Tikrit University

College of Petroleum Processes Engineering

Department of Petroleum Refining Engineering

Specialized Petroleum Processes

Fourth Class

Lecture 1

By

Jasim I. Humadi

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Stages of Petroleum Industry from Oilfield to Market

Petroleum industry is involved different activities. These activities are divided into:

- Upstream activities
- Midstream activities
- Downstream activities

The upstream phase includes exploration, development, production and abandonment activities, whereas the midstream and downstream phases deal with hydrocarbon transportation and trading to refining and marketing (Figure 1).

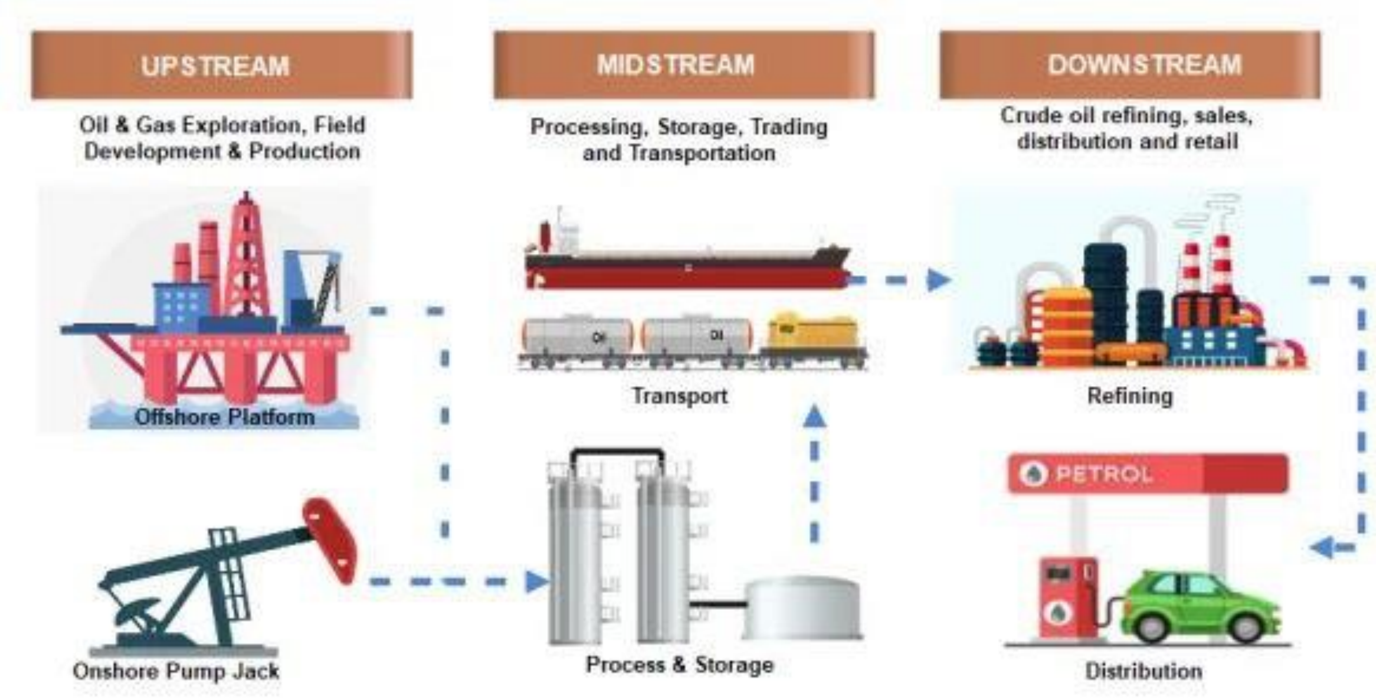


Figure 1: Stages of Petroleum industry

Introduction (Petroleum refining processes)

- Petroleum refining plays an important role in our lives. Most transportation vehicles are powered by refined products such as gasoline, diesel, aviation turbine kerosene (ATK) and fuel oil. Petroleum has remained an important aspect of our lives and will do so for the next four or five decades. The fuels that are derived from petroleum supply more than half of the world total supply of energy. Gasoline, kerosene, and diesel oil provide fuel for automobiles, tractors, trucks, aircraft, and ships. Fuel oil and natural gas are used to heat homes and commercial buildings, as well as to generate electricity. Petroleum products are the basic materials used for the manufacture of synthetic fibers for clothing and in plastics, paints, fertilizers, insecticides, soaps, and synthetic rubber. The uses of petroleum as a source of raw material in manufacturing are central to the functioning of modern industry.
- Petroleum refining is a unique and critical link in the petroleum supply chain, from the wellhead to the pump. The other links add value to petroleum mainly by moving and storing it (e.g., lifting crude oil to the surface; moving crude oil from oil fields to storage facilities and then to refineries; moving refined products from refinery to terminals and end-use locations, etc.).
- Refining adds value by converting crude oil (which in itself has little end-use value) into a range of refined products, including transportation fuels. The primary economic objective in refining is to maximize the value added in converting crude oil into finished products. Figure 2 is explained the basic units in petroleum refineries.
- Petroleum refineries are large, capital-intensive manufacturing facilities with extremely complex processing schemes. They convert crude oils and other input streams into dozens of refined (co-)products, such as Liquefied petroleum gases (LPG), Gasoline, Jet fuel, Kerosene (for lighting and heating), Diesel fuel, Petrochemical feed stocks, Lubricating oils and waxes, Home heating oil, Fuel oil (for power generation, marine fuel, industrial and district heating), and Asphalt (for paving and roofing uses).

