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 hydro processing 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 compound.

Disadvantages of Metallic Compounds:

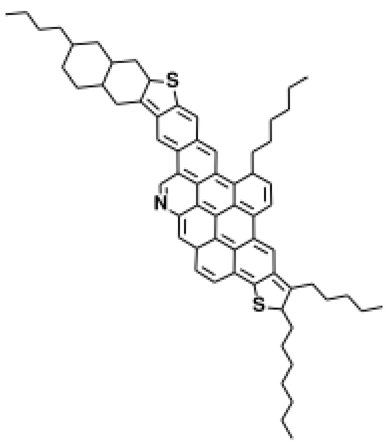
1. Affected on catalyst activity.
2. Reduced the yield of the gasoline
3. Form ash deposits – power generation plants.
4. Causes corrosion of metal equipment and machinery in oil refineries.

Asphaltenes

Asphaltenes are defined as the fraction of crude oil that is insoluble in light alkanes (n-pentane or n-heptane) but soluble in aromatic solvents (e.g., toluene or benzene)

Composition: They consist of complex molecules containing carbon, hydrogen, nitrogen, oxygen, and sulfur, often with trace metals like nickel and vanadium.

Structure: Asphaltenes are highly aromatic and contain polycyclic aromatic hydrocarbons (PAHs) with aliphatic side chains. They form aggregates due to strong intermolecular interactions



An example of possible structure for an asphaltene molecule

Properties of Asphaltenes:

1. **Molecular Weight**: Typically range from 500 to 2000 g/mol, but they can form larger aggregates.
2. Polarity: Highly polar due to heteroatoms (N, O, S) and functional groups.
3. **Solubility**: Insoluble in light alkanes (e.g., n-pentane, n-heptane) and Soluble in aromatic solvents (e.g., toluene, benzene).
4. **Color**: Dark brown to black.
5. Density: Higher than other crude oil components.

Disadvantages of Asphaltenes:

1. **Deposition**:
   - Asphaltenes can precipitate and deposit in pipelines, wells, and production equipment, leading to blockages and reduced flow efficiency.
2. **Refining Challenges**:
   - Asphaltenes contribute to fouling in refineries, clogging heat exchangers and catalysts.
   - They increase the viscosity of heavy crude oils, making transportation and processing more difficult.
3. **Environmental Impact**:
   - Asphaltenes are difficult to degrade and can persist in the environment, contributing to pollution.

Resins

Resins are polar molecules in the molecular weight range of 500–1000, which are insoluble in liquid propane but soluble in n-heptane. The resin molecules surround the asphaltene clusters (micelles) and suspend them in liquid oil. Because each asphaltene is surrounded by a number of resin molecules, the content of resins in crude oils is higher than that of the asphaltenes.

Resins fraction of crude oil comprises polar molecules often containing heteroatoms such as nitrogen, oxygen, or sulfur. The resin fraction is soluble in light alkanes such as pentane and heptane, but insoluble in liquid propane. The H/C ratio of resins is between 1.2 and 1.7 times higher than that of asphaltenes; the H/C ratio of asphaltenes is between 0.9 and 1.2. Resins are structural similar to asphaltenes, but smaller in molecular weight. The resin fraction is very important with regard to crude oil properties. Naphthenic acids are commonly regarded as a part of the resin fraction

Differences between Resins and asphaltenes

1- **Solubility**:
    - **Resins** are soluble in light alkanes (n-pentane or n-heptane) and are more soluble in crude oil.
    - **Asphaltenes** are insoluble in light alkanes but soluble in aromatic solvents like toluene.

2- **Molecular Weight**:
    - Resins generally have lower molecular weights compared to asphaltenes.
    - Asphaltenes are larger and more complex, with higher molecular weights.

3- **Polarity**:
    - Resins are less polar than asphaltenes, though both contain polar functional groups.

4- **Physical State**:
    - Resins are typically viscous liquids or semi-solids.

- Asphaltenes are solid or semi-solid and can precipitate out of solution under certain conditions (changes in pressure, temperature, or composition).

