2.1 Petroleum Definition:

Petroleum (also called crude oil) is a naturally mixture of hydrocarbons, generally in the liquid state, that may also include compounds of sulfur, nitrogen, oxygen, and metals and other elements (ASTM D-4175). Inorganic sediment and water may also be present. The elementary composition of crude oil usually falls within the following ranges:

<table>
<thead>
<tr>
<th>Element</th>
<th>Percent by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>84–87</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>11–14</td>
</tr>
<tr>
<td>Sulfur</td>
<td>0–3</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0–0.6</td>
</tr>
</tbody>
</table>

Crude oils are classified as:

- paraffin base,
- naphthene base,
- asphalt base,
There are some crude oils which have up to 80% aromatic content, and these are known (as aromatic-base oil). Attempts have been made to define or classify petroleum based on various distillation properties when combined with another property such as density. It has been suggested that a crude should be called asphaltic if the distillation residue contained less than 2% wax and paraffinic if it contained more than 5%.

**COMPOSITION OF PETROLEUM**

Crude oils and high-boiling crude oil fractions are composed of many members of a relatively few homologous series of hydrocarbons. Petroleum is essentially a mixture of hydrocarbons, and even the non-hydrocarbon elements are generally present as components of complex molecules predominantly hydrocarbon in character, but containing small quantities of oxygen, sulfur, nitrogen, vanadium, nickel, and chromium. The hydrocarbons present in crude petroleum are classified into three general types: 1-paraffins, 2-naphthenes, 3-and aromatics. In addition, there is a fourth type, olefins, that is formed during processing by the dehydrogenation of paraffins and naphthenes.
Paraffins:

- 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 paraffins 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.2). 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. 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 isoctane (2,2,4-trimethyl pentane) is 100.
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 \( \text{C}_n\text{H}_{2n} \). Olefins are generally undesirable in finished products because: (the double bonds are reactive and the compounds are more easily oxidized and polymerized to form gums and varnishes).

In gasoline boiling-range fractions, some olefins are desirable because olefins have higher research octane numbers than paraffin compounds with the same number of...
carbon atoms. Olefins containing five carbon atoms have high reaction rates with compounds in the atmosphere that form pollutants and, even though they have high research octane numbers, are considered generally undesirable.

- Some diolefins (containing two double bonds) are 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.

**Naphthenes (Cycloparaffins)**

- Cycloparaffin hydrocarbons in which all of the available bonds of the carbon atoms are saturated with hydrogen are called naphthenes. There are many types of naphthenes present in crude oil, but, except for the lower-molecular-weight compounds such as cyclopentane and cyclohexane, are generally not handled as individual compounds.

- They are classified according to boiling range and their properties determined with the help of correlation factors such as the KW factor or CI. Some typical naphthenic compounds are shown in Figure 3.
Aromatics

- The aromatic series of hydrocarbons is chemically and physically very different from the paraffins and cycloparaffins (naphthenes). Aromatic hydrocarbons contain a benzene ring which is unsaturated but very stable and frequently
behaves as a saturated compound. Some typical aromatic compounds are shown in Figure 4.

- The cyclic hydrocarbons, both naphthenic and aromatic, can add paraffin side chains in place of some of the hydrogen attached to the ring carbons and form a mixed structure. These mixed types have many of the chemical and physical characteristics of both of the parent compounds, but generally are classified according to the parent cyclic compound.

![Chemical structures of aromatic hydrocarbons](image)

*Benzene, Toluene, Ethylbenzene, Ortho-xylene, Meta-xylene, Para-xylene, Cumene, Naphthalene*

*Figure 4. Aromatic hydrocarbons in crude oil.*
CRUDE OIL PROPERTIES

Crude petroleum is very complex and, except for the low-boiling components, no attempt is made by the refiner to analyze for the pure components contained in the crude oil. Relatively simple analytical tests are run on the crude and the results of these are used with empirical correlations to evaluate the crude oils as feedstocks for the particular refinery. The more useful properties are:

**API Gravity**

The density of petroleum oils is expressed in the United States in terms of API gravity rather than specific gravity; it is related to specific gravity in such a fashion that an increase in API gravity corresponds to a decrease in specific gravity. The units of API gravity are °API and can be calculated from specific gravity by the following:

\[
°API = \frac{141.5}{sp.gr} - 131.5 \quad (1)
\]

In equation (1), specific gravity and API gravity refer to the weight per unit volume at 60°F as compared to water at 60°F. Crude oil gravity may range from less than 10API to over 50API but most crudes fall in the 20 to 45API range. API gravity always refers to the liquid sample at 60°F (15.6°C).
Crude oils can generally be classified according to gravity as shown in table 2.

