



كليــــة: التكنولوجيا قســــم: هندسة الطرائق وبتروكيمياء

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Chapter I: Refinery processes

I.1 Crude oil

Definition: Crude oil is a multicomponent mixture consisting of more than 10⁸ compounds.

Petroleum refining refers to the separation as well as reactive processes to yield various valuable **products**. Therefore, a key issue in the petroleum refining is to deal with multicomponent feed streams and multicomponent product **streams**.

Usually, in chemical plants, we encounter streams not possessing more than 10 components, which is not the case in petroleum refining. Therefore, characterization of both crude, intermediate product and final product streams is very important to understand the processing operations effectively.

Element	Composition (wt%)
Carbon	83-87
Hydrogen	10-14
Sulphur	0.05-6
Nitrogen	0.1-0.2
Oxygen	0.05-2
NI	<120 ppm

 Table1 : elemental composition of crude oils

Note : ppm: La partie par million (le **ppm**)/ **parts-per-million** (**ppm**, 10^{-6}). (1 **ppm** = 1 mg/kg).



Figure 1: Simplified flow chart of crude oil refinery processes.

I.2 Overview of Refinery processes

Primary crude oil cuts in a typical refinery include **gases**, light/heavy **naphtha**, **kerosene**, light gas oil, heavy gas oil and **residue**. From these intermediate refinery product streams several final product streams such as **fuel gas**, **liquefied petroleum gas** (**LPG**), **gasoline**, **jet fuel**, **kerosene**, **auto diesel**, **lubricants**, **bunker oil**, **asphalt** *and* **coke** are obtained.

The entire refinery technology involves careful manipulation of various feed properties using both chemical and physical changes. Conceptually, a process refinery can be viewed upon as a

combination of both physical and chemical processes or unit operations and unit processes respectively.

Typically, the dominant physical process in a **refinery** is **the distillation process** that enables the removal of **lighter components** from the **heavier components**.

Other chemical processes such as **alkylation** and **isomerization** are equally important in the **refinery engineering** as these processes enable the reactive transformation of various functional groups to desired functional groups in the product streams.



Figure 2. Pathways to petroleum utilization.

I.3 Feed and Product characterization

The characterization of petroleum process **streams** is approached from both chemistry and **physical properties perspective**. The chemistry perspective indicates **to characterize** the **crude oil** in terms of the functional groups such as **olefins, paraffins, naphthenes, aromatics** and **resins.** The dominance of one or more of the functional groups in various petroleum processing streams is indicative of the desired product quality and characterization. For instance, the lighter **fractions** of the **refinery** consist of only **olefins** and **paraffins.**

On the other hand, products such as petrol should have high **octane number** which is a characteristic feature of **olefinic** and aromatic **functional groups** present in the product stream.

The physical characterization of the crude oil in terms of **viscosity**, **density**, **boiling point curves** is equally important. These properties are also indicative of the quality of the product as well as the feed.

Therefore, in petroleum processing, obtaining any **intermediate** or a product stream with a defined characterization of several properties indicates whether it is diesel or petrol or any other product.

This is the most important characteristic feature of **petroleum processing** sector in contrary to the **chemical process sector.**

I.4 Important characterization properties

Numerous important feed and product characterization properties in refinery engineering include - API gravity - Viscosity - Sulfur content - Octane number.

I.4.1 API gravity

API gravity of petroleum fractions is a measure of density of the stream. Usually measured at 60 $^{\circ}$ F, the API gravity is expressed as

°API = 141.5/specific gravity – 131.5

where specific gravity is measured at 60 °F.

According to the above expression, 10 °API gravity indicates a specific gravity of 1 (equivalent to water specific gravity). In other words, higher values of API gravity indicate lower specific gravity and therefore lighter crude **oils** or refinery products and vice-versa.

As far as **crude oil** is concerned, lighter API gravity value is desired as more amount of **gas fraction, naphtha** and **gas** oils can be produced from the **lighter crude oil than with the heavier crude oil**.

Therefore, crude oil with high values of API gravity are expensive to procure due to their quality.

I.4.2 Sulfur content

Since crude oil is obtained from **petroleum reservoirs**, **sulphur** is present in the crude oil. Usually, crude oil has both organic and inorganic sulphur in which the inorganic sulphur dominates the composition.

Typically, crude oils with high **sulphur** content are termed as **sour crude**. On the other hand, crude oils with low sulphur content are termed as sweet crude.

Typically, crude oil sulphur content consists of 0.5 - 5 wt % of sulphur. Crudes with sulphur content lower than 0.5 wt % are termed as sweet crudes. It is estimated that about 80 % of world crude **oil reserves** are **sour**.

I.4.3 Viscosity

Viscosity is a measure of the **flow properties** of the **refinery stream**. Typically in the refining industry, viscosity is measured in terms of centistokes (termed as **cst**). Usually, the viscosity measurements are carried out at 100 °F and 210 °F.