- The transportation fuels have the highest value; fuel oils and asphalt the lowest value. Many refined products, such as gasoline, are produced in multiple grades, to meet different specifications and standards (e.g., octane levels, sulfur content).
- More than 660 refineries, in 116 countries, are currently in operation, producing more than 85 million barrels of refined products per day. Each refinery has a unique physical configuration, as well as unique operating characteristics and economics. A refinery's configuration and performance characteristics are determined primarily by the refinery's location, vintage, availability of funds for capital investment, available crude oils, product demand (from local and/or export markets), product quality requirements, environmental regulations and standards, and market specifications and requirements for refined products.
- Most refineries in North America are configured to maximize gasoline production, at the expense of the other refined products. Elsewhere, most of the existing refining capacity and virtually all new capacity is configured to maximize distillate (diesel and jet fuel) production and, in some areas, petrochemical feedstock production, because these products are enjoying the fastest demand growth in most regions of the world.

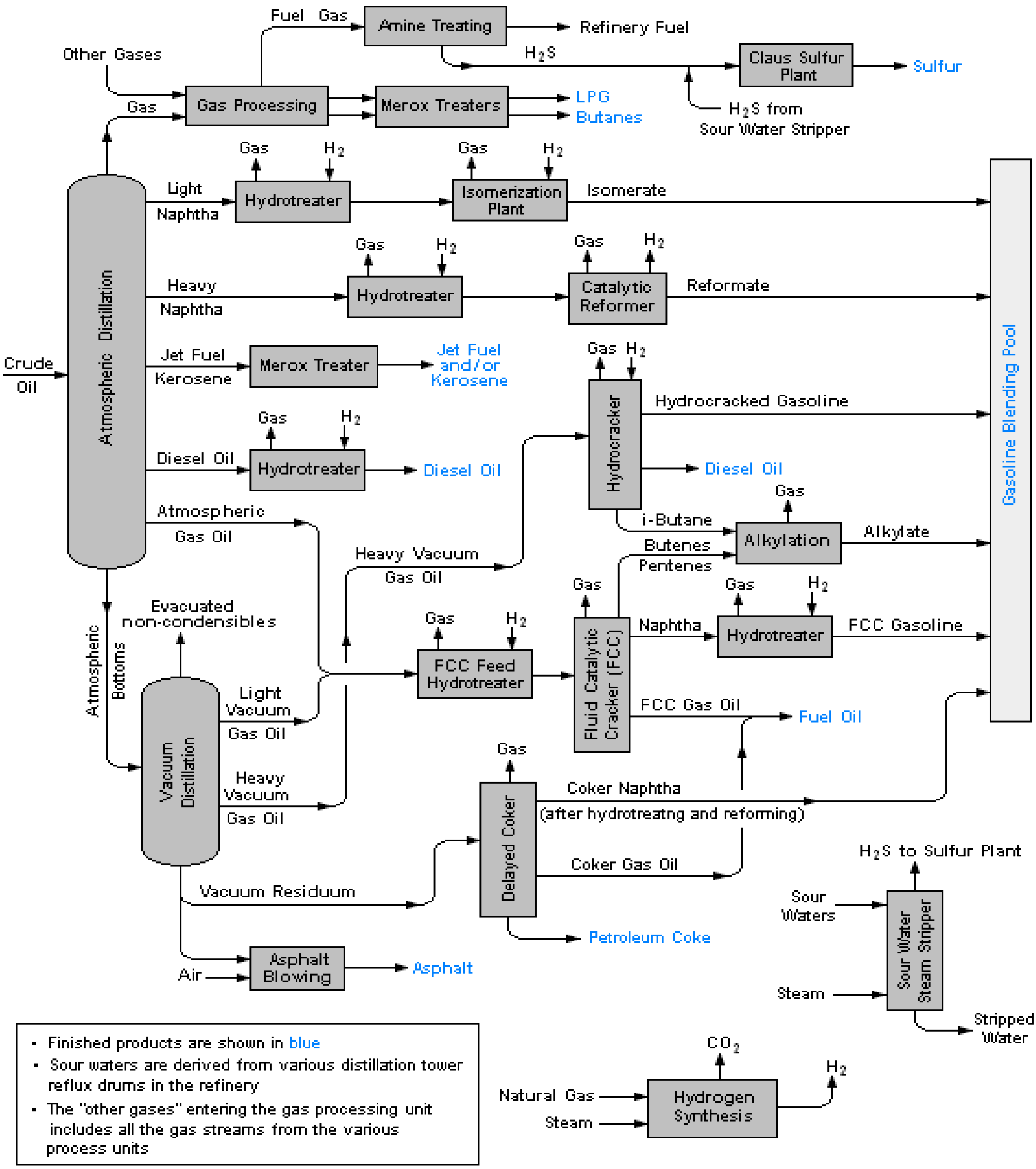


Figure 1: Petroleum Refinery

Composition and Classification of Crude Oils

Crude oil is a complex liquid mixture made up of a vast number of hydrocarbon compounds that consist mainly of carbon and hydrogen in differing proportions. In addition, small amounts of organic compounds containing sulfur, oxygen, nitrogen and metals such as vanadium, nickel, iron and copper are also present (See Table below).

