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:

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

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.

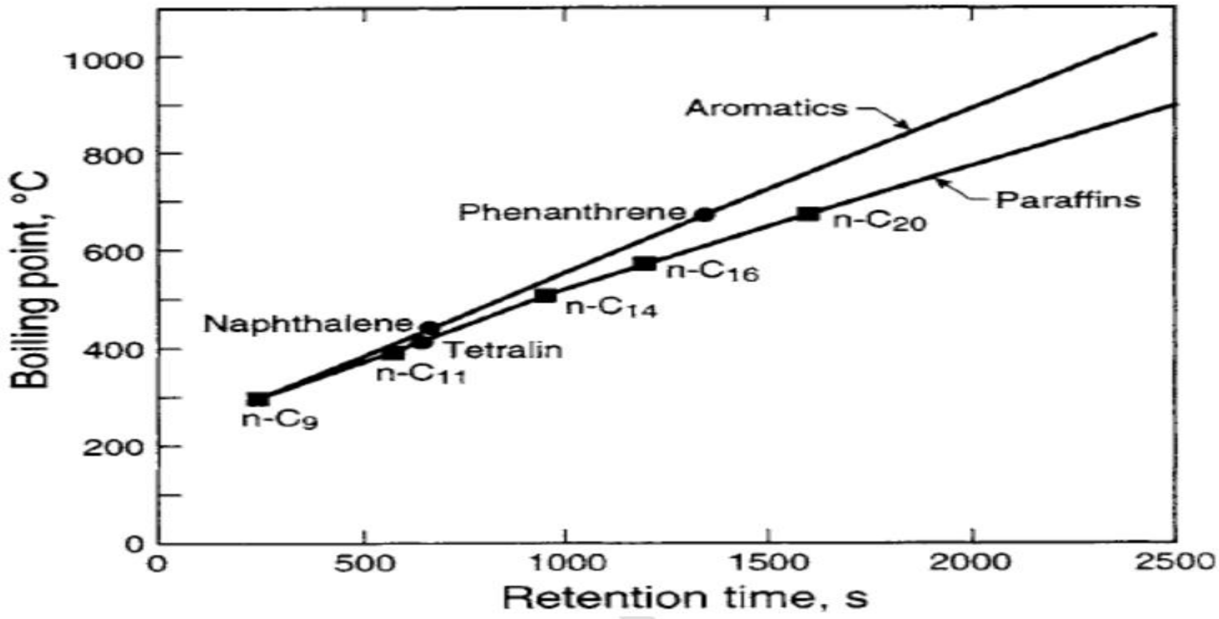

Fig.: Hydrocarbon boiling points, determined from GC retention times.

Thermal properties

The thermal properties of petroleum are those properties (or characteristics) that determine how petroleum will behave (or react) when it is subjected to excessive heat or heat fluctuations over time.

As with all properties of petroleum, a collection of standard test methods is instrumental in the evaluation and assessment of the thermal properties.

These standards allow petroleum refineries and other geological and chemical processing plants to appropriately examine and process petroleum in a safe and efficient manner.

Cloud Point

The cloud point is the lowest temperature at which wax crystals begin to form by a gradual cooling under standard conditions. As temperature decreases below the cloud point, formation of wax crystals is accelerated. Therefore, low cloud point products are desirable under low-temperature conditions.

Factors Influencing Cloud Point:

- **Crude Composition**: Paraffinic crudes (high wax content) have higher cloud points, while asphaltic or naphthenic crudes typically exhibit lower values.
- **Cooling Rate**: Faster cooling can slightly lower the observed cloud point due to super cooling effects.
- **Impurities**: Solids or water content may influence crystallization kinetics.

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.

Factors Affecting Pour Point:

- **Composition**: Crude oils with high paraffin (wax) content tend to have higher pour points.
- **Impurities**: The presence of water, sediments, or asphaltenes can influence the pour point.

- **Cooling Rate**: Faster cooling can result in a slightly lower pour point due to supercooling effects.

Freezing Point:

Freezing point is the temperature at which liquid solidifies at 1 atm pressure.

Importance of Freezing Point in Industry

1. **Cold Climate Operations**:
   - In Arctic or subsea environments, crude oil must be maintained above its freezing point to prevent solidification and ensure flow.
2. **Pipeline Design**:
   - Insulation or heating systems are often used to keep the oil above its freezing point during transportation.
3. **Safety and Efficiency**:
   - Solidified oil can block pipelines, damage equipment, and pose safety risks, making the freezing point a critical parameter for operational planning.

Factors Influencing Freezing Points:

- **Composition**: Crude oils with higher paraffin (wax) content tend to have higher freezing points.
- **Impurities**: The presence of water, sediments, or other contaminants can alter the freezing point.
- **Pressure**: While freezing point is defined at 1 atm, changes in pressure can affect the temperature at which solidification occurs.

Example:

- A crude oil with a high paraffin content might have a cloud point of 20°C, a pour point of 15°C, and a freezing point of 10°C. This means:
  - At 20°C, wax crystals begin to form (cloud point).
  - At 15°C, the oil stops flowing (pour point).
  - At 10°C, the oil solidifies completely (freezing point).

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:

$TF = 15.48 + 0.70704 T_{10}$

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.

Aniline point (AP)

Aniline point of a petroleum fraction is defined as the minimum temperature at which equal volumes of aniline and the oil are completely miscible.

The higher aniline point with the lower aromatic content and the higher paraffin content. Aniline is an aromatic compound with a structure of a benzene molecule where one atom of hydrogen is replaced by the -NH2 group (C_6H_5-NH_2).

The aromatic content in petroleum fraction may be calculated from aniline point by the following formula:

$$\mathbf{o/oA = 692.4 + 12.15\,(\boldsymbol{SG})\,(\boldsymbol{AP}) - 794\,(\boldsymbol{SG}) - 10.4\,(\boldsymbol{AP})}$$

Where: %A is the percent aromatic content, SG is the specific gravity, and AP is the aniline point in °C