I.4.4 Octane number

Though irrelevant to the **crude oil stream**, the **octane number** is an important property for many intermediate streams that undergo blending later on to produce **automotive gasoline**, **diesel** etc. Typically, gasoline tends to **knock the engines**. The knocking tendency of the gasoline is defined in terms of the maximum compression **ratio** of the engine at which the knock occurs. Therefore, high quality gasoline will tend to knock at higher compression ratios and vice versa.

Chapter II: Petroleum refining processes

II.1 Petroleum

The petroleum that is pumped out of the ground at locations around the world is a complex mixture of several thousand **organic compounds**, including **straight-chain alkanes**, **cycloalkanes**, **alkenes**, and **aromatic hydrocarbons** with four to several hundred carbon atoms.

The identities and relative abundances of the components vary depending on the source.

So Texas crude oil is somewhat different from Saudi Arabian crude oil.

In fact, the analysis of petroleum from different deposits can produce a "fingerprint" of each, which is useful in tracking down the sources of spilled crude oil.

For example, Texas crude oil is "sweet," meaning that it contains a small **amount** of **sulfurcontaining molecules**, whereas Saudi Arabian crude oil is "sour," meaning that it contains a relatively large amount of sulfur-containing molecules.

Physical Processing Typical Refinery Capacity: ~50,000 bbl/day Distillation Chemical Processing Cracking + Reforming Residual Jet fuel fuel oil (~10%) (~10%) Distillate Gasoline fuel oil (~40%) (~20%)

Figure 3. Schematic representation of a petroleum refinery.

II.2 Crude chemistry

Crude oil

Fundamentally, crude oil consists of 84 - 87 wt % **carbon**, 11 - 14 % **hydrogen**, 0 - 3 wt % **sulphur**, 0 - 2 wt % **oxygen**, 0 - 0.6 wt % nitrogen and metals ranging from 0 - 100 ppm. Understanding thoroughly the fundamentals of **crude chemistry** is very important in various **refining processes**.

The existence of compounds with various **functional groups** and their dominance or reduction in various **refinery** products is what is essentially targeted in various **chemical** and **physical processes** in **the refinery**. Based on chemical analysis and existence of various functional groups, refinery crude can be broadly categorized into about 9 categories summarized as:

II.2.1 Paraffins:

Paraffins refer to alkanes such as methane, ethane, propane, n and iso butane, n and iso pentane. These compounds are primarily obtained as a gas fraction from the crude distillation unit.

Ex: Methane, ethane, Propene.

II.2.2 Olefins:

Alkenes such as ethylene, propylene and butylenes are highly chemically reactive. They are not found in mentionable quantities in crude oil but are encountered in some refinery processes such as alkylation.



Ethylene : C₂H₄

II.2.3 Naphthenes:

Naphthenes or cycloalkanes such as cyclopropane, methyl cyclohexane are also present in the **crude oil.**



 $Cyclopropane \ : C_3H_6$

II.2.4 Aromatics:

Aromatics such as **benzene**, toluene o/m/p-xylene are also available in the crude oil.

Benzene : C_6H_6





petroleum distillation tower

petroleum fractions

Figure 3. The Distillation of Petroleum

(a) This is a diagram of a distillation column used for separating petroleum fractions.

(b) Petroleum fractions condense at different temperatures, depending on the number of

carbon atoms in the molecules, and are drawn off from the column. The most volatile

components (those with the lowest boiling points) condense at the top of the column, and the least volatile (those with the highest boiling points) condense at the bottom.

Table2: Petroleum fractions

Number of carbons	Boiling point range	Uses
1-4	0-30°C	Bottled and natural gas
5-10	30-180°C	Gasoline
10-16	180-260°C	Kerosene for home heaters,
		jet fuel
16-60	260-350°C	Diesel fuel, feedstock for
		cracking
>60	350-575°C	Motor oil, feedstock for
		cracking
>70	>490°C	Candles, fuel oil for ships
		and power stations
>80	>580°C	Roofing tar, road tar

II.3 Gasoline

Petroleum is converted to useful products such as gasoline in three steps: **distillation**, **cracking**, and **reforming**.

Part (a) in Figure 3 "The Distillation of Petroleum" shows a cutaway drawing of a column used in the petroleum industry for separating the components of crude oil.

The petroleum is heated to approximately 400°C (750°F), at which temperature it has become a mixture of liquid and vapor.

This mixture, called the feedstock, is introduced into the refining tower. **The most volatile components (those with the lowest boiling points) condense at the top of the column where it is cooler, while the less volatile components condense nearer the bottom**.

Some materials are so nonvolatile that they collect at the bottom without evaporating at all.

Thus the composition of the liquid condensing at each level is different. These different fractions, each of which usually consists of a mixture of compounds with similar numbers of carbon atoms, are drawn off separately. Part (b) in Figure 3 "The Distillation of Petroleum" shows the typical fractions collected at refineries, the number of carbon atoms they contain, their boiling points, and their ultimate uses. These products range from gases used in natural and bottled gas to liquids used in fuels and lubricants to gummy solids used as tar on roads and roofs.

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