CRUDE OIL - COMPOSITION, CLASSIFICATION & CHARACTERIZATION

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INTRODUCTION

Crude oils are derived from the transformation of the remains of plants, marine algae and bacteria into hydrocarbons under the prevailing conditions of high temperature and high pressure and are formed hundreds of millions of years ago. The hydrocarbons so formed occur in the liquid phase as crude oil and in the gaseous phase as natural gas. Usually they are available in the sub-surface of the earth in the porous rocks known as sedimentary basins.

COMPOSITION

Crude oil is a complex liquid mixture consists of approximately 85% Carbon and 12% Hydrogen by weight, the balance being made up of compounds of Sulphur, Nitrogen, Oxygen and metals. Hydrogen to Carbon ratios affect the physical properties of crude oil. As the Hydrogen to Carbon ratio decreases, the specific gravity and the boiling point of the hydrocarbons increase.

The three main types of hydrocarbons found in crude oil are:

- Paraffins (alkanes)
- Naphthenes (alicyclic alkanes)
- Aromatics

The Sulphur content of crude oils varies from 0.05-10% by weight. Crude oils contain Sulphur in the form:

- Elemental Sulphur
- Dissolved Hydrogen Sulphide (H_2S)
- Carbonyl Sulphide (COS),
- Organic forms (Mercaptans RSH, sulphides and disulphides in lighter fractions, thiophenes, polynuclear aromatic compounds in heavier fractions)

Sulphur compounds cause corrosion, act as catalyst poisons and release Sox during combustion when present in petroleum fuel products, thereby causing environmental pollution.

The Oxygen content of crude oil is usually less than 2wt %. Oxygen in crude oil occurs as alcohols, ethers, carboxylic acids, ketones, phenolic compounds, esters etc.

Crude oils contain very low amounts of nitrogen compounds like pyridines and pyrroles. They are very stable and hard to remove. They act as poisons to cracking catalysts.

Minute amounts of oil-soluble metallic compounds of iron, nickel and vanadium exist in crude oil. Zinc, Titanium, Calcium and magnesium appear in the form of organometallic soaps. They also cause catalyst poisoning.

Asphaltenes and Resins

Asphaltenes are dark brown friable solids that have no definite melting point and usually leave carbonaceous residue on heating. They lead to coke formation and metal deposition on the catalyst surface causing catalyst deactivation in the subsequent refining steps.

Resins are polar molecules having molecular weight in the range of 500-1000, which are responsible for dissolving and stabilizing asphaltenes in petroleum.

CLASSIFICATION

Crude oils have been discovered in commercial qualities on all continents of the world and there are over 1500 different types of crude oils produced. The main differences between crude oils stem from either the predominant hydrocarbon type, or the proportion of light and heavy hydrocarbons or the extent to which substances other than hydrocarbons are present.

The classification based on extent to which the main hydrocarbon types occur in a particular crude oil

CLASSIFICATION TYPE	COMPOSITION
Paraffinic (P)	P >75%
Naphthenic (N)	N >75%
Aromatic (A)	A >50%
Asphaltic (As)	As >50%

Subclassifications of mixed crude types such as Paraffinic-Naphthenic (P-N), Naphthenic-aromatic (N-A) and Aromatic-Asphaltic (A-As) also exist.

The different types of crude oil are classified based on the **American Petroleum Institute** (API) gravity ,

TYPE	^{0}API
Light crude oil	> 31.1 °API
Medium oil	22.3 °API - 31.1 °API
Heavy oil	< 22.3 °API

Because density is a measure of weight per volume, API can be used to calculate how many barrels of crude can be extracted from a metric ton of a given oil. A metric ton of West Texas Intermediate, with an API of 39.6, will produce 7.6 barrels (at 42 gallons each). The calculation is:

Barrels per metric ton = 1/[(141.5/(API + 131.5) x 0.159]

API stands for the American Petroleum Institute, which is the major United States trade association for the oil and natural gas industry. The API represents about 400 corporations in the petroleum industry and helps to set standards for production, refinement, and distribution of petroleum products. They also advocate on behalf of the industry. One of the most important standards that the API has set is the method used for measuring the density of petroleum. This standard is called the API gravity.

