**Petroleum properties**

**Petroleum:** is a complex mixture of hydrocarbons that occur in the sedimentary rocks in the form of gases (natural gas), liquids (crude oil), semisolids (bitumen), or solids (wax or asphaltite). It is the main source of energy for industry, heating, and transportation and it also provides the raw materials for many produce such as polymers, plastics, and many other products. The word petroleum, derived from the Latin words petra and oleum, means literally rock oil and a special type of oil called oleum. In general terms, petroleum (conventional crude oil) ranges from a brownish green to black liquid.

**Importance of petroleum**

1. It represents the major sources for energy in the world (45% crude oil and 15% natural gases).
2. Electrical power generation.
3. Fuel for cars, ships and airliners.
4. Fuel for heating and cooking.
5. It is used in petrochemicals industrials to produce various useful materials such as clothes, plastics, drugs, pipes……etc.
6. It used for lubrication of different types of engines.

**Origin of Petroleum**

There are two assumptions explaining the formation of petroleum:

A) Inorganic hypothesis:

This hypothesis assumes that the oil hydrocarbon compounds produced from reaction hot water vapor with metal carbides which will form the hydrocarbon substances under high pressure and temperature as follows:

\[ \text{Al}_4\text{C}_3 + 12\text{H}_2\text{O} \rightarrow 4\text{Al(OH)}_3 + 3\text{CH}_4 \]

\[ \text{CH}_4 \rightarrow \text{petroleum} \]

\[ \text{CaC}_2 + 2\text{H}_2\text{O} \rightarrow \text{C}_2\text{H}_2 + \text{Ca(OH)}_2 \]

\[ \text{C}_2\text{H}_2 \rightarrow \text{petroleum} \]
B) Organic hypothesis:

This hypothesis assume that the petroleum is formed from the decomposition of the animals and plants dead which converted to liquids and gases hydrocarbon by effect the high temperature, pressure and catalyst (as a small microscopic beings). Some sources suggest this hypothesis to explain the formation of the Arabian Gulf's petroleum.

*Composition of crude oil*

The composition of petroleum obtained from the well is variable and depends not only on the original composition of the oil *in situ* but also on the manner of production and the stage reached in the life of the well or reservoir.

<table>
<thead>
<tr>
<th>Element</th>
<th>Amount, wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon, C</td>
<td>82-87</td>
</tr>
<tr>
<td>Hydrogen, H</td>
<td>11-14</td>
</tr>
<tr>
<td>Sulfur, S</td>
<td>0.06-8</td>
</tr>
<tr>
<td>Nitrogen, N</td>
<td>0.02-1.7</td>
</tr>
<tr>
<td>Oxygen, O</td>
<td>0.08-1.82</td>
</tr>
<tr>
<td>Metals (Ni and V),</td>
<td>0-0.14</td>
</tr>
</tbody>
</table>

The presence of these impurities is undesirable, the negative impact on the processing and refining operations and this is what requires the establishment of a special purification and handling devices i.e. gas separation, dehydration, desalting, desulfurization, heating and separation of wax by solvent and all operations that would increase the cost.

1. *Hydrocarbons components*

Hydrocarbons constitute the essential components of petroleum; their molecules contain only carbon and hydrogen they are grouped into many chemical families according to their structure. All structure are based on the quadrivalency of carbon. The carbon-carbon molecule chains can be as follows:

- Either linked by a single $c - c$ (given suffix “- ane”)
- On linked by multiple bonds (are said to be unsaturated)
  - Double $c = c$ (given suffix “- ene”)
  - Or triple $c \equiv c$ (given suffix “- yne”)
1.1. Paraffin or alkanes

The paraffin series of hydrocarbons is characterized by the rule that the carbon atoms are connected by a single bond and the other bonds are saturated with hydrogen atoms. The general formula for paraffin is \( C_nH_{2n+2} \).

The simplest paraffin is methane, \( CH_4 \), followed by the homologous series of ethane, propane, normal and isobutane, normal, iso-, and neopentane, etc. (Fig. 1). First three compounds are gases while compounds up to C16 are liquids and beyond that, they assume semisolid consistency. Well beyond C30 assume the shape solid blocks or crystalline forms.