**Table 2: Classification of crude oils**

<table>
<thead>
<tr>
<th>Crude Category</th>
<th>Gravity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Light crudes</td>
<td>API &gt; 38</td>
</tr>
<tr>
<td>Medium crudes</td>
<td>38 &gt; API &gt; 29</td>
</tr>
<tr>
<td>Heavy crudes</td>
<td>29 &gt; API &gt; 8.5</td>
</tr>
<tr>
<td>Very heavy crudes</td>
<td>API &lt; 8.5</td>
</tr>
</tbody>
</table>

**Carbon Residue, Asphaltene Content %**

The carbon residues of petroleum and petroleum products serve as an indication of the propensity of the sample to form carbonaceous deposits (thermal coke) under the influence of heat.

The carbon residue is roughly related to the asphalt content of the crude and to the quantity of the lubricating oil fraction that can be recovered. In most cases the lower the carbon residue, the
more valuable the crude. This is expressed in terms of the weight percent carbon residue by either the Ramsbottom (RCR) or Conradson (CCR) ASTM test procedures (D-524 and D-189).

The asphaltene fraction 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.

**Characterization Factors**

There are several correlations between yield and the aromaticity and paraffinic content of crude oils, but the two most widely used are the UOP or Watson “characterization factor” ($K_W$) and the U.S. Bureau of Mines “correlation index” (CI).

\[ K_W = \frac{T_B}{G} \]  \hspace{1cm} (2)

\[ CI = \frac{87.552 + 473.7G - 456.8}{T_B} \]  \hspace{1cm} (3)

$T_B$ = mean average boiling point, °R

$G$ = specific gravity at 60°F.
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 $K_W$ and vary from 10.5 for highly naphthenic crude to 12.9 for paraffinic base crude.

The correlation index is useful in evaluating individual fractions from crude oils. The CI scale is based upon straight-chain paraffins having a CI value of 0 and benzene having a CI value of 100. The CI values are not quantitative, but the lower the CI value, the greater the concentrations of paraffin hydrocarbons in the fraction; and the higher the CI value, the greater the concentrations of naphthenes and aromatics.

**Sulfur Content, wt%**

Sulfur content and API gravity are two properties which have had the greatest influence on the value of crude oil, although nitrogen and metals contents are increasing in importance. The sulfur content is expressed as percent sulfur by weight and varies from less than 0.1% to greater than 5%. Crudes with greater than 0.5% sulfur generally
require more extensive processing than those with lower sulfur content. Although the term “sour” crude initially had reference to those crudes containing dissolved hydrogen sulfide independent of total sulfur content, it has come to mean any crude oil with a sulfur content high enough to require special processing. There is no sharp dividing line between sour and sweet crudes, but 0.5% sulfur content is frequently used as the criterion.

**Viscosity and Pour Point**

**Viscosity** and **pour point** determinations are performed principally to ascertain the handling (flow) characteristics of petroleum at low temperatures. There are, however, some general relationships of crude oil composition that can be derived from pour point and viscosity data. Commonly, the lower the pour point of a crude oil the more aromatic it is, and the higher the pour point the more paraffinic it is. Viscosity is usually determined at different temperatures (e.g., 25°C/77°F, and 100°C/212°F) by measuring the time for a volume of liquid to flow under gravity through a calibrated glass capillary viscometer (ASTM D-445).
In the test, the time for a fixed volume of liquid to flow under gravity through the capillary of a calibrated viscometer under a reproducible driving head and at a closely controlled temperature is measured in seconds.

The **kinematic viscosity** is the product of the measured flow time and the calibration constant of the viscometer. Conversion of the kinematic viscosity in centistokes (cSt) at any temperature to Saybolt Universal viscosity in Saybolt Universal seconds (SUS) at the same temperature and for converting kinematic viscosity in centistokes at 122 and 210°F to Saybolt Furol viscosity in Saybolt Furol seconds (SFS) at the same temperatures (ASTM D-2161) is available through formulae.

The **viscosity index** (ASTM D-2270, IP 226): is a widely used measure of the variation in kinematic viscosity due to changes in the temperature of petroleum between 40°C and 100°C (104°F and 212°F). For crude oils of similar kinematic viscosity, the higher the viscosity index the smaller is the effect of temperature on its kinematic viscosity. The accuracy of the calculated viscosity index is dependent only on the accuracy of the original viscosity determination.

The **pour point** of petroleum: is an index of the lowest temperature at which the crude oil will flow under specified conditions. It is a rough indicator of the relative paraffinicity and aromaticity of the crude. The lower the pour point, the lower the paraffin content and the greater the content of aromatics.
Water, salt and Sediment

Considerable importance is attached to the presence of water or sediment in petroleum because they lead to difficulties in the refinery, for example, corrosion of equipment, uneven running on the distillation unit, blockages in heat exchangers, and adverse effects on product quality in heat exchangers, and adverse effects on product quality.