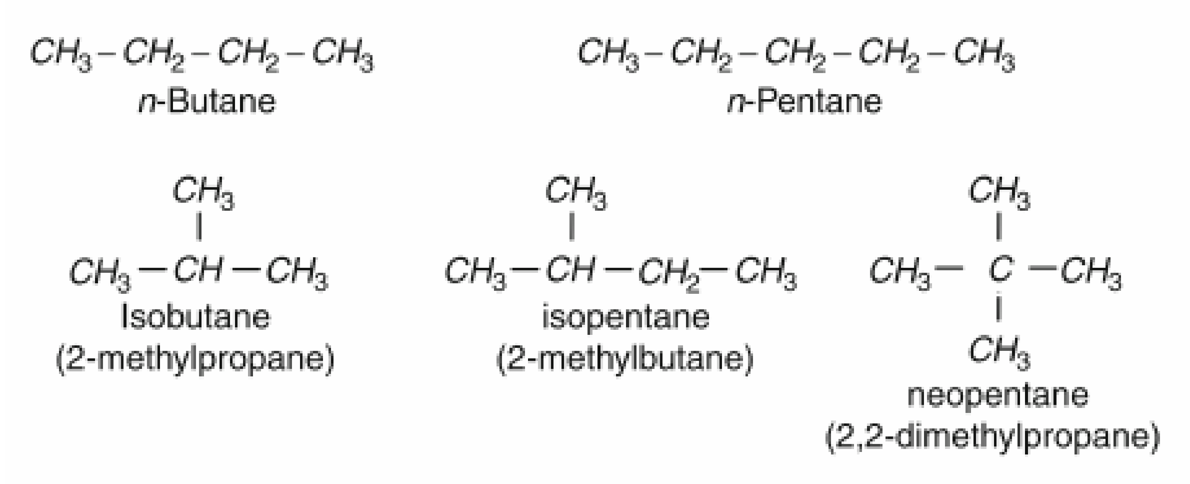
Element	Composition (wt%)
Carbon	83.0–87.0
Hydrogen	10.0–14.0
Sulphur	0.05–6.0
Nitrogen	0.1–0.2
Oxygen	0.05–2.0
Ni	$<$120 ppm
V	$<$1200 ppm

There are three main classes of hydrocarbons. These are based on the type of carbon–carbon bonds present. These classes are:

- Saturated hydrocarbons contain only carbon–carbon single bonds. They are known as paraffins (or alkanes) if they are acyclic, or naphthenes (or cycloalkanes) if they are cyclic.
- Unsaturated hydrocarbons contain carbon–carbon multiple bonds (double, triple or both). These are unsaturated because they contain fewer hydrogens per carbon than paraffins. Unsaturated hydrocarbons are known as olefins. Those that contain a carbon–carbon double bond are called alkenes, while those with carbon–carbon triple bond are alkyenes.
- Aromatic hydrocarbons are special class of cyclic compounds related in structure to benzene.

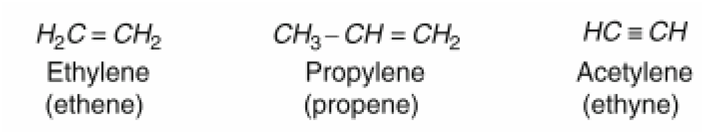
1-Paraffins

General formula: CnH2n+2 (n is a whole number, usually from 1 to 20), straight or branchedchain molecules, can be gasses or liquids at room temperature depending upon the molecule. For example, methane, ethane, propane, butane, isobutane, pentane, hexane



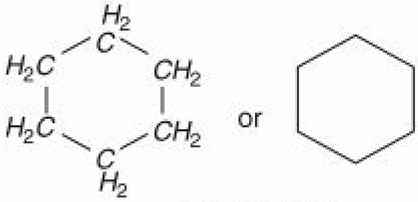
2- Olefins (also known as alkenes)

General formula: CnH2n (n is a whole number, usually from 1 to 20), linear or branched chain molecules containing one carboncarbon double-bond, can be liquid or gas. For example: ethylene, butene, isobutene.



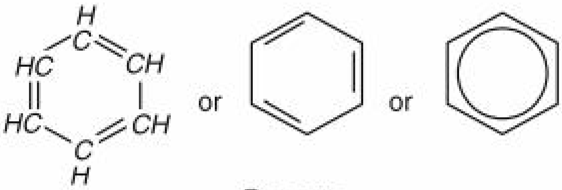
3- Naphthenes (cycloalkanes)

General formula: CnH2n (n is a whole number usually from 1to 20), ringed structures with one or more rings, rings contain only single bonds between the carbon atoms, typically liquids at room temperature. For example: cyclohexane, methyl cyclopentane .