When the number of carbon atoms in the molecule is greater than three, several hydrocarbons may exist which contain the same number of carbon and hydrogen atoms but have different structures. C4 exhibits only two isomers, and C5 exhibits three isomers as shown here:

![Figure 1 Paraffin in crude oil](image)

This is because carbon is capable not only of chain formation, but also of forming single- or double- branched chains which give rise to isomers that have significantly different properties. For example, the motor octane number of n-octane is 17 and that of isooctane is 100.

1.2. Cycloparaffin hydrocarbons (Naphthenes)

These are saturated ring compounds bearing in which all of the available bonds of the carbon atoms are saturated with hydrogen. Some typical naphthenic compounds are shown in Figure 2. The importance of ring structure starts with 5 carbon ring atoms. Naphthenic exhibits both the properties of saturated paraffin and unsaturated aromatics like sp. gr., viscosity, thermal characteristics.
The general formula for cycloparaffins having a single ring is $C_nH_{2n}$. There also exist cycoparaffins with two, three or four etc. rings attached. Hence decalin has two rings attached to each other and the general formula is is $C_nH_{2n-2}$.

### 1.3. Aromatics

The aromatic series of hydrocarbons is chemically and physically very different from the paraffins and cycloparaffins (naphthenes). The first and smallest of the aromatic hydrocarbons is benzene ring which is unsaturated but very stable and frequently behaves as a saturated compound in addition to toluene, xylene, cumene etc. Some typical aromatic compounds are shown in Figure 3. Aromatics are usually having high boiling points, low freezing point, high octane number, high viscosity and these burns with a red flame with much soot.
The general formula is the $C_nH_{2n-6}$, and hydrogen atoms can be substituted in the following ways:

- Either by alkyl groups which are designated by letter R, which is equivalent to $C_nH_{2n+1}$ to give alkyl-aromatic. The prefixes *ortho*, *meta* and, *para* are used to show positions of substitutes on the ring. Therefor C8H10 or dimethyl benzenes (xylenes) are represented as below:

\[
\begin{align*}
\text{Orthoxylene} & \quad \begin{array}{c}
\text{H} \\
\text{H} \\
\text{C}=\text{C} \\
\text{C} \\
\text{CH}_3 \\
\end{array} \\
\text{Metaxyylene} & \quad \begin{array}{c}
\text{H} \\
\text{H} \\
\text{C}=\text{C} \\
\text{C} \\
\text{CH}_3 \\
\text{CH}_3 \\
\end{array} \\
\text{Paraxyylene} & \quad \begin{array}{c}
\text{H} \\
\text{H} \\
\text{C}=\text{C} \\
\text{C} \\
\text{CH}_3 \\
\end{array}
\end{align*}
\]

- In this instance a second aromatic ring can be substituted for two adjacent hydrogen atoms giving condensed polynuclear aromatic, for example:

\[
\begin{align*}
\text{Naphthalene} & \quad \begin{array}{c}
\text{H} \\
\text{H} \\
\text{C}=\text{C} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{H} \\
\text{H} \\
\end{array} \\
\text{Anthracene} & \quad \begin{array}{c}
\text{H} \\
\text{H} \\
\text{C}=\text{C} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{H} \\
\text{H} \\
\end{array}
\end{align*}
\]
Properties of Petroleum and Natural Gas
2nd Stage/Chemical Eng. Dept.
Asst. Professor Hameed Hussein Alwan

Table 1 summarize data for these aromatic hydrocarbons

<table>
<thead>
<tr>
<th>Overall formula</th>
<th>Structural formula</th>
<th>Molecular weight</th>
<th>Boiling point °C (1 atm.)</th>
<th>Specific gravity (liquid)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>C₆H₆</td>
<td>78.1</td>
<td>80.1</td>
<td>0.884</td>
</tr>
<tr>
<td>Toluene</td>
<td>C₇H₈</td>
<td>92.1</td>
<td>110.6</td>
<td>0.871</td>
</tr>
<tr>
<td>Ethyl benzene</td>
<td>C₈H₁₀</td>
<td>106.2</td>
<td>136.2</td>
<td>0.871</td>
</tr>
<tr>
<td>o-xylene</td>
<td>C₈H₁₀</td>
<td>106.2</td>
<td>144.4</td>
<td>0.884</td>
</tr>
<tr>
<td>o-xylene</td>
<td>C₈H₁₀</td>
<td>106.2</td>
<td>139.1</td>
<td>0.868</td>
</tr>
<tr>
<td>o-xylene</td>
<td>C₈H₁₀</td>
<td>106.2</td>
<td>138.4</td>
<td>0.865</td>
</tr>
</tbody>
</table>

1.4 Olefins (Alkenes)

Olefins do not naturally occur in crude oils but are formed during the processing. They are very similar in structure to paraffins but at least two of the carbon atoms are joined by double bonds. The general formula is CₙH₂ₙ. Olefins containing five carbon atoms have high reaction rates with compounds in the atmosphere that form pollutants. The first four compounds are gases and up to C15 are liquids and beyond that are solid.