Classification of Petroleum:

1- Classification as a hydrocarbon resource

Petroleum is referred to generically as a fossil energy resource and is further classified as a hydrocarbon resource. For illustrative (or comparative) purposes in this text, coal and oil shale kerogen have also been included in this classification. However, the inclusion of coal and oil shale under the broad classification of hydrocarbon resources has required (incorrectly) that the term hydrocarbon be expanded to include the macro molecular non-hydrocarbon hetero atomic species that constitute coal and oil shale kerogen. The use of the term organic sediments would be more correct. The inclusion of coal and oil shale kerogen in the category hydrocarbon resources is because these two natural resources (coal and oil shale kerogen) will produce hydrocarbons in high-temperature processing. Therefore, if coal and oil shale kerogen are to be included in the term hydrocarbon resources, it is more appropriate that they be classed as hydrocarbon-producing resources under the general classification of organic sediments. Thus, fossil energy resources are divided into two classes:

(1) Naturally occurring hydrocarbons (petroleum, natural gas, and natural waxes).

(2) Hydrocarbon sources (oil, shale, and coal) may be used to generate hydrocarbons by applying conversion processes.

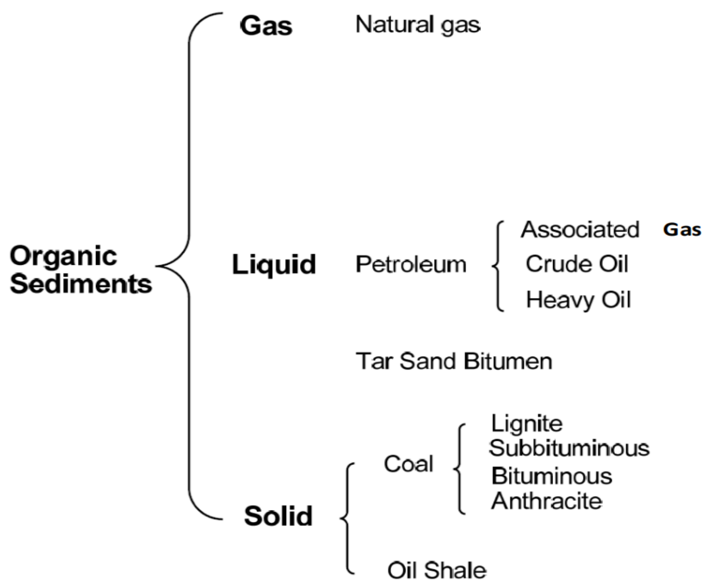


Fig.: Classification of the earth's organic sediments according to hydrocarbon occurrence and Production

The hydrocarbon constituents, separated from petroleum and natural gas, are the hydrocarbon constituents that exist in the reservoir. Naturally occurring hydrocarbons are major contributors to petroleum and natural gas composition. Coal and kerogen do not enjoy this means of separation, and thermal decomposition methods must be applied before producing hydrocarbons. These hydrocarbon products, generated by the thermal process, are not naturally occurring hydrocarbons

2- Classification by:

- Kw
- API
- C.I
- VGC
- S content
- paraffin content
- Molecular Weight
- Pour point
- Carbon Residue
- Salt Content
- Flash point

- **Watson or UOP characterization factor (Kw):** is the oldest of factors and it is defined as

$$\mathbf{Kw} = \frac{(\mathbf{1.8}\boldsymbol{Tb})^{\mathbf{1/3}}}{\boldsymbol{S}}$$

T_b is the boiling temperature (in Rankine **(°R)**) in degrees Rankine, °R = °F + 459.67

S is the standard specific gravity (15.6°/15.6° C).

This characterization factor, which was initially introduced by the research personnel of the Universal Oil Products Company (UOP), This factor is a useful empirical parameter for characterizing the chemical nature and behavior of petroleum fractions, particularly in refining and processing. It is based on the relationship between the **specific gravity** (density) and the **boiling point** of hydrocarbons, as well as their **hydrogen-to-carbon (H/C) ratio**.

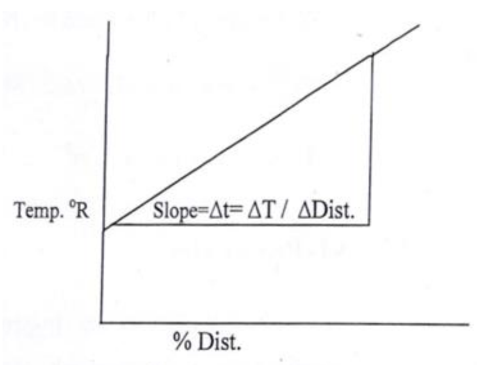
Crude oil classificated by Watson characterization factor as follows:

- **Paraffinic Hydrocarbons**: Have high *Kw* values (typically > 12.5). These hydrocarbons are saturated, with a high H/C ratio, and are chemically stable.
- **Naphthenic Hydrocarbons**: Have intermediate *Kw* values (typically between 11 and 12.5). These contain cyclic structures and have a moderate H/C ratio.
- **Aromatic Hydrocarbons**: Have low *Kw* values (typically < 11). These are unsaturated, with a low H/C ratio, and are more reactive.

