Basic products of crude oil:

The basic products from fractional distillation are:

Liquid petroleum gas (LPG):

Liquified petroleum gas is a group of hydrocarbon-based gases derived from crude oil refining or natural gas fractionation. They include ethane, ethylene, propane, propylene, normal butane, butylene, isobutane and isobutylene. For convenience of transportation, these gases are liquefied through pressurization.

Properties of LPG

LPG: liquefied petroleum gases (C2, C3, C4)

Pure LPG has no smell, but for safety an odorant agent, a mercaptan, is added to aid leak detection at very low concentrations.

LPG have high heating value (propane, 95 MJ/m3; butane, 121 MJ/m3) compared with that of natural gas (38 MJ/m3).

LPG as a liquid can be stored in a relatively small spherical or cylindrical vessels.

The low sulfur and very low levels of nitrogen oxides (NOx) emissions during its combustion make LPG a most environmentally friendly source of energy.

Automotive LPG, or auto-gas, refers to the LPG used in automotive applications.

The disadvantage is that LPG has a lower heating value per unit volume compared to gasoline, and thus the vehicle has to refuel more frequently.

Naphtha

Naphtha: is the fraction with boiling points between 38 °C and 180 °C and molecules generally having carbon numbers 5 to 12.

The fraction is typically 15–30% of crude oil by weight. It is used mainly as a feedstock for other processes:

- In the refinery for producing additives for high octane gasoline.
- A diluent for transporting very heavy crude.
- Feedstock to the petrochemical olefins chain.
- Feedstock for many other chemicals.

Naphtha cut may be classified by its boiling range or by its end use:

Light straight run (LSR) naphtha (C5 to 80°C), highly paraffinic (80 vol %), has a low RON ≤ 60, and feedstock for isomerization unit to make a light gasoline (RON ≈ 80).

Wide straight run (WSR) naphtha (C7-180°C), the heaviest part is used as a feedstock for the catalytic reforming unit for the production of reformate (high gasoline RON ≈ 98).

Gasoline

Gasoline is classified by octane ratings (conventional, oxygenated and reformulated) into three grades: Regular, Midgrade and Premium.

1- Regular gasoline: Gasoline having an antiknock index, i.e. octane rating, greater than or equal to 85 and less than 88.
2- Mid-grade gasoline: Gasoline having octane rating, greater than or equal to 88 and less than or equal to 90.
3- Premium gasoline: Gasoline having octane rating greater than 90.
   Premium and regular-grade motor gasoline are used depending on the octane rating. In addition, aviation gasoline, which is a complex mixture of relatively volatile hydrocarbons, is blended with additives to form suitable fuel for aviation engines.

Properties of Gasoline

(C5 - C11) 40-200°C finished product

Volatile flammable liquid hydrocarbon blend used as a fuel in spark- internal combustion engines ICE

Gasoline is a mixture of n-butane, reformate, isomerate, alkylate, gasoline form catalytic cracker, and coker gasoline.

Straight run gasoline cut contains: 50 percent alkanes (n and iso paraffins), 40 percent cyclic alkanes (naphthenes) and 10 percent aromatics.

Flash point: -45°C.

Auto-ignition temperature: 495°F (257°C).

Vapor density: 3 to 4 times that of air.
Viscosity: Slightly less than water.

Kerosene

Kerosene is a light petroleum distillate that is used in space heaters, cook stoves and water heaters and which is suitable for use as a light source.

Kerosene has a maximum distillation temperature of 204˚C (400˚F) at the 10% recovery point, a final boiling point of 300˚C (572˚F), and a minimum flash point of 37.8˚C (100˚F). The two grades are recognized by ASTM Specification D3699. A kerosene-type jet fuel-based product is having a maximum distillation temperature of 204˚C (400˚F) at the 10% recovery point and a final maximum boiling point of 300˚C (572˚F) and meeting ASTM Specification D1655.