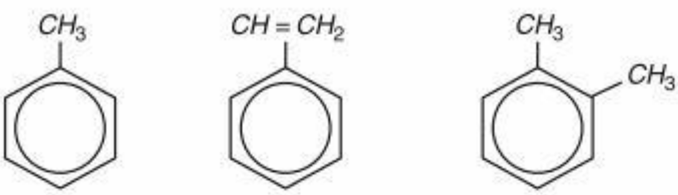


4-Aromatics

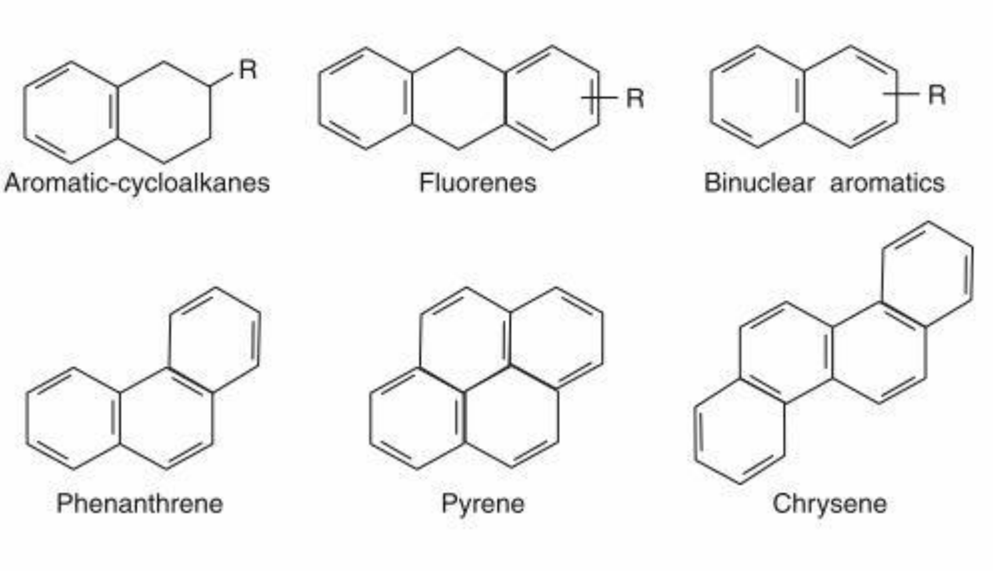
General formula: C6H5 - Y (Y is a longer, straight molecule that connects to the benzene ring), ringed structures with one or more rings, rings contain six carbon atoms, with alternating double and single bonds between the carbons, typically liquids. For examples benzene, naphthalene.



Crude oils from various origins contain different types of aromatic compounds in different concentrations. Light petroleum fractions contain mono-aromatics, which have one benzene ring with one or more of the hydrogen atoms substituted by another atom or alkyl groups. Examples of these compounds are toluene and xylene.

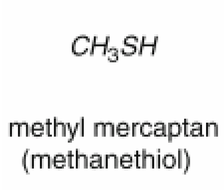


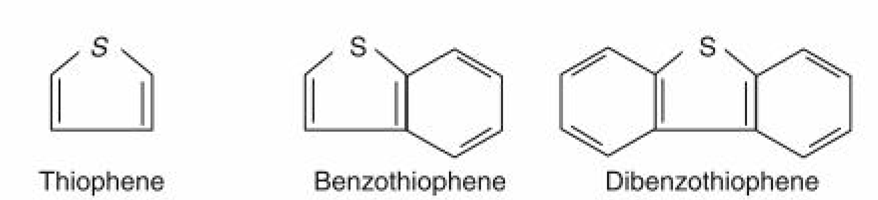
More complex aromatic compounds consist of a number of benzene rings. These are known as polynuclear aromatic compounds. They are found in the heavy petroleum cuts, and their presence is undesirable because they cause catalyst deactivation and coke deposition during processing, besides causing environmental problems when they are present in diesel and fuel oils. Examples of polynuclear aromatic compounds are shown below.

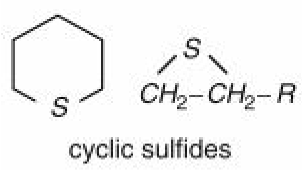


5- Sulfur Compounds

The Sulfur content of crude oils varies from less than 0.05 to more than 10 wt% but generally falls in the range 1–4 wt%. Crude oil with less than 1 wt % sulfur is referred to as low sulfur or sweet, and that with more than 1 wt% sulfur is referred to as high sulfur or sour. Crude oils contain sulfur heteroatoms in the form of elemental sulfur S, dissolved hydrogen sulphide H2S, carbonyl sulphide COS, inorganic forms and most importantly organic forms, in which sulfur atoms are positioned within the organic hydrocarbon molecules. Sulfur compounds lead to environmental pollution, decreases the life of machinery, corrodes of pipes, machines and equipment, affecting the additives used for the purpose of increasing the octane number, reduce the activity of Tetra Ethyl Lead (TEL) added to gasoline. As a result, the engine metal will erode and leads to destruct the metallic parts. Also, their emissions are very dangerous to human safety and environment. In addition, these impurities cause catalyst poisoning and reduce the catalyst activity. Sulfur containing constituents of crude oils vary from simple mercaptans, also known as thiols, to sulphides and polycyclic sulphides (Mercaptans (R–SH), sulphides (R–S–R'), disulphides (R–S–S–R'), Thiophenes)