As it can be observed in this table there is an overlap between the ranges of this factor for various hydrocarbon families. As a result, the use of this factor will not allow us to identify every hydrocarbon uniquely by a number.

Where:

% Distillate	Temp. oF
0	T0: IBP
10	T1
20	T2
30	T3
40	T4
50	T5
60	T6
70	T7
80	T8
90	T9
95	T10:FBP



IBP:Initial Boiling Point at 0% distillate

FBP:Final Boiling Point at stop distillate.

$T_{av.volume}$ (T1 +T2+T3+T 4+T 5+T 6+T7 +T8+79) / 9

Δt=Slope = (T9-T1)/ (90- 10) = (T9-T1)/ 80

API gravity

The American Petroleum Institute gravity, or API gravity, is a measure of how heavy or light a petroleum liquid is compared to water: if its API gravity is greater than 10, it is lighter and floats on water; if less than 10, it is heavier and sinks

The API gravity scale is inversely related to density, meaning that liquids with higher API gravity are lighter (less dense) than those with lower API gravity.

The formula to calculate API gravity from Specific Gravity (SG) is:

$$\mathbf{API} = \frac{\mathbf{141.5}}{\mathbf{Sp.Gr\ at\ 60°F}} - \mathbf{131}$$

Specific gravity(Sp.Gr) is the ratio of the density of the liquid to the density of water at 60°F (15.6°C).

the specific gravity of petroleum liquids can be derived from their API gravity value as

$$\mathbf{SG\ at\ 60°F} = \frac{\mathbf{141.5}}{\mathbf{API\ gravity + 131.5}}$$

the crude oil classification will be as follows:

when API gravity > 38 crude oil is light

API gravity = 33 - 38 intermediate crude oil

API gravity < 33 heavy crude oil.

API<8.5 Very heavy crudes

Crude oil is classified as light, medium or heavy, according to its measured API gravity.

API gravity determines the grade or quality of crude oils. It is an inverse measure lighter the crude, higher the API gravity, and vice versa.

1- Helps determine the quality and market value of crude oil.
2- Used in refining processes to classify and process different types of crude oil.
3- API gravity helps in planning the transportation and storage of crude oil and petroleum products.

Density is defined as mass per unit volume of a fluid. Density is a state function and, for a pure compound, depends on both temperature and pressure and is shown by ρ. Liquid densities decrease as temperature increases but the effect of pressure on liquid densities at moderate pressures is usually negligible. Liquid density for hydrocarbons is usually reported in terms of specific gravity (SG) or relative density defined as:

$$\mathrm{SG} = \frac{\text{Density of liqued at temparature T}}{\textit{Density of water at temparature T}}$$

Since the standard conditions adopted by the petroleum industry are 60°F (15.5° C) and 1 atm, specific gravities of liquid hydrocarbons are normally reported at these conditions. Water density at 60°F is 0.999 or almost 1 g/cm3 thus:

$$\mathrm{SG}\ (60^{\circ}/60^{\circ}\mathrm{F}) = \frac{Density\ of\ liqued\ at\ 60^{\circ}F\ in\ g/cm3}{0.999 g/cm3}$$

Water density at 60°F is 0.999 or almost 1 g/cm^3; therefore, values of specific gravities are nearly the same as the density of liquid at 15.5°C in s/cm^3. the specific gravity is useful in terms of API gravity, characterization factor and indication of fluid flow of petroleum.

The definition of specific gravity for gases is somewhat different. The specific gravity of a gas is proportional to the ratio of molecular weight of gas (Mg) to the molecular weight of air (28.97)

$$\mathrm{SGg} = \frac{\mathrm{Mg}}{28.97}$$

Viscosity

Dynamic viscosity (μ) is the force in dynes required to move a plane of 1 cm^2 area at a distance of 1 cm from another plane of 1 cm^2 area in 1 sec (is the tangential force per unit area required to move one horizontal plane with respect to another plane). In the cgs system, the unit of viscosity is the poise (gm/cm.s) or centipoise (0.01 P). Fluidity is simply the reciprocal of viscosity.