Specific gravity is a ratio of the density of one substance to the density of a reference substance, usually water. The API gravity is nothing more than the standard specific gravity used by the oil industry, which compares the density of oil to that of water through a calculation designed to ensure consistency in measurement. Less dense oil or "light oil" is preferable to more dense oil as it contains greater quantities of hydrocarbons that can be converted to gasoline. The API scale for gravity was adapted to be used in hydrometers for measuring even small differences in the specific gravity of liquids

API gravity is calculated using the specific gravity of an oil, which is nothing more than the ratio of its density to that of water (density of the oil/density of water). Specific gravity for API calculations is always determined at 60 degrees Fahrenheit/ 15.6 degrees Centigrade. API gravity is found as follows:

API gravity = (141.5/Specific Gravity) – 131.5

Though API values do not have units, they are often referred to as degrees. So the API gravity of West Texas Intermediate is said to be 39.6 degrees. API gravity moves inversely to density, which means the denser an oil is, the lower its API gravity will be. An API of 10 is equivalent to water, which means any oil with an API above 10 will float on water while any with an API below 10 will sink.

The API gravity is used to classify oils as light, medium, heavy, or extra heavy. As the "weight" of an oil is the largest determinant of its market value, API gravity is exceptionally important. For the purposes of the SPR (Strategic Petroleum Reserve), sour crude oils are defined as those containing more than 0.5 mass % total sulfur, and sweet crude oils are defined as those containing a maximum of 0.50 mass % total sulfur.

Crude oil can also be referred to as sour or sweet, based on the sulfur content of the unrefined oil. Determining the sulfur content in crude oil is an important assessment of quality. Sulfur must be removed when refining crude. If it is not, when released into the atmosphere, it can cause pollution and acid rain.

Furthermore, high sulfur content can lead to the degradation of metals used in the refining process. When working with crude that contains hydrogen sulfide, it can also be dangerous because it poses a breathing hazard. Crude oil with a sulfur content greater than 0.5% is considered sour; less than 0.5% is sweet.

Light, sweet crude is more expensive than heavier, sourer crude because it requires less processing and produces a slate of products with a greater percentage of value-added products, such as gasoline, diesel, and aviation fuel. Heavier, sourer crude typically sells at a discount to lighter, sweeter grades because it produces a greater percentage of lower value-added products with simple distillation and requires additional processing to produce lighter products.

CHARACTERIZATION :-

A crude oil assay (determination of certain physical and chemical properties) is performed at the refinery to determine its quality. There are various types of assays, which vary considerably in the amount of experimental information determined. Some include yields and properties of the streams used as feed for catalytic reforming (naphtha) and catalytic cracking (gas oils). Others give additional details for the potential production of lubricant oil and/or asphalt. At a minimum, the assay should contain a distillation curve (typically, TBP distillation) for the crude oil and a specific gravity curve. The most complete assay includes experimental characterization of the entire crude oil fraction and various boiling-range fractions. A typical crude assay should include API Gravity, Total Sulfur (% wt), Pour Point (°C), Viscosity @ 20°C (cSt) & @ 40°C (cSt), Nickel (ppm), Vanadium (ppm), Total Nitrogen (ppm), Total Acid Number (mgKOH/g), Distillation Data, Characterization factor K_{UOP}, K_W

The most common applications of petroleum assays are:

- To provide extensive detailed experimental data for refiners to establish the compatibility of a crude oil for a particular petroleum refinery

- To anticipate if the crude oil will fulfill the required product yield, quality, and production.
- To determine if during refining the crude oil will meet environmental and other standards.
- To help refiners to make decisions about changes in plant operation, development of product schedules, and examination of future processing ventures.
- To supply engineering companies with detailed crude oil analyses for their process design of petroleum refining plants.
- To facilitate companies' crude oil pricing and to negotiate possible penalties due to impurities and other nondesired properties.

Petroleum and its products are tested according to the methods and equipment specified by the American Society for Testing and Materials (ASTM)

Physical Property

1. API gravity is expressed as the relation developed by the American Petroleum Institute, as:

   $^{0}API = 141.5/s - 131.5$

   where 's' is the specific gravity of the oil measured with respect to water both at $60^{0}F$ ($15.6^{0}C$) The greater the specific gravity the lower is the API gravity. The price of oil is fixed depending on the API gravity as it is an easily measured entity and is directly related to the presence of lighter hydrocarbons.