- 1-butene  \( \text{CH}_2\equiv\text{CH} - \text{CH}_2 - \text{CH}_3 \)
- cis 2-butene  \( \text{CH}_3 - \text{C}\equiv\text{C} - \text{CH}_3 \)  
  \( \text{H} \quad \text{H} \)  
- trans 2-butene  \( \text{CH}_3 - \text{C} = \text{C} - \text{CH}_3 \)  
  \( \text{H} \)  
- isobutene  \( \text{CH}_3 \backslash \text{C} = \text{C} \backslash \text{CH}_3 \)  
  \( \text{CH}_3 \)  

1.5 Diolefins

It containing two double bonds is also formed during processing, but they react very rapidly with olefins to form high-molecular-weight polymers consisting of many simple
unsaturated molecules joined together. Diolefins are very undesirable in products because they are so reactive they polymerize and form filter and equipment plugging compounds. These are represented by the formula C\textsubscript{n}H\textsubscript{2n-2}.

Normally absent or in trace amounts in crude oil, products of conversion processes such as diolefins, acetylenes, etc., are encountered. Table 2 gives the physical properties of some of them. Noteworthy is 1-3butadine:

CH\textsubscript{2}=CH-CH=CH\textsubscript{2} as well as isoprene; CH\textsubscript{2}=C(CH\textsubscript{3})-CH=CH\textsubscript{2}, the basic monomers for a number of polymers.

<table>
<thead>
<tr>
<th>Overall formula</th>
<th>Structural formula</th>
<th>Molecular weight</th>
<th>Boiling point °C (1 atm.)</th>
<th>Specific gravity (liquid)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene</td>
<td>C\textsubscript{2}H\textsubscript{4}</td>
<td>(\text{C} = \text{C})</td>
<td>28.0</td>
<td>-103.7</td>
</tr>
<tr>
<td>Propylene</td>
<td>C\textsubscript{3}H\textsubscript{6}</td>
<td>(\text{C} - \text{C} = \text{C})</td>
<td>42.1</td>
<td>-47.7</td>
</tr>
<tr>
<td>1-Butene</td>
<td>C\textsubscript{4}H\textsubscript{8}</td>
<td>(\text{C} = \text{C} - \text{C} - \text{C})</td>
<td>56.1</td>
<td>-6.3</td>
</tr>
<tr>
<td>Cis 2-Butene</td>
<td>C\textsubscript{4}H\textsubscript{8}</td>
<td>(\text{C} = \text{C})</td>
<td>56.1</td>
<td>3.7</td>
</tr>
<tr>
<td>Trans 2-Butene</td>
<td>C\textsubscript{4}H\textsubscript{8}</td>
<td>(\text{C} = \text{C})</td>
<td>56.1</td>
<td>0.8</td>
</tr>
<tr>
<td>Isobutene</td>
<td>C\textsubscript{4}H\textsubscript{8}</td>
<td>(\text{C} - \text{C} = \text{C})</td>
<td>56.1</td>
<td>-6.9</td>
</tr>
<tr>
<td>1-Pentene</td>
<td>C\textsubscript{5}H\textsubscript{10}</td>
<td>(\text{C} = \text{C} - \text{C} - \text{C} - \text{C})</td>
<td>70.1</td>
<td>30.0</td>
</tr>
<tr>
<td>1,3-Butadiene</td>
<td>C\textsubscript{4}H\textsubscript{6}</td>
<td>(\text{C} = \text{C} = \text{C})</td>
<td>54.1</td>
<td>-4.4</td>
</tr>
<tr>
<td>Isoprene</td>
<td>C\textsubscript{5}H\textsubscript{8}</td>
<td>(\text{C} = \text{C} - \text{C} = \text{C})</td>
<td>68.1</td>
<td>34.1</td>
</tr>
<tr>
<td>Cyclopentadiene</td>
<td>C\textsubscript{5}H\textsubscript{8}</td>
<td>(\text{C} = \text{C} - \text{C} - \text{C})</td>
<td>66.0</td>
<td>40.0</td>
</tr>
</tbody>
</table>

