to flow more easily through the well.
2. **Beam Pump Extraction** (Extraction au moyen de pompe à balancier)
   This technique uses a mechanical beam pump (also known as a "nodding donkey") to lift oil from the reservoir to the surface. The pump operates with a counterbalance system, providing a continuous pumping motion.
3. **Submersible Pump Extraction** (Extraction au moyen de pompe immergée)
   This method involves a pump that is placed directly in the wellbore, submerged in the oil. The pump helps lift the oil to the surface, particularly in cases where there is insufficient natural pressure.
4. **Water Injection Extraction** (Extraction par l’injection d’eau)
   This technique involves injecting water into the reservoir to maintain pressure and push the oil toward the production well. The water helps displace the oil, increasing the overall recovery rate.

These techniques are often used in combination, depending on the reservoir's characteristics and the production stage.

9.3. Tertiary Extraction (Activated Production)

Tertiary extraction is also an assisted recovery method. It is based on more complex technologies, such as injecting CO_2, nitrogen, miscible chemical solvents, or steam into the reservoir. The goal is to lower the oil's surface tension so that it detaches more easily from the rock. The overall recovery rate can reach 40 to 50% of the oil in place.