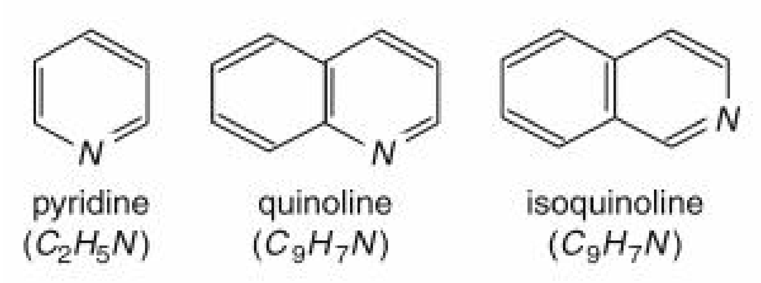






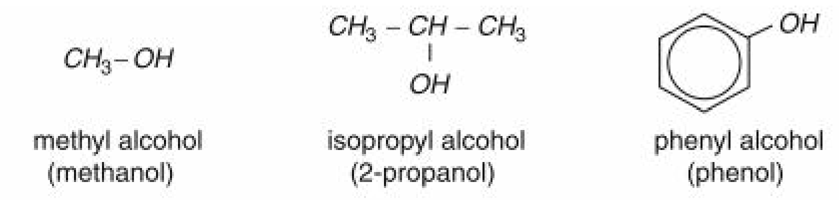
6-Nitrogen Compounds

Crude oils contain very low amounts of nitrogen compounds, less than 1%, The nitrogen compounds in crude oils may be classified as basic or non-basic. Basic nitrogen compounds consist of pyridines. The greater part of the nitrogen in crude oils is the non-basic nitrogen compounds, which are generally of pyrrole types. The decomposition of nitrogen compounds in catalytic cracking and hydrocracking processes forms ammonia and cyanides that can cause corrosion.



7- Oxygen Compounds

Less than 1% (found in organic compounds such as carbon dioxide, phenols, ketones, carboxylic acids) occur in crude oils in varying amounts.



8- Metals Compounds

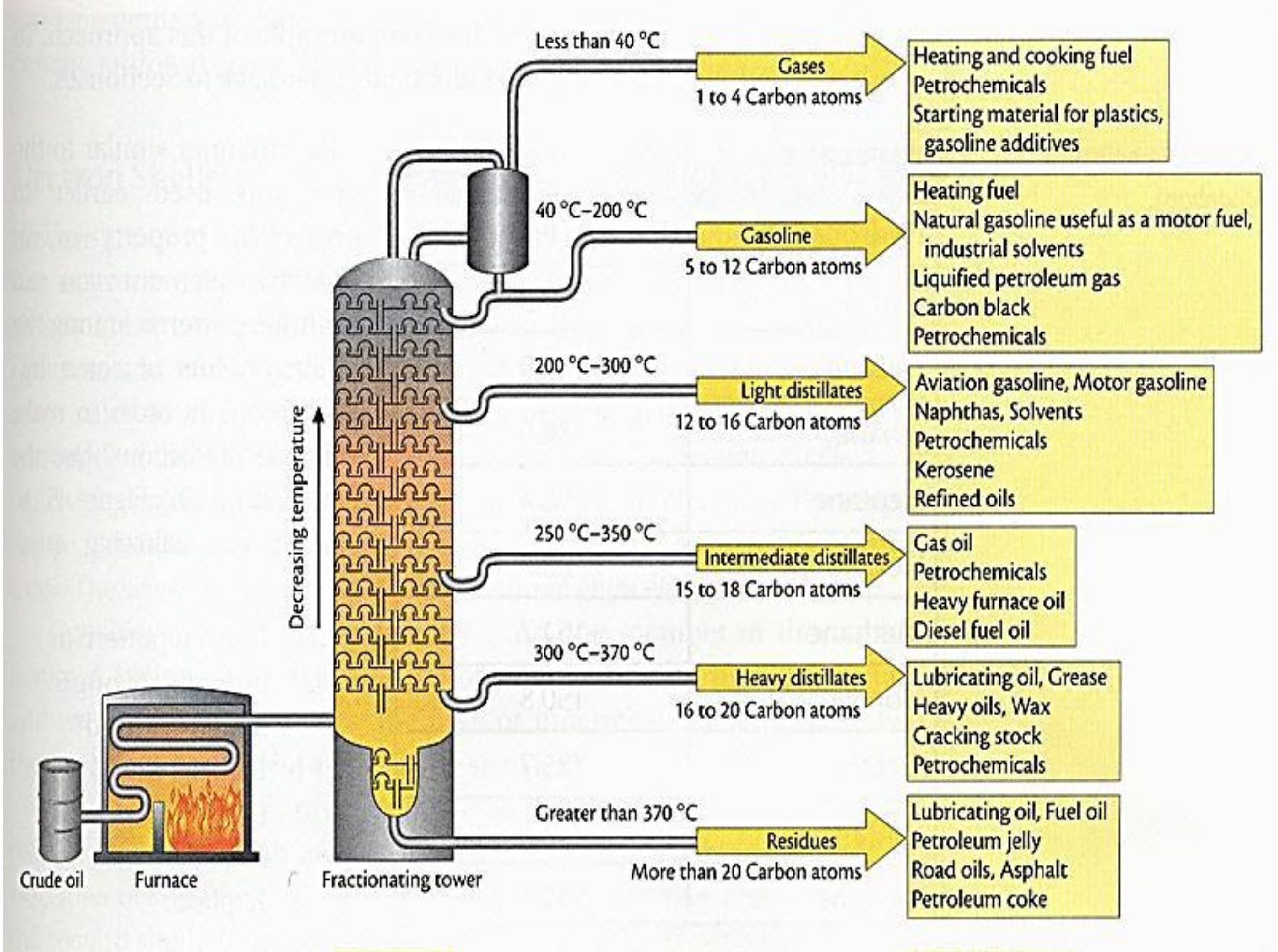
Metallic compounds exist in all crude oil types in very small amounts. Their concentration must be reduced to avoid operational problems and to prevent them from contaminating the products. Metals affect many upgrading processes. They cause poisoning to the catalysts used for hydroprocessing and cracking. Even minute amounts of metals (iron, nickel and vanadium) in the feedstock to the catalytic cracker affect the activity of the catalyst and result in increased gas and coke formation and reduced gasoline yields. Burning heavy fuel oils in refinery furnaces and boilers can leave deposits of vanadium oxide and nickel oxide in furnace boxes, ducts, and tubes. It is also desirable to remove trace amounts of arsenic, vanadium, and nickel prior to processing as they can poison certain catalysts.