Table 2 physical properties of selected unsaturated hydrocarbons

2. Nonhydrocarbon Components

Crude oils contain amounts of organic nonhydrocarbon constituents, the most important are the organic sulfur, nitrogen, and oxygen compounds. Traces of metallic compounds are also found in all crudes. The presence of these impurities is harmful and may cause problems to certain catalytic processes. Fuels having high sulfur and nitrogen levels cause pollution problems in addition to the corrosive nature of their oxidization products.
2.1 Sulfur compounds
The presence of sulfur compounds in finished petroleum products often produces harmful effects. For example, in gasoline, sulfur compounds promote corrosion of engine parts. Sulfur in crude oils is mainly present in the form of organosulfur compounds. Hydrogen sulfide (H2S) is the only important inorganic sulfur compound found in crude oil. Its presence, however, is harmful because of its corrosive nature. Organosulfur compounds may generally be classified as acidic and non-acidic.

1. Mercaptanes
These are acidic sulfur compounds classified of two types:
   A. Mercaptanes that contains aliphatic or cyclohydrocarbon (called thiols R-SH) examples are methyl, ethyl, and propyl mercaptane, and cyclohexylthiol.

   ![Methyl mercaptan and Cyclohexylthiol](image)

   B. Mercaptanes that contains aromatic hydrocarbon (called thiophenols) such as phenol mercaptane.

2. Thiophenes
These are non-acidic sulfur compounds found in crude fractions, contains thiophene rings with one or more benzene rings examples are thiophene, benzothiophene.

![Thiophene, Benzothiophene, Dibenzothiophene](image)

3. Organic Sulfides
These compounds are of two types, the noncyclosulfide and the cyclosulfides:
These compounds are less corrosive but may have high effect if exists in gasoline as they can react with tetra ethyl lead and then reduce its octane no.

4. Disulfide

Disulfide R-S-S-R’ always present with low percentage in crude oils that only contains mercaptanes, and vice versa. The reason of this case is the oxidation of mercaptanes with atmosphere during process production of crude oil from wells.

The sulfur content of petroleum is an important property and varies widely within the rough limits 0.1% w/w to 3.0% w/w, and sulfur content up to 8.0% w/w has been noted for tar sand bitumen. Compounds containing this element are among the most undesirable constituents of petroleum because they can give rise to plant corrosion and atmospheric pollution. Because many organic sulfur compounds are not thermally stable, hydrogen sulfide H₂S is often produced during crude processing. Petroleum can evolve H₂S during distillation as well as low-boiling sulfur compounds. H₂S has the ability to dissolve in water producing sulfurous acid H₂SO₃ causing high corrosion in equipment.

Usually sulfur does not exceed 5%. there is an effect of sulfur in increasing the density of crude as shows in this correlation:

\[
\rho = 0.0087(S\%)^2 + 0.0607(S\%) + 0.7857
\]

Some information of Iraqi crude

Sulfur contains in Basrah -2.05%

API =33.9

Sour crudes contain a high percentage of H₂S. High-sulfur crudes are less desirable because treating the different refinery streams for acidic H₂S increases production costs. Sulfur concentration can range from 0.1 to more than 8 weight percent.
<table>
<thead>
<tr>
<th>Country</th>
<th>S% content</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kuwait</td>
<td>2.48</td>
</tr>
<tr>
<td>Iraq</td>
<td>1.85</td>
</tr>
<tr>
<td>Saudi Arabia</td>
<td>1.60</td>
</tr>
<tr>
<td>Iran</td>
<td>1.40</td>
</tr>
<tr>
<td>Qatar</td>
<td>1.05</td>
</tr>
<tr>
<td>Libya</td>
<td>0.45</td>
</tr>
<tr>
<td>Nigeria</td>
<td>0.25</td>
</tr>
<tr>
<td>Algeria</td>
<td>0.14</td>
</tr>
</tbody>
</table>

### 2.2 Oxygen and nitrogen

Oxygen and nitrogen do not occur in free state either in crude or in fractions. Oxygen occurs as oxygenated compounds like phenols, cresols, naphthenic acid, sulphonate, sulphate, and sulfoxide. Nitrogen exists in the form of indole, pyridine, quioline, and amine.