Types of viscosity:

1- Dynamic viscosity (μ) with units (poise or g/ (cm.s)

2- Kinematic viscosity (*v*) with unit (stoke or cm^2/s).

Dynamic viscosity is the resistance to movement of one layer of a fluid over another. The unit of dynamic viscosity is Pa s. Usually, it is measured in centipoise (cP)

Many types of instruments have been proposed for the determination of dynamic viscosity. The simplest and most widely used are capillary types, and the viscosity is derived from the Hagen-Poiseuille equation

$$\boldsymbol{\eta} = \frac{\boldsymbol{\pi}\mathbf{R}^{2}\boldsymbol{\Delta}\mathbf{Pt}}{\mathbf{8LV}}$$

Where η is the absolute (dynamic) viscosity

ΔP is the pressure drop along the ends of capillary tube (gm/cm^2)

R radius of capillary tube (cm).

t the time of liquid flow through capillary tube (sec)

L the capillary tube length (cm)

V volume of flow liquid through capillary tube (ml)

Kinematic viscosity is defined as the ratio of absolute viscosity to absolute density (p) at the same temperature in the following form:

$$\nu = \frac{\mu}{\rho}$$

It can be measurement by viscometer (U-tube device) by following equation:

$$\nu = c.t$$

Where:

ν: Kinematic viscosity

C: Viscometer constant (mm^2/s^2)

t: time required to passing the oil through the limited marks in viscometer (s)

Factors Affecting Viscosity:

1- Molecular weight
2- density
3- impurity content
4- temperature

Viscosity Index:

The viscosity index is a number indicating the effect of change of temperature on the kinematic viscosity of an oil. A high viscosity index signifies a relatively small change of kinematic viscosity with temperature. Viscosity index increasing with paraffin and decreasine with naphthene.

What Does the Viscosity Index Measure?

- The Viscosity Index quantifies the rate of change of viscosity with temperature.
- A high VI indicates that the oil's viscosity changes **less** with temperature (i.e., it is more stable).
- A low VI indicates that the oil's viscosity changes **more** with temperature.

How is the Viscosity Index Calculated?

The Viscosity Index is calculated using the kinematic viscosities of the oil at two standard temperatures: 40°C and 100°C. The formula is based on empirical relationships and is standardized by organizations like ASTM (ASTM D2270)

Steps to Calculate VI:

Measure Kinematic Viscosity:

- **Determine ν40 and ν100 using a viscometer**
- **Determine L and H**

1. Measure the kinematic viscosity of the oil at **40°C (ν_{40})** and **100°C (ν_{100})**.
2. Use the following formulas:
    - If $\nu_{100} \leq 70$ cSt:

$$\mathbf{VI} = \frac{(\mathbf{L} - \boldsymbol{\nu}\mathbf{40})}{(\mathbf{L} - \mathbf{H})} \times \mathbf{100}$$

- If $\nu_{100} > 70$ cSt

$$\mathbf{VI} = \frac{(\mathbf{L} - \boldsymbol{\nu}\mathbf{40})}{(\mathbf{L} - \mathbf{H})} \times \mathbf{100} + \frac{(\boldsymbol{\nu}\mathbf{100} - \mathbf{100})}{\mathbf{0.85}}$$

Where:

- L and H are constants obtained from ASTM D2270 tables based on ν_{100}.
- L = Viscosity of a low VI oil at 40°C.
- H = Viscosity of a high VI oil at 40°C

Paraffinic Oils (VI ≈ 100)

- **Structure:** Dominated by straight-chain alkanes.

Properties:

- High VI (low viscosity change with temperature).
- Good oxidative stability
- High pour point (may solidify at low temperatures unless additives are used).

Naphthenic Oils (VI ≈ 0)

Structure: Dominated by cyclic hydrocarbons (naphthenes)

Properties:

- Low VI (high viscosity change with temperature).
- Excellent low-temperature fluidity (low pour point).
- Good solvency for additives and contaminants

Example Calculation

Given:

- ν_{40}=120 cStv
- ν_{100}=15 cStv

Step 1: Find L and H from ASTM Tables:

For ν_{100} =15cSt:

- L=200
- H=150

Step 2: Calculate VI:

Since $\nu_{100} \leq 70$cSt, use the first formula

$$\mathbf{VI = \frac{(L - \nu 40)}{(L - H)} \times 100}$$

$$\mathbf{VI = \frac{(200 - 100)}{(200 - 150)} \times 100}$$

So, the Viscosity Index of the oil is **160**

Correlation Index (C.I indicator of the aromaticity of a crude oil)

The Correlation Index (C.I.) is a numerical value used to characterize the aromaticity and hydrocarbon composition of crude oil fractions. It serves as an indicator of the types of hydrocarbons present in a crude oil sample, particularly distinguishing between paraffinic, naphthenic, and aromatic compounds.