9- Asphaltenes and Resins Compounds

Asphaltenes are dark brown friable solids that have no definite melting point and usually leave carbonaceous residue on heating. They are made up of condensed polynuclear aromatic layers linked by saturated links. The presence of high amounts of asphaltenes in crude oil can create tremendous problems in production because they tend to precipitate inside the pores of rock formations, well heads and surface processing equipment's. They may also lead to transportation problems because they contribute to gravity and viscosity increases of crude oils. Resins are polar molecules have high molecular weight, which are insoluble in liquid propane but soluble in n-heptane. It is believed that the resins are responsible for dissolving and stabilizing the solid asphaltenes molecules in petroleum.

Petroleum fractions from crude distillation unit

Typical petroleum products with their carbon atom and boiling ranges:



To understand the diversity contained in crude oil, and to understand why refining crude oil is important in our society, look through the following list of products that come from crude oil:

1- Liquefied Petroleum Gas (LPG)

- used for heating, cooking, making plastics
- small alkanes (1 to 4 carbon atoms)
- commonly known by the names methane, ethane, propane, butane
- boiling range < 90 degrees Fahrenheit / < 27 degrees Celsius
- often liquified under pressure to create LPG (liquefied petroleum gas)

2- Gasoline

- motor fuel
- liquid
- mix of alkanes and cycloalkanes (5 to 7 carbon atoms)
- boiling range = 90-220 degrees Fahrenheit / 27-93 degrees Celsius

3- Kerosene

- fuel for jet engines and tractors; starting material for making other products
- liquid
- mix of alkanes (10 to 15 carbons) and aromatics
- boiling range = 315-450 degrees Fahrenheit / 177-293 degrees Celsius

4- Diesel Fuel

- used for diesel fuel and heating oil, starting material for making other products
- liquid
- alkanes containing 13-18 carbon atoms
- boiling range = 450-650 degrees Fahrenheit / 293-315 degrees Celsius

5- **Lubricating oil**

- used for motor oil, grease, other lubricants
- Liquid
- long chain (20 to 50 carbon atoms) alkanes, cycloalkanes, aromatics
- boiling range = 572 to 700 degrees Fahrenheit / 300 to 370 degrees Celsius

6- **Fuel oil**

- used for industrial fuel; starting material for making other products
- liquid
- long chain (16 to 40 carbon atoms) alkanes, cycloalkanes, aromatics
- boiling range = 650-800 degrees Fahrenheit / 315-565 degrees Celsius

7- **Residual oil**

- coke, asphalt, tar, waxes; starting material for making other products
- solid
- multiple-ringed compounds with 40 or more carbon atoms
- boiling range = greater than 800 degrees Fahrenheit / 565 degrees Celsius