### 2.2 Nitrogen Compounds

Organic nitrogen compounds occur in crude oils either in a simple heterocyclic form as in pyridine (C₅H₅N) and pyrrole (C₄H₅N), or in a complex structure as in porphyrin. The nitrogen content in most crude is very low and does not exceed 0.1 wt%. In some heavy crude, however, the nitrogen content may reach up to 0.9 wt%. Nitrogen compounds are more thermally stable than sulfur compounds and accordingly are concentrated in heavier petroleum fractions and residues. Light petroleum streams may contain trace amounts of nitrogen compounds, which should be removed because they poison many processing catalysts. During hydrotreatment of petroleum fractions, nitrogen compounds are hydrodenitrogenated to ammonia and the corresponding hydrocarbon.

For example, pyridine is denitrogenated to ammonia and pentane:

\[
\text{Pyridine} + 5 \text{H}_2 \rightarrow \text{NH}_3 + \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3
\]
Nitrogen compounds in crudes may generally be classified into basic (alkaline) and non-basic categories. Basic nitrogen compounds are mainly those having a pyridine ring, and the non-basic nitrogen compounds have a pyrrole structure. Both pyridine and pyrrole are stable compounds due to their aromatic nature. The following are examples of basic organic nitrogen compounds.

![Basic Nitrogen Compounds](image1)

**Basic Nitrogen Compounds**

- Pyridine
- Quinoline
- Isoquinoline
- Acridine

![Non-Basic Nitrogen Compounds](image2)

**Non-Basic Nitrogen Compounds**

- Pyrrole
- Indole
- Carbazole
- Benzocarbazole

Porphyrrins are non-basic nitrogen compounds. The porphyrin ring system is composed of four pyrrole rings joined by =CH- groups. The entire ring system is aromatic. Many metal ions can replace the pyrrole hydrogens and form chelates. Almost all crude oils and bitumens contain detectable amounts of vanadyl and nickel porphyrins. Porphyrrins can be cracked at temperatures ranging from 200 to 250°C. The basic structural unit of porphyrrins is as following:

![Porphyrrin Structure](image3)
Separation of nitrogen compounds is difficult, and the compounds are susceptible to alteration and loss during handling. However, the basic low molecular weight compounds may be extracted with dilute mineral acids.

2.3 Oxygen Compounds

Oxygen compounds in crude oils are more complex than the sulfur types. However, their presence in petroleum streams is not poisonous to processing catalysts.

Acidic oxygen compounds found in crude oils are weakly acidic such as carboxylic acids, cresylic acid, phenol, and naphthenic acid. Naphthenic acids are mainly cyclopentane and cyclohexane derivatives having a carboxyalkyl side chain. Naphthenic acids in the naphtha fraction have a special commercial importance and can be extracted by using dilute caustic solutions. The total acid content of most crude is generally low, but may reach as much as 3% as in some California crudes.

Non-acidic oxygen compounds such as esters, ketones, and amides are less abundant than acidic compounds. They are of no commercial value. The following shows some of the oxygen compounds commonly found in crude oils:

2.4 Metallic Compounds
Many metals occur in crude oils. Some of the more abundant are Ca, Mg, Na, Al, Fe, V, and Ni. They are present either as inorganic salts, such as Na and Mg chlorides, or in the form of organometallic compounds, such as those of Ni and V (as in porphyrins). The presence of Ca and Mg can form salts or soaps with carboxylic acids. These compounds act as emulsifiers, and their presence is undesirable. Even trace amounts of these metals can be deleterious to refining processes, especially processes in which catalysts are used. Although metals in crudes are found in trace amounts, their presence is harmful and should be removed. When crude oil is processed, Na and Mg chlorides produce hydrochloric acid, which is very corrosive. Desalting crude oils is a necessary step to reduce these salts.

Trace components such as metallic constituents, can also produce adverse effects in refining either (1) by causing corrosion or (2) by affecting the quality of refined products. Nickel and vanadium along with iron and sodium (from the brine) are the major metallic constituents of crude oil. These metals can be determined by atomic absorption spectrophotometric methods (ASTM D-5863). Vanadium V and Ni are poisons to many catalysts and should be reduced to very low levels. Most of the V and Ni compounds are concentrated in the heavy residues. Solvent extraction processes are used to reduce the concentration of heavy metals in petroleum residues.