The Correlation Index is calculated based on the boiling point and specific gravity of a crude oil fraction. It is defined as:

$$\mathbf{C.I = 473.7\ SGat\ 60}°\mathrm{F}\mathbf{ - 456.8 + \frac{48640}{Boiling\ point(in\ °R)}}$$

where:

- Specific Gravity is measured at 60°F (15.6°C).
- Boiling Point is in degrees Rankine (°R = °F + 459.67).

Interpretation of C.I. Values

1- C.I. = 0 normal paraffinic based crude oil
2- C.I = 0-15 (n-paraffinic crude oil)
3- C.I = 15 – 50 (paraffinic and aromatic mixture)
4- C.I > 50 (aromatic crude oil)
5- C.I = 100 (benzene)

Molecular Weight

the relationship between the molecular weight of oil compounds and their average boiling point is well-established and is a fundamental concept in petroleum chemistry and refining. This relationship is based on the principle that as the molecular weight of hydrocarbons increases, their boiling points also increase. This is due to the stronger intermolecular forces (e.g., van der Waals forces) in larger molecules, which require more energy (higher temperatures) to overcome and transition from the liquid to the vapor phase.

Figure, illustrates the increase of boiling points with the increase of molecular weights among n-alkanes and condensed aromatics.

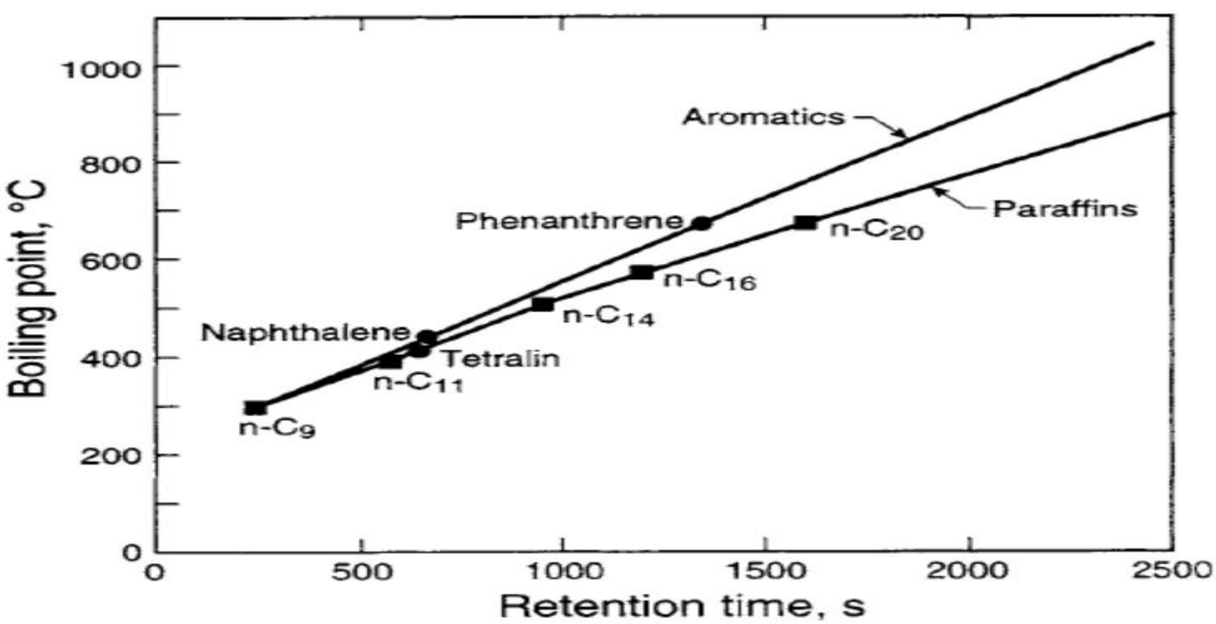


Fig.: Hydrocarbon boiling points, determined from GC retention times.