2. The Characterization Factor (CF)

   The Characterization Factor is commonly used with API gravity to judge the quality and physical properties of crude oil and its products.

   $$CF = K_{UOP} = (VABP)^{1/3}/s$$

   $VABP=(T10\%+T30\%+T50\%+T70\%+T90\%)/5$ where VABP (in degree Fahrenheit) is the volume average boiling point of the sample's' is the specific gravity of the oil at $15.6^{0}C$.

Relationship of Type of Hydrocarbon to the Characterization Factor

K Factor	Type of Hydrocarbon
12.15 – 12.90	Paraffinic
11.50-12.10	Naphthenic-paraffinic
11.00-11.45	Naphthenic
10.50-10.90	Aromatic-naphthenic
10.00-10.45	Aromatic

T10% → 1st volume & temp

The temperatures should be measured following ASTM, D86 distillation methods

The characterization factor thus provides a means for roughly identifying the general origin and nature of petroleum.

The U.S. Bureau of Mines Correlation Index (BMCI) or (CI) is useful for characterization of crude oil fractions. CI is defined in terms of Mean Average Boiling Point (T_b) in K and specific gravity (SG) at 60°F as shown in the following equation:

$$CI = 48{,}640/T_b + 473.7SG - 456.8$$

According to this CI scale, all n-paraffins have a CI value of 0, while cyclohexane (the simplest naphthene), has a CI value of 50, and benzene has a CI value of 100. 0-15 indicates a predominance of paraffinic hydrocarbons; 15-50 indicates a predominance either of napthenes or of mixtures of paraffins, napthenes, and aromatics. CI>50 indicates the predominance of aromatic character. For a petroleum fraction, CI correlates with many characteristics, such as crackability, steam cracking, feed quality and aromaticity.

1. True Boiling Point Distillation
   The boiling point distribution of crude oil is obtained through a batch distillation test ASTM 2892. The distillation is carried out with 15-18 theoretical plates with 5:1 reflux ratio. Below 340^{0}C, the distillation is performed at atmospheric pressure. This test allows for the collection of sample cuts at different boiling point ranges. This cut can be subjected to physical and chemical measurement.

2. Pour point
   The pour point is defined as the maximum temperature at which the sample will flow. It indicates how easy or difficult it is to pump the oil, especially in cold weather. A lower pour point means that the paraffin content is low. Pour points for the whole crude & fractions boiling point above 232^{0}C are determined by standard tests like ASTM D97.

3. Cloud Point
   The cloud point is the maximum temperature at which the oil becomes hazy or cloudy due to the onset of wax crystallization or solidification. This is tested in a standard tube in an ice bath. The tube fitted with a thermometer is placed in the bath. At intervals, the test tube is removed (without disturbing the oil) to observe cloudiness. The temperature is reported to be the cloud point.

4. Viscosity
   The resistance to flow or the pumpability of the crude oil or petroleum fraction is indicated by the viscosity. More viscous oils create a greater pressure drop when they flow in pipes. Viscosity measurement is expressed in terms of kinematic viscosity in centistokes (cSt). The viscosity is measured at 37.8^{0}C by ASTM D445 & by ASTM D446 at 99^{0}C.

5. 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 the calibration curve. In addition, the boiling point distribution of light & heavy petroleum cuts can also be done by gas chromatography by the standard method ASTM D5307.

Other physical properties of importance include the Flash point, Smoke point, Reid Vapour Pressure, Refractive Index, Total Acid Number, Penetration, Water, Salt and Sediment.

Chemical Properties

1. Elemental Analysis

Carbon, hydrogen, nitrogen and sulphur content of crude oil can be determined by elemental analysis. S in a sample is estimated by X-ray fluorescence combustion method.

2. Carbon Residue

The carbon residue of a crude oil is the weight percent of coke that remains after evaporation and cracking of the sample in absence of air. The carbon residue indicates the asphaltene content of the oil.

3. Detailed Hydrocarbon Analysis (PIONA)

A chromatogram can be used to calculate the paraffin, isoparaffin, olefins and aromatic content of the sample.

NMR and Mass Spectroscopy techniques are also used to determine hydrocarbon families, sulphur containing compounds

The assay data represents typical properties of crude oil and some physical and chemical properties of the derived fractions.

CONCLUSION

Thus, the aforementioned facts and information on crude oil can help us identify and characterize the different kinds of crudes in order to achieve beneficial outcome from their appropriate application. These facts enable us to determine the steps of refining, products and their corresponding quantity that can be derived from a particular crude oil.

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