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.

\[
\begin{align*}
\text{CH}_3\text{SH} & \quad \text{Methyl mercaptan} \\
\text{Cyclohexylthiol} & 
\end{align*}
\]

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

\[
\begin{align*}
\text{SH} & 
\end{align*}
\]

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.
3. **Organic Sulfides**

These compounds are of two types, the noncyclosulfide and the cyclosulfides:

![Chemical Structures](image)

- **Dimethyl sulfide**
- **Ethyl Methyl Sulfide**
- **Thiocyclohexane**

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.

![Dimethyl disulfide](image)

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 H$_2$S. High-sulfur crudes are less desirable because treating the different refinery streams for acidic H$_2$S 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 (C$_5$H$_5$N) and pyrrole (C$_4$H$_5$N), 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:
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**

![Pyridine, Quinoline, Isoquinoline, Acridine](image)

**Non-Basic Nitrogen Compounds**

![Pyrrole, Indole, Carbazole, Benzocarbazole](image)

Porphyrids 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. Porphyrids can be cracked at temperatures ranging from 200 to 250°C. The basic structural unit of porphyrids is as following:
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.

\[
\text{CH}_2(\text{CH}_2)_n\text{COOH} \\
\text{An aliphatic carboxylic acid}
\]

Some acidic oxygen compounds

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 $\text{Na}^+, \text{Ba}^{2+}, \text{Mg}^{2+}, \text{Al}^{3+}, \text{Ca}^{2+}, \text{K}^+, \text{Si}^{2+}$ and negative ions $\text{Cl}^-, \text{Br}^-, \text{SO}_4^{2-}, \text{HCO}_3^-, \text{CO}_3^{2-}, \text{NO}_2^{-1}$ 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.