Sediment in petroleum can be determined simultaneously (ASTM D-96, ASTM D-4007, IP 359) by:

1. the centrifuge method.
2. an extraction method (ASTM D-473, IP 53)
3. or by membrane filtration.

Most of the salts are dissolved in the water, and the remainder is present in the oil as fine crystals. Chlorides of magnesium, calcium and sodium are the most common salts. The presence of salts causes problems in processing, such as corrosion, erosion and plugging of equipment, and catalyst deactivation.

To determine the composition of the salts present, it is necessary used:
1- atomic absorption,
2- inductively coupled argon plasma emission spectrophotometry
3- ion chromatography.

Metallic 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. For high-temperature power generators, the presence of vanadium in the fuel may lead to ash deposits on turbine blades and cause severe corrosion, and the deterioration of refractory furnace linings.

Part of the metallic constituents of crude oils exist as inorganic water-soluble salts, mainly as chlorides and sulphates of sodium, potassium, magnesium and calcium. These are removed in desalting operations. More important are metals which are present in form of oil-soluble organometallic compounds. Zinc, titanium, calcium and magnesium appear in the form of organometallic soaps. However, vanadium, nickel, copper and iron are present as
oil-soluble compounds, capable of complexing with pyrrole compounds.

Nitrogen Compounds

Crude oils contain very low amounts of nitrogen compounds. In general, the more asphaltic the oil, the higher its nitrogen content. Nitrogen compounds are more stable than sulphur compounds and therefore are harder to remove. Even though they are present at very low concentrations, nitrogen compounds have great significance in refinery operations. They can be responsible for the poisoning of a cracking catalyst, and they also contribute to gum formation in finished products.

Distillation

1-Fractionation

Distillation of crude oils determines the yield of the products that can be obtained from this crude oil when it is processed in a refinery. A light crude oil will produce higher amounts of gasoline than a heavier crude oil. Different standard distillation tests can be performed on crude oil or petroleum fractions.

2-True Boiling Point Distillation
The boiling point distribution of crude oil (boiling point versus volume or mass percent distilled) is obtained through a batch distillation test ASTM 2892. The distillation apparatus has 15–18 theoretical plates with a 5:1 reflux ratio. For boiling points below 340°C (644 °F) the distillation is performed at atmospheric pressure. The residue is distilled under vacuum (1–10 mm Hg). The boiling points under vacuum are converted to normal boiling points.

The distillation continues to a normal boiling point of 535 °C (995 °F). This test allows for the collection of sample cuts at different boiling point ranges. These cuts can be subjected to physical and chemical measurements.

3–ASTM Distillation

The distillation of petroleum cuts is done in a simple distillation apparatus which does not have a fractionation column. For light cuts (gasoline, kerosene, diesel and heating oil) the distillation is run at atmospheric pressure under ASTM D86 test. For heavier fractions an ASTM D1160 test at reduced pressure is employed.
4-Simulated Distillation by Gas Chromatography

The boiling point distribution of the whole crude oil can be determined by an injection of the sample in a gas chromatograph which separates the hydrocarbons in boiling point order. The retention time is related to the boiling point through a calibration curve. The results of this test are comparable to the true boiling point tests. In addition, the boiling point distribution of light and heavy petroleum cuts can also be done by gas chromatography. One of the standards methods of measurements is ASTM D5307.

Usually seven fractions provide the basis for a reasonably thorough evaluation of the distillation properties of the feedstock (as shown in table 3):

1. Gas, boiling range: <15.5°C (60°F)
2. Gasoline (light naphtha), boiling range: 15.5–149°C (60–300°F)
3. Kerosene (medium naphtha), boiling range: 149–232°C (300–450°F)
5. Light vacuum gas oil, boiling range: 343–371°C (650–700°F)
6. Heavy vacuum gas oil, boiling range: 371–566°C (700–1050°F)
7. Residuum, boiling range: >566°C (1050°F)
### Table 3  Fractions Obtained from Arabian Crude