2.5 Wax Content

Petroleum with high wax content presents difficulties in handling and pumping as well as producing distillate and residual fuels of high pour point and lubricating oils that are costly to dewax.

All the standard methods for the determination of wax involve precipitating the wax from solvents such as methylene chloride or acetone under specified conditions of solvent-to-oil ratio and temperature. Such measurements give compared results that are often useful in characterizing the wax content of petroleum or for investigating factors involved in flow problems. On the other hand, the wax appearance point (ASTM D-3117) may be determined by cooling of a sample under defined conditions with stirring. The temperature at which the wax first appears is the wax appearance point.
2.6 Brine Water content

The knowledge of the content of salt in crude oil is important in deciding whether and to what extent the crude oil needs desalting. The salt content of crude oil is highly variable and results principally from production practices used in the field. Production of crude oil and natural gas is usually associated with the production of water. The produced water may be water that exists within the petroleum reservoir as natural water or bottom water. Alternatively, water may be produced as a result of water-flooding operations, where water is injected into the reservoir to enhance the recovery.

The most associated soluble salts in water is sodium chloride NaCl and several positive ions of Na⁺, Ba²⁺, Mg²⁺, Al³⁺, Ca²⁺, K⁺, Si²⁺ and negative ions Cl⁻, Br⁻, SO₄²⁻, HCO₃⁻, CO₃⁻, NO₂⁻ molecules are suspension in crude oil with extremely high concentrations of dissolved salt ions nearly 300–300 000 ppm.

Salt in crude oil may be damaging in several ways. Even in small concentrations, salts will accumulate in stills, heaters, and exchangers, leading to fouling that requires expensive cleanup. More importantly, during flash vaporization of crude oil certain metallic salts can be hydrolyzed to hydrochloric acid according to the following reactions:

\[ 2\text{NaCl} + \text{H}_2\text{O} \rightarrow 2\text{HCl} + \text{Na}_2\text{O} \]
\[ \text{MgCl}_2 + \text{H}_2\text{O} \rightarrow 2\text{HCl} + \text{MgO} \]

The hydrochloric acid evolved is extremely corrosive, necessitating the injection of a basic compound, such as ammonia, into the overhead lines to minimize corrosion damage. Salts and evolved acids can also contaminate both overhead and residual products, and certain metallic salts can deactivate catalysts.

2.7 Resins and Asphaltenes Content

Resins and asphaltenes are heavy distillate of crude oils, primarily are a subclass of the aromatics, although some resins may contain only naphthenic rings. They are large molecules consisting primarily of hydrogen and carbon, with one to three sulfur, oxygen, or nitrogen
atoms per molecule. The basic structure is composed of rings, mainly aromatics, with three to ten or more rings per molecule.

The asphaltene fraction (ASTM D-893, ASTM D-2006) is the highest molecular weight, most complex fraction in petroleum. The asphaltene content gives an indication of the amount of coke that can be expected during processing.

In any of the methods for the determination of the asphaltene content, the crude oil or product (such as asphalt) is mixed with a large excess (usually >30 volumes hydrocarbon per volume of sample) of low-boiling hydrocarbon solvents such as n-pentane or n-heptane. After a specified time, the insoluble material (the asphaltene fraction) is separated (by filtration) and dried. The yield is reported as percentage (% w/w) of the original sample.

3. Evaluation of Petroleum

Petroleum can be classified depending on several bases as follows:

3.1 Type of Hydrocarbon

The hydrocarbons found in petroleum are classified into the following types:

- Paraffin base, i.e., saturated hydrocarbons with straight or branched chains, but without any ring structure
- Naphthene base, i.e., saturated hydrocarbons containing one or more rings, each of which may have one or more paraffin side-chains (more correctly known as alicyclic hydrocarbons)
- Aromatic-base oils, i.e., hydrocarbons containing one or more aromatic nuclei such as benzene, naphthalene, and phenanthrene ring systems that may be linked up with (substituted) naphthalene rings or paraffin side-chains.
- Asphalt base, or mixed base.