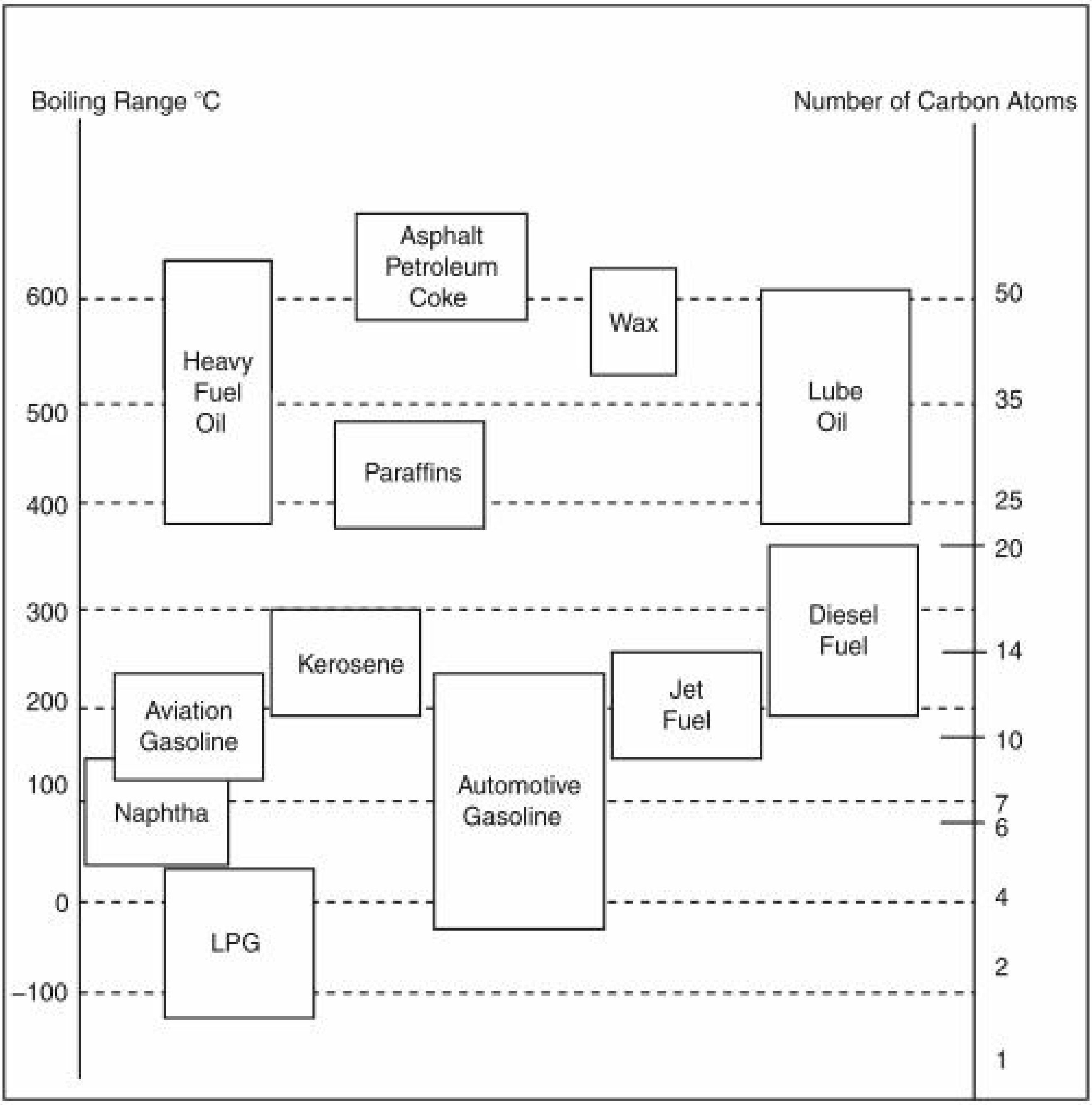


Figure 3: The relation between boiling point and number of carbon atoms in petroleum fractions.

Classification of Crude Oil

Classification of crude oil refers to natural and type of crude oil (**type of hydrocarbons in crude oil**) by simplified tests. Four mainly methods are used

A- Watson or UOP characterization factor (Kw):

Watson characterization factor (Kw) can be calculated from the following equation:

$$K_w = \frac{\sqrt[3]{MeABP}}{Sp.Gr\ @\ 60°F} \quad \dots .1$$

Kw = Watson characterization factor

MeABP = mean average boiling point temperature in Rankin = **VABP - Δ**

VABP = volume average boiling point temperatures in °F.

VABP can be calculated as the average of the five boiling temperatures at 10, 30, 50, 70 and 90 percent distilled.

Sp.Gr. 60/60°F = Specific Gravity at 15°C (60 °F) = **density crude oil @ 60°F / density of water @ 60°F**

$$Sp.Gr\ @\ 60°F = \frac{141.5}{API+131.5} \quad \dots .2$$

Crude oil classifications by Watson characterization factor as follows:

1- Kw = 12.15 – 13 paraffinic (or light) based crude oil

2- Kw = 11.1 – 12.0 mixed (or intermediate) based crude oil

3- Kw = 10 – 11.0 naphthenic (asphaltic or heavy) based crude oil

B- (API gravity)

API = American Petroleum Institute

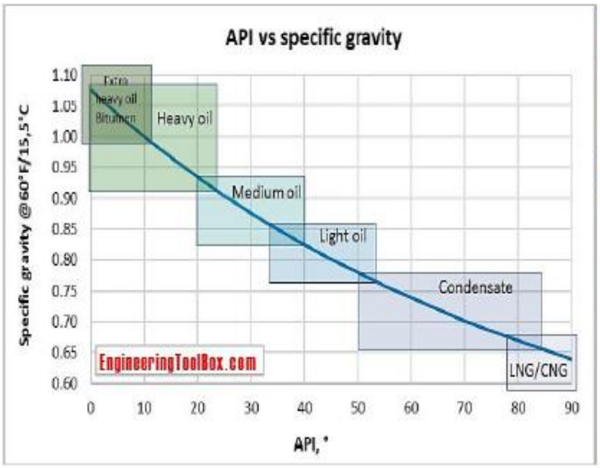
$$API = \frac{141.5}{Sp.Gr.@\ 60°F} - 131.5 \quad \dots .3$$

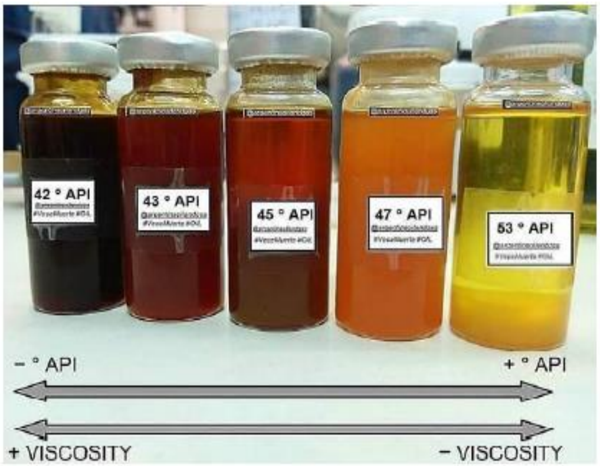
At atmospheric (1 atm), the crude oil classification will be as follows:

1- API gravity > 40 paraffinic (or light) based crude oil

2- API gravity = 33 - 40 mixed (or intermediate) based crude oil

3- API gravity < 33 naphthenic (asphaltic or heavy) based crude oil





C- Correlation Index (C.I)

This method based on the percentages of various hydrocarbons types in the crude oil which are classified into paraffinic or aromatic according to following

$$C.I = 473.7\, SG\ at\ 60F - 456.8 + \frac{48680}{ABP\ °K} \quad ....4$$

ABP: average boiling point in Kelvin

The crude oil can be classified as follow as:

1. C.I. = 0 (normal paraffinic based crude oil)

2. C.I = 0-15 (predominance of n-paraffinic crude oil)

3. C.I = 15 – 50 (paraffinic and aromatic mixture)

4. C.I > 50 (predominance of aromatic crude oil)

5. C.I = 100 benzene (Aromatic)

D- Classification by Viscosity-Gravity Constant

The viscosity gravity constant is of particular value in indicating a predominantly paraffinic or cyclic composition. **The lower the index number**, **the more paraffinic the stock**; for example, napthenic lubricating oil distillates have VGC = 0.876 while raffinate obtained by solvent distillation of lubricating oil distillate has VGC ~ 0.840

$$VGC = \frac{10\ Sp.Gr - 1.0752\ \log(v_{38} - 38)}{10 - \log(v - 38)} \quad ....5$$

V is the saybolt viscosity at 38° C (100°F). For oils so heavy that low-temperature viscosity is difficult to measure, an alternative formula has been proposed in which the **99°C (210°F) saybolt viscosity is used**.

$$VGC = \frac{Sp.Gr - 0.24 - 0.022\ \log(v_{99} - 35.5)}{0.755} \quad ....6$$

The Saybolt universal viscosity (SUS) is the time in seconds required for the flow of 60 ml of petroleum from a container, at a constant temperature, through a calibrated orifice.

VGC:

1) 0.70-0.79 paraffinic hydrocarbon.

2) 0.80-0.90 naphthenic base.

3) 0.91-1.31 aromatic base.

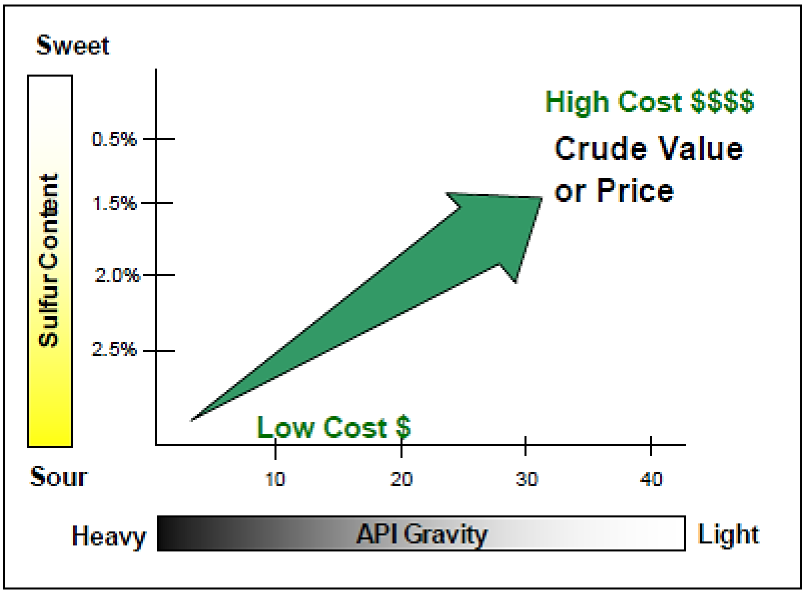
C varies for paraffinic hydrocarbons from 0.74 0.75, for naphthenic from 0.89 to 0.94, and for aromatics from0.95 to 1.13

E - Sulfur Content

• If crude has **less than 0.5%** sulfur content, then it will be considered as **sweet crude oil.**

• **If crude has greater than 2.5% sulfur, then it will be sour crude oil.**

• **Crude with sulfur content between these two end points is called intermediate.**



F- Technological Classification of Petroleum

According to technological classification, the oil can be classified as:

• **Low sulfur oil** containing not more than 0.5% of the sulfur, whereby the gasoline fraction contains less than 0.1% sulfur and diesel fraction less than 0.2%.

• **High sulfur oil** containing over 2% of sulfur.

• **Low paraffinic oil** containing less than 1.5% of paraffins. This type of oil can be used for production of jet and winter diesel fuels without deparaffinization.

• **Medium paraffinic oil** containing over 1.5% and fewer than 6% of paraffins. This type of oil can be used for production of jet and summer diesel fuels without deparaffinization.

• **High paraffinic oil** containing over 6% of paraffins. This type of oil can be used for production of diesel and jet fuels only after deparaffinization.