<table>
<thead>
<tr>
<th>Fractions</th>
<th>Percent yield</th>
<th>No. of carbon atoms in molecule</th>
<th>Boiling range (°F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gases (dry/wet)</td>
<td>2</td>
<td>1–2</td>
<td>−260 to −130 dry</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3–4</td>
<td>−55 to 30 wet</td>
</tr>
<tr>
<td>Naphtha</td>
<td>20–26</td>
<td>5–12</td>
<td>90–360</td>
</tr>
<tr>
<td>Kerosene</td>
<td>7–12</td>
<td>10–15</td>
<td>320–460</td>
</tr>
<tr>
<td>Diesel oil</td>
<td>10–14</td>
<td>12–20</td>
<td>400–600</td>
</tr>
<tr>
<td>Wax distillate</td>
<td>15–20</td>
<td>17–22</td>
<td>500–700</td>
</tr>
<tr>
<td>Residuum</td>
<td>35–40</td>
<td>20–90</td>
<td>600+</td>
</tr>
</tbody>
</table>

### Table 1.2  Crude distillation products (Gary and Handwerk, 2001)

<table>
<thead>
<tr>
<th></th>
<th>Yield (wt%)*</th>
<th>True boiling temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atmospheric distillation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Refinery gases (C₁ – C₂)</td>
<td>0.10</td>
<td>–</td>
</tr>
<tr>
<td>Liquid petroleum gases (LPG)</td>
<td>0.69</td>
<td>–</td>
</tr>
<tr>
<td>Light straight run (LSR)</td>
<td>3.47</td>
<td>32–82 (90–180 °F)</td>
</tr>
<tr>
<td>Heavy straight run (HSR)</td>
<td>10.17</td>
<td>82–193 (180–380 °F)</td>
</tr>
<tr>
<td>Kerosene (Kero)</td>
<td>15.32</td>
<td>193–271 (380–520 °F)</td>
</tr>
<tr>
<td>Light gas oil (LGO)</td>
<td>12.21</td>
<td>271–321 (520–610 °F)</td>
</tr>
<tr>
<td>Heavy gas oil (HGO)</td>
<td>21.10</td>
<td>321–427 (610–800 °F)</td>
</tr>
<tr>
<td>Vacuum distillation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vacuum gas oil (VGO)</td>
<td>16.80</td>
<td>427–566 (800–1050 °F)</td>
</tr>
<tr>
<td>Vacuum residue (VR)</td>
<td>20.30</td>
<td>+566 (+1050 °F)</td>
</tr>
</tbody>
</table>

*The yields quoted here depend on feed composition and properties. In this case feed API was 26.3.
petroleum gas describes liquefied petroleum gas, natural gas and refinery gas, the composition of each gas varies (Table 1):

<table>
<thead>
<tr>
<th>Product</th>
<th>Lower Carbon Limit</th>
<th>Upper Carbon Limit</th>
<th>Lower Boiling Point °C</th>
<th>Upper Boiling Point °C</th>
<th>Lower Boiling Point °F</th>
<th>Upper Boiling Point °F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Refinery gas</td>
<td>C₁</td>
<td>C₄</td>
<td>-161</td>
<td>-1</td>
<td>-259</td>
<td>31</td>
</tr>
<tr>
<td>Liquefied petroleum gas</td>
<td>C₃</td>
<td>C₄</td>
<td>-42</td>
<td>-1</td>
<td>-44</td>
<td>31</td>
</tr>
<tr>
<td>Naphtha</td>
<td>C₃</td>
<td>C₁₇</td>
<td>36</td>
<td>302</td>
<td>97</td>
<td>575</td>
</tr>
<tr>
<td>Gasoline</td>
<td>C₄</td>
<td>C₁₂</td>
<td>-1</td>
<td>216</td>
<td>31</td>
<td>421</td>
</tr>
<tr>
<td>Kerosene/diesel fuel</td>
<td>C₅</td>
<td>C₁₅</td>
<td>126</td>
<td>258</td>
<td>302</td>
<td>575</td>
</tr>
<tr>
<td>Aviation turbine fuel</td>
<td>C₈</td>
<td>C₁₆</td>
<td>126</td>
<td>287</td>
<td>302</td>
<td>548</td>
</tr>
<tr>
<td>Fuel oil</td>
<td>C₁₂</td>
<td>&gt;C₂₀</td>
<td>216</td>
<td>421</td>
<td>&gt;343</td>
<td>&gt;649</td>
</tr>
<tr>
<td>Lubricating oil</td>
<td>&gt;C₂₀</td>
<td>&gt;343</td>
<td>&gt;649</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wax</td>
<td>C₁₇</td>
<td>&gt;C₂₀</td>
<td>302</td>
<td>&gt;343</td>
<td>575</td>
<td>&gt;649</td>
</tr>
<tr>
<td>Asphalt</td>
<td>&gt;C₂₀</td>
<td>&gt;343</td>
<td>&gt;649</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coke</td>
<td>&gt;C₅₀*</td>
<td>&gt;1000*</td>
<td>&gt;1832*</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
**Natural gas**

Natural gas is found in petroleum reservoirs as:
- *associated gas*
- in solution with petroleum in the reservoir (*dissolved gas*),
- in reservoirs that contain only gaseous constituents and no (or little) petroleum (*unassociated gas*).