Physical properties:
A pale yellow or clear oily liquid.
Chemical properties:

1- Kerosene consists of 35% paraffins, 60% naphthenes, and 15% aromatics.
2- Flash point: l00°F-165°F (38-74°C).
3- Auto-ignition temperature: 444°F (229°C) & Vapor density: 4.5 times that of air.
4- Smoke point (17 mm) minimum & Pour point: 0°F (-18°C).
5- Kerosene used in space heaters, cook stoves, and suitable for use as a light source.
6- Kerosene used in aircrafts is called “aviation turbine fuel ATF.” Kerosene was considered as aviation fuel because of:
    - High flash point: allowed safer handling, transportation, and storage of fuel.
    - Lower volatility compared with that of naphtha.
    - Very low freezing point, allowing planes to fly at high altitudes.

Three main grades of turbine fuels are in use for civil commercial aircrafts:

- Jet A-1
- Jet A
- Jet B

Jet A-1 is a kerosene cut: has flash point ≈ 100°F and a freezing point ≈ -47°C. Jet A-1 meets the specifications of ASTM D 1655.

Jet A is identical to Jet A-1: with a higher freezing point (-40°C).

Jet B is a wide-cut distillate fuel containing naphtha and kerosene fractions.

It can be used as an alternative to Jet A-1, but it has a lower flash point and higher flammability. It is more difficult to handle. It is used in very cold weather operations. It is generally produced to Canadian specifications CAN/CGSB 3.23.

Military Jet Fuel Specifications

The major difference between military fuels and commercial fuels is the use of additives, such as anti-icing, corrosion inhibitors, lubricity improvers, antioxidants, thermal stability improvers, and conductivity improvers.

JP-4: blend of 60 vol% LSR naphtha and medium straight run naphtha, and 40 % straight run kerosene. JP-4 has corrosion inhibitor and anti-icing additives. JP-4 meets the requirements of U.S military specifications MIL-DTL-5624U grade JP-4. It also meets requirements of British specifications DEF STN 91-88 AVTAG/FSII. JP-4 can be considered the military equivalent of Jet B.

JP-5: is a high flash point kerosene meeting the requirements of U.S. military specifications MIL DTL-5624U grade JP-5. JP-5 also meets the requirements of British specifications DEF STN 91-87 AVTUR /FSII. JP-5 is mainly used by the U.S. Navy for its aircrafts. Its high flash point provides a higher degree of safety in fuel handling.

JP-7: is a highly refined, high thermal stability fuel developed in the 1960s to meet the high heat sink demand of supersonic air crafts and missiles.

- It is thermally stable to 550°F.

- It has high flash, very low aromatic content (maximum 5%), a high hydrogen content, and a high heat of combustion.
- It is a blend of kerosene coming from hydrocracker and straight run desulfurized kerosene for HDS process.

Diesel oil

The quality of diesel fuels can be expressed as cetane number or cetane index. The cetane number (CN) is expressed in terms of the volume percent of cetane ($C_{16}H_{34}$) which has high ignition (CN = 100) in a mixture with alpha-methyl naphthalene ($C_{11}H_{10}$) which has low ignition quality (CN = 0). Diesel fuel includes:

1- diesel (Super-diesel) which has cetane number of 45 and it is used in high speed engines, trucks and buses.
2- diesel has 40 cetane number. Railroad diesel fuels are similar to the heavier automotive diesel fuels, but have higher boiling ranges up to 400˚C (750 ˚F) and lower cetane numbers (CN = 30).

Physical properties

A yellow viscous liquid used for compression ICE

(boiling range 200-340°C) (C11 – C20)

Chemical properties

- It consists of 30% (paraffins), 45% (naphthenes) and 25% aromatics.
- AGO must go through a distillate hydrotreater unit to remove sulphur.

Fuel Oil

The term fuel oil includes any liquid fuel that is burned in a furnace or boiler to generate heat (heating oils), or used in an engine to generate power (as motor fuels)

Physical properties

Very viscous, dark liquid.