<table>
<thead>
<tr>
<th>Classification by Chemical Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition of 250 °C-300 °C (480 °F-570 °F)</td>
</tr>
<tr>
<td>----------------------------------------</td>
</tr>
<tr>
<td>&gt; 46 , &lt; 61</td>
</tr>
<tr>
<td>&gt; 42 , &lt; 45</td>
</tr>
<tr>
<td>&gt; 15 , &lt; 26</td>
</tr>
<tr>
<td>&gt; 27 , &lt; 35</td>
</tr>
<tr>
<td>&lt; 8</td>
</tr>
</tbody>
</table>
3.2 Mallison classification

Mallison classified the crude on the basis of residuum, a material left behind after distillation of fractions (wax content). Crude oils are considered to be asphaltic if the distillation residue contains less than 2% wax. On the other hand, a crude oil is considered paraffinic if it contains more than 5% wax. نسبه البرافين في المحتوى الشمسي

Accordingly:

- Residue containing more than 5% parafins is paraffinic crude
- Residue containing less than 2% parafins is naphthenic base
- Residue containing 2-5% parafins is considered as mixed base.

3.3 The U.S. Bureau of Mines has developed a system which classifies the crude according to two key fractions obtained in distillation: No. 1 from 482 to 527°F (250 to 275°C) at atmospheric pressure and No. 2 from 527 to 572°F (275 to 300°C) at 40 mmHg pressure. The gravity of these two fractions is used to classify crude oils into types as shown below.

<table>
<thead>
<tr>
<th>Key fraction</th>
<th>Boiling point</th>
<th>Pressure</th>
<th>API</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. 1</td>
<td>482-527°F</td>
<td>1 atm.</td>
<td>&gt; 40 (Paraffinic base) 33 &lt; API &lt; 40 (Intermediate base) API &lt; 33 (Naphthenic base)</td>
<td></td>
</tr>
<tr>
<td>No. 2</td>
<td>527-572°F</td>
<td>1 atm.</td>
<td>&gt; 30 (Paraffinic base) &lt; 22 (Naphene Base) 22 &lt; API &lt; 30 (Intermediate base)</td>
<td>The presence of wax is noted by cloud point (if below 5°F) it indicates little wax (wax free)</td>
</tr>
<tr>
<td></td>
<td>733-779°F</td>
<td>40-mm Hg</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.4 Specific Gravity and API Gravity

Specific gravity and API gravity are expressions of the density or weight of a unit volume of liquid fuels. Specific gravity and API (American Petroleum Institute) gravity refer to the weight per unit volume at 60°F as compared to water at 60°F (15.6°C).

Density of a liquid is defined as the mass of a liquid per unit volume at a given temperature. Specific gravity (or relative density) is the ratio of the density of a liquid to the density of water at a given temperature.

The units of API gravity are °API and can be calculated from specific gravity by the following:

\[
API \, Gravity = \frac{141.4}{sp. \, gr. @ 60^\circ F / 60} - 131.5
\]
For a blend, the API gravity is given as:

\[(\text{API})_{\text{mix}} = (\text{API})_a \cdot W_a + (\text{API})_b \cdot W_b + (\text{API})_c \cdot W_c + \ldots.\]

\(\text{API}_a\) is API gravity of component A, \(W\) is the weight fraction of the mixture.
3.5 Correlation Index (CI)

It is related to boiling point and sp.gr, and it can be calculated as below:

\[ CI = \frac{48640}{T_B} + 473.7 \times S - 456.8 \]

Where, \( T_B \)= boiling point (K) in degrees Kelvin

\( S \)=Sp. Gravity at 60 (°F)

The normal paraffin series is given a value of CI = 0 and for aromatics is given as CI = 100. Thus, Values for the index between 0 and 15 indicate a predominance of paraffin hydrocarbons in the fraction. A value from 15 to 50 indicates predominance of either naphthenes or of mixtures of paraffins, naphthenes, and aromatics. An index value more than 50 indicates a predominance of aromatic species. The value is not quantitative hence a relative indication of the groups is only possible.