The hydrocarbon content varies from mixtures of methane and ethane with very few other constituents (*dry gas*) to mixtures containing all of the hydrocarbons from methane to pentane and even hexane (C₆H₁₄) and heptane (C₇H₁₆) (*wet gas*). In both cases, some carbon dioxide (CO₂) and inert gases, including helium (He), are present together with hydrogen sulfide (H₂S) and a small quantity of organic sulfur. Raw natural gas varies greatly in composition (Table 3.2), and the constituents can be several of a group hydrocarbons (Table 3.3) and non-hydrocarbons.
Carbon dioxide in excess of 3% is normally removed for reasons of corrosion prevention. Hydrogen sulfide is also removed, and the odor of the gases must not be objectionable.
so mercaptan content is important and the odor of the gases must not be objectionable so mercaptan content is important.

The natural gas after appropriate treatment for acid gas reduction, odorization, and hydrocarbon and moisture dew point adjustment would then be sold within prescribed limits of pressure, calorific value, and possibly Wobbe index [cv/(sp. gr.)].

**Refinery gas**

*Refinery gas* is the noncondensable gas that is obtained during distillation or treatment (cracking, thermal decomposition) of petroleum. It consists mainly of hydrogen (H₂), methane (CH₄), ethane (C₂H₆), propane (C₃H₈), butane (C₄H₁₀), and olefins (RCH=CHR₁, where R and R¹ can be hydrogen or a methyl group) and may also include off-gases from petrochemical processes (Table 3). Olefins such as ethylene (ethene, CH₂=CH₂, boiling point: −104°C, −155°F), propene (propylene, CH₃CH=CH₂, boiling point: −47°C, −53°F), butene (butene-1, CH₃CH₂CH=CH₂, boiling point: −5°C, 23°F) iso-butylene [(CH₃)₂C=CH₂, boiling point −6°C, 21°F], *cis*– and *trans*-butene-2 (CH₃CH=CHCH₃, boiling point: −1°C, 30°F), and butadiene (CH₂=CHCH=CH₂, boiling point: −4°C, 24°F) as well as higher-boiling olefins are produced by various refining processes.
Residual refinery gases, usually in more than one stream, which allows a degree of quality control, are treated for hydrogen sulfide removal, and gas sales are usually on a thermal content (calorific value, heating value) basis with some adjustment for variation in the calorific value and hydrocarbon type.

Liquefied Petroleum Gas

*Liquefied petroleum gas* (LPG) is a mixture of the gaseous hydrocarbons propane (CH$_3$CH$_2$CH$_3$, boiling point: –42°C, –44°F) and butane (CH$_3$CH$_2$CH$_2$CH$_3$, boiling point: 0°C, 32°F) that are produced during natural gas refining, petroleum stabilization, and petroleum refining.

The propane and butane can be derived:

- from natural gas or
- from refinery operations
  - but in the latter case substantial proportions of the corresponding olefins will be present and must be separated. The hydrocarbons are normally liquefied under pressure for transportation and storage.
Liquefied petroleum gas is usually available in different grades (usually specified as:
- Commercial Propane
- Commercial Butane
- Commercial Propane-Butane (P-B) Mixtures
- Special Duty Propane.

*Commercial Propane* consists of propane and/or propylene, *Commercial Butane* is mainly composed of butanes and/or butylene
Both must be free from:
1. harmful amounts of toxic constituents
2. free from mechanically entrained water
Analysis by gas chromatography is possible.

*Commercial Propane-Butane mixtures* are produced to meet particular requirements such as (volatility, vapor pressure, specific gravity, hydrocarbon composition, sulfur and its compounds, corrosion of copper, residues, and water content). These mixtures are used as fuels, analysis by gas chromatography is possible.

*Special Duty Propane* is intended for use in spark-ignition engines, and the specification includes a minimum *motor octane number* to ensure satisfactory antiknock performance.

*Liquefied petroleum gas* and *liquefied natural gas* can stored and transported as a liquid and then vaporized and used as a gas. To achieve this, liquefied petroleum gas must be maintained at a moderate pressure but at ambient temperature. The liquefied natural gas can be at ambient pressure but must be maintained at a temperature of roughly −1 to 60°C (30–140°F).
The contaminants of liquefied petroleum gas are:

- The contaminants of liquefied petroleum gas are controlled at a level at which they do not corrode fittings and appliances or impede the flow of the gas. For example, hydrogen sulfide (H₂S) and carbonyl sulfide (COS) should be absent but Organic sulfur such as dimethyl sulfide (CH₃SCH₃) and ethyl mercaptan (C₂H₅SH) are commonly used at a concentration of up to 50 ppm, required for adequate odorization.