Chemical properties

- It consists of 15% (paraffins), 15% polar compounds, containing nitrogen, oxygen, or sulfur, 25% aromatics, 45% (naphthenes).
- Viscosity: 180 cSt to 450 cSt at 120°F.
- Flash point above 65°C (150°F).

Residual Fuel Oil

It is mainly composed of vacuum residue. Critical specifications are viscosity and sulphur content. Low sulphur residues are in more demand in the market.

- have boiling points above (450°C)
- These cuts cannot be vaporized in the atmospheric distillation tower because they begin to crack or break down.
- Atmospheric bottoms is sent to a secondary distillation tower, the vacuum distillation unit.

Vacuum residue VR

Vacuum residue from crude oil distillation can be split into: 50-60 wt% saturates and aromatic, 25 wt% resins, and 20 wt% asphaltenes. Asphaltenes are high-molecular compounds insoluble in n-hexane and n-pentane.

Disadvantages of asphaltenes in crude oil

- block the pores of rock formations, well heads and surface processing equipment.
- Transportation problems because they increase gravity and viscosity of crude oils.
- Coke formation and metal deposition on catalyst surface causing catalyst deactivation.

Evaluation of Crude Oil

Evaluation of crude oil is important for refiners because it gives the following types of information:

1- Base and general properties of the crude oil.
2- Presence of impurities such as sulfur, salt, and emulsions which cause general difficulties in processing.
3- Operating or design data. Primarily this necessitates curves of temperature and gravity vs. percent distilled.
4- Curves of the properties of the fractions vs. percent distilled (mid per cent curves) or the average properties of a series of fractions vs. percentage yield (yield curve)
5- Finished products. Having established the general properties and yield by means of distillation and property curves and exploring the economy of the various break ups of the crude oil.

Fractionation distillation:

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.

True Boiling Point Distillation (TBP)

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.