Pour point

The pour point is defined as the lowest temperature at which the sample will flow and is a rough indicator of the relative paraffinicity and aromaticity of the crude.
A lower pour point means that the paraffin content is low and greater content of aromatics.
To estimate the pour point of petroleum fractions from viscosity, molecular weight, and specific gravity, the following form is used for this purpose:

$$T_P = 130.47[SG^{2.970566}] \times [M^{(0.61235-0.47357SG)}] \times v_{38(100)}^{(0.310331-0.32834SG)}]$$

where
Tp is the pour point (ASTM D 97) in kelvin,
M is the molecular weight,
$V_{38(100)}$ is the kinematic viscosity at 37.8°C (100˚F) in cSt.

Carbon Residue, wt%

Carbon residue is the residue left after evaporating and pyrolyzing a sample under specific conditions. It represents the amount of carbonaceous material that does not volatilize and remains as a solid residue.
Carbon residue provides insight into the heavy fraction of petroleum, including asphaltenes, resins, and other high-molecular-weight compounds.

It is a critical parameter for assessing the quality of fuels and feedstocks for refining processes, as high carbon residue can lead to fouling, coking, and catalyst deactivation.

Factors Influencing Carbon Residue

1- Composition of the Sample

- High concentrations of asphaltenes, resins, and heavy polycyclic aromatic hydrocarbons (PAHs) increase carbon residue.
- Lighter fractions (e.g., naphtha, gasoline) have negligible carbon residue, while heavy fractions (e.g., vacuum residue, bitumen) have high carbon residue

2-Heteroatom Content:

the presence of nitrogen, oxygen, and sulfur in the sample can increase carbon residue, as these elements tend to form stable, non-volatile compounds during pyrolysis

3-Thermal Stability:

- Samples with low thermal stability (e.g., highly aromatic or unsaturated compounds) are more likely to form carbon residue.

Typical Carbon Residue Values:

- Light Distillates (gasoline, naphtha): < 0.1%
- Middle Distillates (diesel, kerosene): 0.1–0.5%
- Heavy Oils (vacuum gas oil): 1–5%
- Residual Fuels (vacuum residue, bitumen): 5–20%

There are two main methods for determining carbon residue:

- Conradson Carbon Residue (CCR):
  - The sample is heated in a crucible under controlled conditions until all volatile matter is evaporated, and the residue is weighed.
  - Commonly used for heavy oils and residues.
- Ramsbottom Carbon Residue (RCR):
  - The sample is heated in a glass bulb, and the residue is weighed after pyrolysis.
  - Often used for lighter fractions and distillates.

Salt Content, lb/1000 bbl

If the salt content of the crude, when expressed as NaCl, is greater than 10 lb/1000 bbl, it is generally necessary to desalt the crude before processing. If the salt is not removed, severe corrosion problems may be encountered. If residua are processed catalytically, desalting is desirable at even lower salt contents of he crude. Although it is not possible to have an accurate conversion unit between lb/1000 bbl and ppm by weight because of the different densities of crude oils, 1 lb/1000 bbl is approximately 3 ppm.

Sulfur Content, wt%

Sweet crude oil: If crude has less than 0.5% (5000 ppm) sulphur content.
Sour crude oil: If crude has greater than 2.5% (25000 ppm) sulphur.

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.

Flash point

Flash point is the minimum temperature at which vapor pressure of the hydrocarbon is sufficient to produce the vapor needed for spontaneous ignition of the hydrocarbon with the air with the presence of an external source, i.e., spark or flame. From this definition, it is clear that hydrocarbons with higher vapor pressures (lighter compounds) have lower flash points.

Generally flash point increases with an increase in boiling point. Flash point is an important parameter for safety considerations, especially during storage and transportation of volatile petroleum products (i.e., LPG, light naphtha, gasoline) in a high-temperature environment.

The flash point can be estimated using the following equation:

$$TF = 15.48 + 0.70704T_{10}$$

Where T_{10} is normal boiling point for petroleum fractions at 10 vol% distillation temperature. Both temperatures (T_{10} and flash point (TF) in Kelvin).

Example: A kerosene product with boiling range of 175-260°C from Mexican crude oil has the API gravity of 43.6 and T_{10} is 499.9K. Estimate its flash point and compare with the experimental value of 59°C.

Solution: By using the last equation, TF = 60.4°C, which is in good agreement with the experimental value of 59°C.