- Liquefied petroleum gas may also be contaminated by higher-boiling constituents such as the constituents of middle distillates to lubricating oil must be prevented from reaching unacceptable levels.

- Olefins and especially diolefins are prone to polymerization and should be removed.

**SAMPLING**

Sampling liquefied petroleum gas from a liquid storage system is complicated by existence of two phases (gas and liquid), and the composition of the supernatant vapor phase will, differ from the composition of the liquid phase. The sampling of gaseous constituents and of liquefied gases is the subject of a variety of sampling methods such as:

- the manual method
- the floating piston cylinder method
- and the automatic sampling.

- Sampling methane (CH₄) and ethane (C₂H₆) hydrocarbons is usually achieved using stainless steel cylinders
- For sampling propane (C₃H₈) and butane (C₄H₁₀) hydrocarbons is by the use of piston cylinders.
Piston cylinders or pressurized steel cylinders are recommended for high vapor-pressure sampling where significant amounts of low-boiling gases are present, whereas atmospheric sampling may be used for samples having a low vapor pressure.

PROPERTIES AND TEST METHODS

1- Calorific Value (Heat of Combustion)

A fuel's calorific value measures the energy it releases when it burns in oxygen. A bomb calorimeter measures this energy by using it to heat a known mass of water. Or

Definitions:
- a) Gross Calorific Value of a gas the quantity of heat liberated by the combustion of unit volume of gas.
- b) net calorific Value of a gas is the gross calorific value minus the latent in the water produced by combustion of hydrogen in the gas above atmospheric temperature.

Units:
- Mega joule per cubic meter at s .t .p .(MJ m\(^{-3}\))
- B.t.u./ft\(^3\) s .t .p
- K cal/ m\(^3\) s .t .p

There are various types of test methods are available for the direct determination of calorific value(ASTM D-900, ASTM D-1826, ASTM D-3588, ASTM D-4981). The most important of these are the Wobbe index [WI; or Wobbe number = calorific value/ (specific gravity)].
3. Density

The density of light hydrocarbons can be determined by several methods including
- a hydrometer method (ASTM D-1298)
- and a pressure hydrometer method.

Sulfur

The manufacturing processes for liquefied petroleum gas are designed of the sulfur compounds are removed. The total sulfur level is therefore considerably lower than for other petroleum fuels, and a maximum limit for sulfur content helps to define the product more completely. The sulfur compounds that are mainly responsible for corrosion are:
- hydrogen sulfide,
- carbonyl sulfide,
- and, sometimes, elemental sulfur.

Control of the total sulfur content, hydrogen sulfide, and mercaptans ensures that the product is not corrosive. Hydrogen sulfide can be detected by its action on moist lead acetate paper, and a procedure is also used as a measure of sulfur compounds.
Volatility and Vapor Pressure

- Volatility is expressed in terms of the temperature at which 95% of the sample is evaporated and presents a measure of the least volatile component present (ASTM D-1837).

- Vapor pressure (IP 410) is, therefore, a measure of the most extreme low-temperature conditions under which initial vaporization can take place.

- The residue (ASTM D-1025, ASTM D-2158, IP 317), that is, nonvolatile matter, is a measure of the concentration of contaminants boiling above 37.8°C (100°F) that may be present in the gas.

- For natural gasoline, the primary criteria are volatility (vapor pressure) and knock performance. Determination of the vapor pressure (ASTM D-323,) and distillation profile (ASTM D-216, IP 191) is essential. Knock performance is determined by both the motor method (ASTM D-2700, IP 236) and the research method (ATSM-2699, IP 237).
Water

It is a fundamental requirement that liquefied petroleum gas should not contain free water (ASTM D-2713). Dissolved water may give trouble by:

- forming hydrates
- and giving moisture vapor in the gas phase. Both of these will lead to blockages.

Test methods are available to determine the presence of water using electronic moisture analyzers (ASTM D-5454), dew-point temperature (ASTM D-1142).
NAPHTHA

*Naphtha* is a liquid petroleum product that boils from about 30°C (86°F) to approximately 200°C (392°F), although there are different grades of naphtha within this extensive boiling range that have different boiling ranges. Naphtha is difficult to define precisely because it can contain varying amounts of its constituents (paraffins, naphthenes, aromatics, and olefins) in different proportions, in addition to the potential isomers of the paraffins that exist in the naphtha boiling range (Tables 1 and 2).