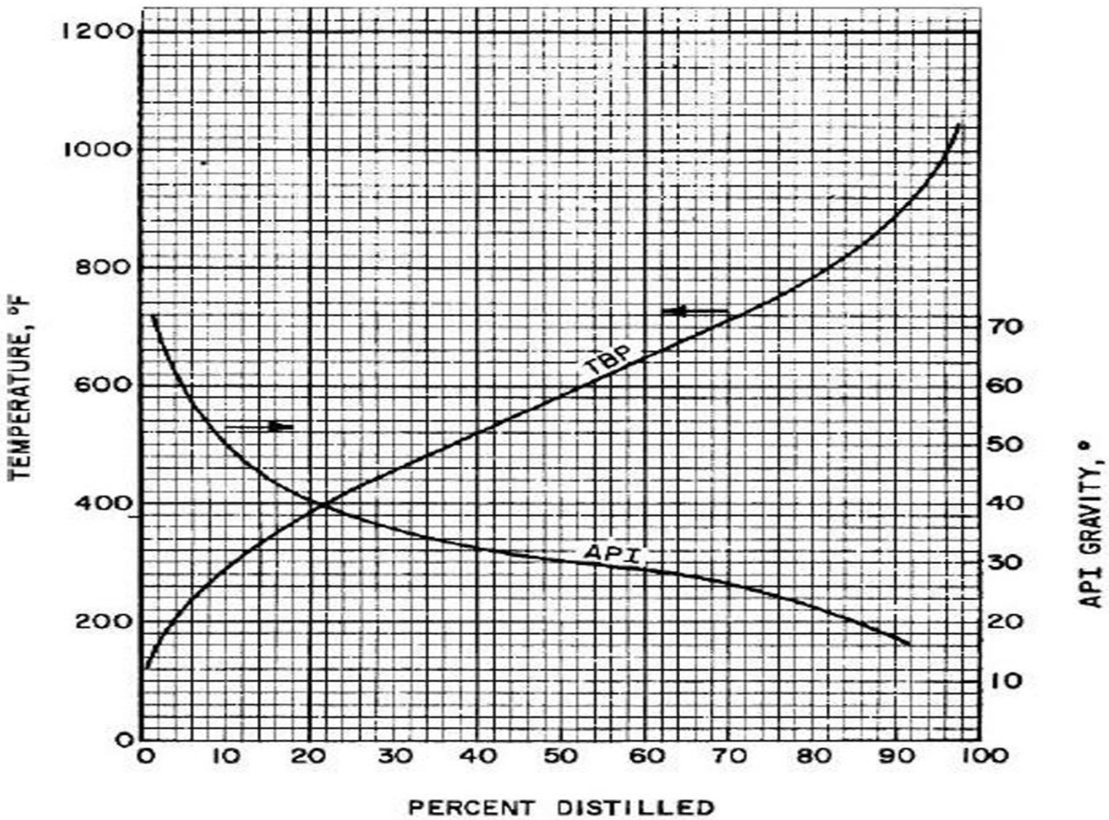

Fig.:TBP and gravity- mid percent curves. Hasting Field, Texas crude: gravity 31.7 oAPI; sulfur, 0.15 wt%.

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.

Chemical Analysis of Crude oil

1- Elemental Analysis

Carbon, hydrogen and nitrogen content of a petroleum fraction or crude oil can be determined by elemental analysis. The sample is combusted to carbon dioxide, sulphur dioxide, water and nitrogen oxides. The gases are separated and their quantities determined by different methods. The determination of the sulfur content is of utmost importance as it determines the processing scheme of the crude oil and, thus, the market value of the products. The analytical methods for sulfur determination are numerous and depend on the level of sulfur in the sample. The most widely used methods are based on combustion and X-ray fluorescence. Elemental analysis can be estimated by ASTM D5251. Metal contents such as nickel (Ni), iron (Fe) and vanadium (V) can be also determined by elemental analysis. The methods used are in the category of X-ray fluorescence, atomic absorption and argon plasma. ASTM D5708 can be used for metal determination. Sulphur can be found by the X-ray method by ASTM D2622.

2- Detailed Hydrocarbon Analysis

Detailed component analyses can be performed on petroleum gases and naphtha fractions by gas chromatography using different columns in a prescribed sequence. An internal standard is used to provide concentrations of the different compounds. A chromatogram can be used to calculate the parafins, isoparrafins, olefins and aromatic (PIONA) content of a sample. ASTM D5445 can be used in this case.

3- Hydrocarbon Family Analysis

Although gas chromatography can be used for the determination of individual compounds in naphtha fractions, this cannot be said about heavier cuts. Hydrocarbon family analyses by mass spectroscopy (MS) provide information on the relative amounts of different types of saturated and aromatic hydrocarbons. Examples of hydrocarbon families are paraffins, monocycloparaffins, alkylbenzenes, diaromatics, and the sulphur containing family of compounds like thiophenes. The results can be useful in yield calculations, since the correlations for the different processes contain parameters related to hydrocarbon family type. The ASTM D5368 can be used in this case.

4- Aromatic Carbon Content

The aromaticity of a petroleum cut is defined as the mole fraction of aromatic carbon in the sample as determined by carbon-13 nuclear magnetic resonance (NMR) spectroscopy. The ASTM D5292 can be used in this case.

5- SARA Analysis

The SARA analysis determines the content of saturate aromatics, resins and asphaltenes in crude oils, heavy cuts and residues. This information is useful in refinery design and operation. The analysis is also preparative, meaning that the test provides enough samples of the above four classes of compounds for further testing and analysis by the chemical analysis testing methods mentioned above. The separation of these four classes of compounds is done in different stages. First, asphaltenes is precipitated by n-heptane. The deasphalted oil called maltenes is subjected to liquid chromatography. Liquid chromatography is similar in principles to gas chromatography in that the compounds are eluted from a packed column by a carrier, in this case a liquid instead of a gas. The saturated hydrocarbons are eluted by n-heptane, the aromatics by a 2:1 volume mixture of n-heptane and toluene and the resins by an equal volume mixture of dichloromethane, toluene and methanol. The ASTM D4124 can be used in this case. In Figure 2 a schematic diagram for SARA analysis is shown.