C.I for Parafine =0

C.I for Benzene =100

C.I =0-15 Parafine
C.I = 15-50 either Naphtenes or mix (Parafine + Naphtenes)

C.I = above 50 Aromatic

### 3.6 UOP Characterization Factor (K)

The Universal Oil Product (UOP) characterization factor or Watson ‘‘characterization factor’’ of a hydrocarbon is defined by the following eq.

\[
Kw = \frac{\sqrt[3]{R}}{0.827 \ s} = \frac{\sqrt[3]{T^\circ}}{s}
\]

Where \( R \) and \( T^\circ \) is the average boiling point in degrees Kelvin (\(^\circ\)K = \(^\circ\)C + 273) and Rankine (\(^\circ\)R=\(^\circ\)F + 460) respectively, and \( s \) is the specific gravity at 60 \(^\circ\)F.

It was originally devised to show the thermal cracking characteristics of oils; thus, The Watson characterization factor ranges from less than 10 for highly aromatic materials to almost 15 for highly paraffinic compounds. Crude oils show a narrower range of \( Kw \) and vary from 10.5 for highly naphthenic crude to 12.9 for paraffinic base crude.

- \( K < 10 \) highly aromatic
  - 10.5 for a highly naphthenic crude to 12.9 for a paraffinic base crude
  - 15 for highly paraffinic compounds

| \( K \geq 12.15 \) (Paraffinic Base) | \( K < 11.5 \) (Naphthene Base) | \( K \) between 11.5-12.15 (Intermediate Base) |

K-value of a mixture is defined as follow

\[
K_{mix} = K_1W_1 + K_2W_2 + K_3W_3 + \ldots
\]

Where \( K_n \) are K factor, and \( W_n \) are weight fractions of different components.
3.7 Viscosity Index (V.I)

A series of number ranging from 0-100 which indicate the rate of change of viscosity with temperature.

Paraffinic base C.O  V.I =100
Naphthenic base C.O V.I = 40
Some Naphthenic base C.O V.I =0

Intermediate oils were rated by the formula:

The viscosity index can be calculated using the following formula:

\[ VI = 100 \frac{(L - U)}{(L - H)} \]

Where V indicates the viscosity index, U the kinematic viscosity at 40 °C (104 °F), and L & H are various values based on the kinematic viscosity at 100 °C (212 °F) available in ASTM D2270.

Where L and H are the viscosities of the zero and 100 index reference oils, both having the same viscosity at 998°C (2108°F), and U is that of the unknown, all at 388°C (1008°F).

Example

Calculate viscosity index, VI of oil, the measure kinematic viscosity at 40 °C of the oil whose viscosity index is to be calculated = 73.3 mm2 / s (cSt), and kinematic viscosity at 100° C of the oil whose viscosity index is to be calculated = 8.86mm2 / s(cSt)

From table 1 (by interpolation) L = 119.94
From table (by interpolation) H = 69.48

\[ VI = 100 \frac{(119.94 - 73.30)}{(119.94 - 69.48)} = 92.43 \]

Then say VI = 92
### TABLE 1 Basic Values for L and H for Kinematic Viscosity in 40–100°C System

<table>
<thead>
<tr>
<th>Kinematic Viscosity at 100°C, mm²/s</th>
<th>L</th>
<th>H</th>
<th>Kinematic Viscosity at 100°C, mm²/s</th>
<th>L</th>
<th>H</th>
<th>Kinematic Viscosity at 100°C, mm²/s</th>
<th>L</th>
<th>H</th>
</tr>
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<tbody>
<tr>
<td>2.00</td>
<td>7.994</td>
<td>6.394</td>
<td>2.10</td>
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<td>2.20</td>
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<td>7.944</td>
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### TABLE 2 Values for L and H for Kinematic Viscosity in 100°C System

<table>
<thead>
<tr>
<th>Kinematic Viscosity at 100°C, mm²/s</th>
<th>L</th>
<th>H</th>
<th>Kinematic Viscosity at 100°C, mm²/s</th>
<th>L</th>
<th>H</th>
<th>Kinematic Viscosity at 100°C, mm²/s</th>
<th>L</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.00</td>
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### TABLE 3 Values for L and H for Kinematic Viscosity in 200°C System

<table>
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<th>Kinematic Viscosity at 200°C, mm²/s</th>
<th>L</th>
<th>H</th>
<th>Kinematic Viscosity at 200°C, mm²/s</th>
<th>L</th>
<th>H</th>
<th>Kinematic Viscosity at 200°C, mm²/s</th>
<th>L</th>
<th>H</th>
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Properties of Petroleum and Natural Gas
2nd Stage/Chemical Eng. Dept.
Asst. Professor Hamed Hussein Alwan