<table>
<thead>
<tr>
<th>Product</th>
<th>Lower Carbon Limit</th>
<th>Upper Carbon Limit</th>
<th>Lower Boiling Point °C</th>
<th>Upper Boiling Point °C</th>
<th>Lower Boiling Point °F</th>
<th>Upper Boiling Point °F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Refinery gas</td>
<td>C₁</td>
<td>C₄</td>
<td>−161</td>
<td>−1</td>
<td>−259</td>
<td>31</td>
</tr>
<tr>
<td>Liquefied petroleum gas</td>
<td>C₃</td>
<td>C₄</td>
<td>−42</td>
<td>−1</td>
<td>−44</td>
<td>31</td>
</tr>
<tr>
<td>Naphtha</td>
<td>C₂</td>
<td>C₁₇</td>
<td>36</td>
<td>302</td>
<td>97</td>
<td>575</td>
</tr>
<tr>
<td>Gasoline</td>
<td>C₄</td>
<td>C₁₂</td>
<td>−1</td>
<td>216</td>
<td>31</td>
<td>421</td>
</tr>
<tr>
<td>Kerosene/diesel fuel</td>
<td>C₈</td>
<td>C₁₈</td>
<td>126</td>
<td>258</td>
<td>302</td>
<td>575</td>
</tr>
<tr>
<td>Aviation turbine fuel</td>
<td>C₈</td>
<td>C₁₆</td>
<td>126</td>
<td>287</td>
<td>302</td>
<td>548</td>
</tr>
<tr>
<td>Fuel oil</td>
<td>C₁₂ &gt; C₂₀</td>
<td></td>
<td>216</td>
<td>421</td>
<td>&gt;343</td>
<td>&gt;649</td>
</tr>
<tr>
<td>Lubricating oil</td>
<td>&gt;C₂₀</td>
<td>&gt;C₂₀</td>
<td>&gt;343</td>
<td>&gt;649</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wax</td>
<td>C₁₇ &gt; C₂₀</td>
<td>&gt;C₂₀ &gt; C₅₀</td>
<td>302</td>
<td>&gt;343</td>
<td>&gt;649</td>
<td>&gt;649</td>
</tr>
<tr>
<td>Asphalt</td>
<td>&gt;C₂₀</td>
<td>&gt;343</td>
<td></td>
<td>&gt;649</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coke</td>
<td>&gt;C₅₀*</td>
<td>&gt;1000*</td>
<td></td>
<td>&gt;1832*</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Naphtha is also represented as having a boiling range and carbon number similar to those of gasoline (Fig. 4.1), being a precursor to gasoline.

These fractions are also referred to as *industrial naphtha*. Other solvents include *white spirit*, which is subdivided into *industrial spirit* [distilling between 30°C and 200°C (86°F–392°F)] and *white spirit* [light oil with a distillation range of 135°C–200°C (275°F–392°F)]. The special value of naphtha as a solvent lies in its stability and purity.
PRODUCTION AND PROPERTIES

Naphtha is produced by any one of several methods:

(1) Fractionation of straight-run, cracked, and reforming distillates or even fractionation of crude petroleum.
(2) solvent extraction;
(3) hydrogenation of cracked distillates;
(4) polymerization of unsaturated compounds (olefins);
(5) alkylation processes.

The more common method of naphtha preparation is distillation. Depending on the design of the distillation unit, either one or two naphtha steam may be produced:

(1) a single naphtha with an end point of about 205°C (400°F) and similar to straight-run gasoline
(2) this same fraction divided into a light naphtha and a heavy naphtha. The end point of the light naphtha is varied to suit the subsequent subdivision of the naphtha into narrower boiling fractions and may be of the order of 120°C (250°F).

Sulfur compounds are most commonly removed or converted to a harmless form by chemical treatment from naphtha especially when it used as a solvent. Naphtha with a small aromatic content has a slight odor, but the aromatics increase the solvent power of the naphtha.

Uses of naphtha are:

(1) by paint,
(2) printing ink
(3) polish manufacturers
(4) in the rubber
(5) Adhesive
TEST METHODS

1-Aniline Point

It is used to estimate the aromatic content of naphtha, aromatic compounds exhibit the lowest aniline points and paraffin compounds have the highest aniline points, with cycloparaffins (naphthenes) and olefins having aniline points between the two extremes. In any homologous series the aniline point increases with increasing molecular weight.

2-Density (Specific Gravity)

Density (the mass of liquid per unit volume at 15°C) and the related terms specific gravity (the ratio of the mass of a given volume of liquid at 15°C to the mass of an equal volume of pure water at the same temperature) and relative density (same as specific gravity) are important properties of petroleum products as they are a part of product sales specifications, although they only play a minor role in studies of product composition.