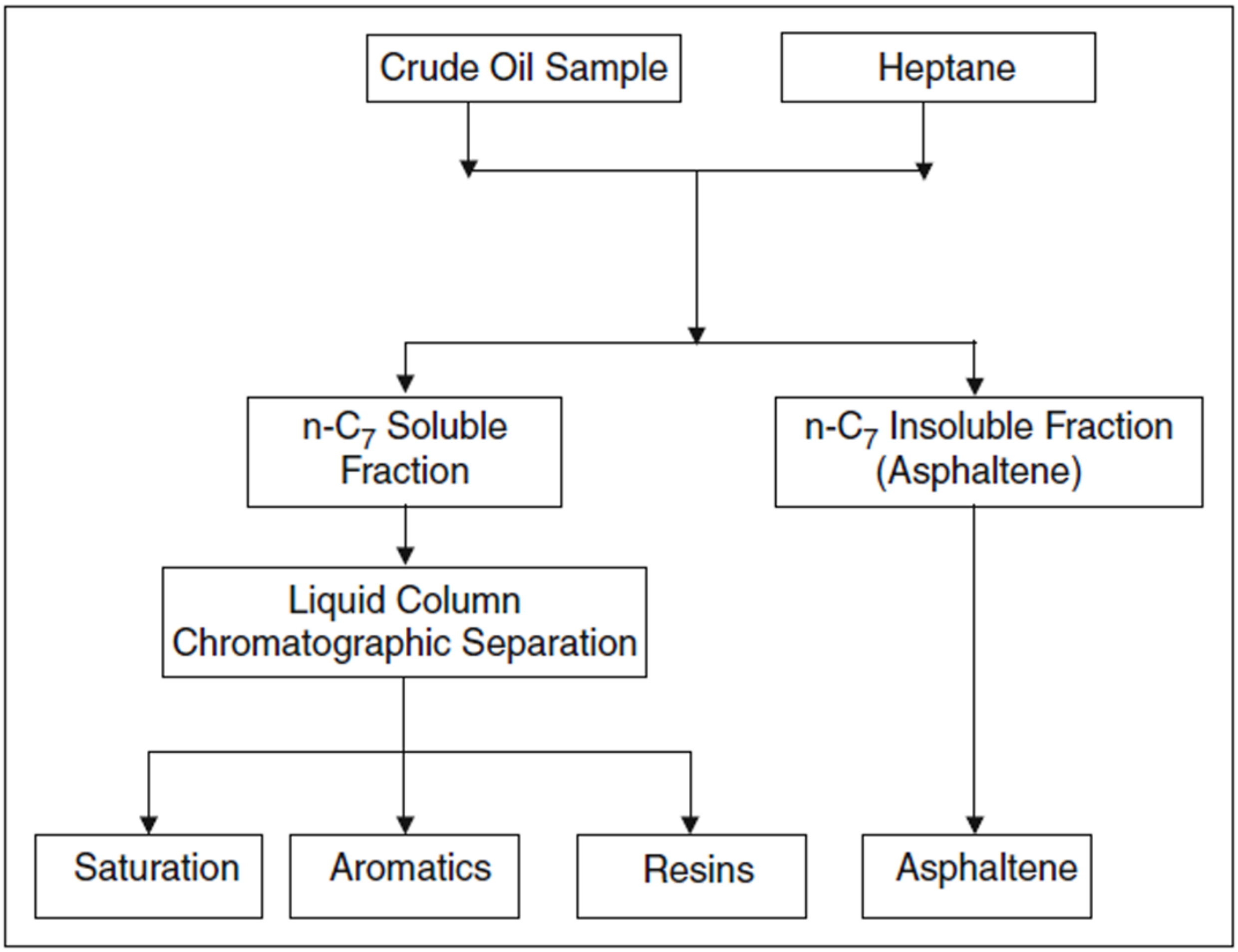

Fig.: Schematic diagram of SARA analysis.