Usually a hydrometer, pycnometer, or digital density meter is used for the determination in all these standards.
The determination of density (specific gravity) (ASTM D-287, ASTM D-891, (Fig. 4.4) provides a check on the uniformity of the naphtha and permits calculation of the weight per gallon. The temperature at which the determination is carried out and for which the calculations are to be made should also be known (ASTM D-1086).

Figure. 1 Density weighing bottle
3-Flash Point

The flash point is the lowest temperature at atmospheric pressure (760 mmHg, 101.3 kPa) at which application of a test flame will cause the vapor of a sample to ignite under specified test conditions. Flash point data can also indicate the possible presence of highly volatile and flammable constituents in a relatively nonvolatile or nonflammable material. The most common method of determining the flash point confines the vapor (closed cup method) until the instant the flame is applied (ASTM D-56) (Fig. 4.5).

An alternate method that does not confine the vapor (open cup method) (ASTM D-92) gives slightly higher values of the flash point.

4-Composition

An indication of naphtha composition may also be obtained from

- The determination of aniline point (ASTM D-1012, IP2), freezing point (ASTMD-852, ASTM D-1015, ASTM D-1493), cloud point (ASTM D-2500), and solidification point (ASTM D-1493). And, although refinery treatment should ensure no alkalinity and acidity (ASTM D-847,
ASTM D-1093, ASTM D-1613, ASTM D-2896, IP 1) and no olefins present, the relevant tests using bromine number (ASTM D-875, ASTM D-1159, IP130 and flame ionization absorption (ASTM D-1319, IP 156) are necessary to ensure low levels (at the maximum) of hydrogen sulfide (ASTM D-853) as well as the sulfur compounds in general (ASTM D-130, ASTM D-849)

The first level of compositional information is group-type totals as deduced by:

- adsorption chromatography (ASTM D-1319, IP 156) to give volume percentage of saturates, olefins, and aromatics in materials that boil below 315°C (600°F).
- spectrophotometric analysis (ASTM D-1017) determination of aromatics in naphtha include a method (ASTM D-5580) using a flame ionization detector and methods in which a combination of gas chromatography and Fourier transform infrared spectroscopy (GC-FTIR) (ASTM D-5986)
5- Kauri-Butanol Value

The kauri-butanol value (ASTM D-1133) is the number of milliliters of the solvent, at 15°C (77°F), required to produce a defined degree of turbidity when added to 20 g of a standard solution of gum kauri resin in n-butylalcohol. The kauri-butanol value of naphtha is used to determine relative solvent power.

For kauri-butanol values of 60 and higher, the standard is toluene, which has an assigned value of 105, whereas for kauri-butanol values less than 60, the standard is a blend of 75% n-heptane and 25% toluene, which has an assigned value of 40. The kauri-butanol value of products that are classified as:

- regular mineral spirits normally varies between 34 and 44
- xylene is 93
- and aromatic naphtha falls in the range 55–108.

6- Evaporation Rate

The evaporation rate is an important property of naphtha, and although there is a significant relation between distillation range and evaporation rate, the relationship is not straightforward.
7–Odor and Color

Naphtha is refined to a low level of odor to meet the specifications for use.

The paraffinic hydrocarbons possess the mildest odor and the aromatics the strongest, the odor level (ASTM D–268, ASTM D–1296, IP89) being related to the chemical character and volatility of the constituents.

Odors caused by the presence of:

- *sulfur compounds* or
- *unsaturated constituents* are excluded by specification.

And apart from certain high-boiling aromatic fractions, which are usually excluded by volatility from the majority of the naphtha fractions, which may be pale yellow in color, naphtha is usually colorless (water white).
8-Volatility

One of the most important physical parameters is the boiling rangedistribution (ASTM D-86). The significance of the distillation test is the indication of volatility, which dictates the evaporation rate, an important property for naphtha used in coatings and similar applications where the premise is that thenaphtha evaporates over time, leaving the coating applied to the surface.

The determination of the boiling range distribution of distillates such as naphtha and gasoline by gas chromatography (ASTM D-3710) not only helps identify the constituents but also facilitates on-line controls at the refinery.

A simple test for the evaporation properties of naphtha is available (ASTM D-381, IP 131), but the volatility of naphtha is generally considered a measure of its drying time in use, and the temperature of use obviously the choice of naphtha.
In choosing naphtha for a particular purpose it is necessary to:

- relate volatility to the fire hazard associated with its use,
- storage
- transport
- and also with the handling of the products arising from the process.

This is normally based on the characterization of the solvent by flash point limits (ASTM D-56, ASTM D-93, IP 34, IP 170).