Crude Oil Refining Processes

Iranian Oil, Gas and Petrochemical Products Exporters' Union

Article — Research ☑
Introduction

During the last 60 years, several correlations have been proposed for determining pressure-volume-temperature (PVT) properties. The most widely used correlations treat the oil and gas phases as a two-component system. Only the pressure, temperature, specific gravity and relative amount of each component are used to characterize the oil’s PVT properties. Crude oil systems from various oil-producing regions of the world were checked in the development of the correlations. These crude oils can exhibit regional trends in chemical composition, placing them into one of the following groups:

- Paraffinic
- Napthenic
- Aromatic

Because of the differences in composition, correlations developed from regional samples, predominantly of one chemical base, may not provide satisfactory results when applied to crude oil's of other regions.
Classification of hydrocarbons regarding their structure

Hydrocarbons are classified according to the structure of the molecule. Paraffin hydrocarbons are characterized by open or straight chains joined by single bonds. Examples are:

- Methane
- Ethane
- Propane
- Decane

Isomers of these compounds, which contain branched chains, are also included as Paraffins. The first four components of the series are gaseous at room temperature and pressure. Compounds ranging from Pentane (C₅H₁₂) through Heptadecane (C₁₇H₃₆) are liquids, while the heavier components are colorless, wax-like solids. Unsaturated hydrocarbons, which consist of Olefins, Diolefins, and Acetylenes, have double and triple bonds in the molecule. These compounds are highly reactive and are not normally present to any great extent in crude oil. Naphthene hydrocarbons are ringed molecules and are also called Cycloparaffins. These compounds, like the Paraffins, are saturated and very stable. They make up a second primary constituent of crude oil. Aromatic hydrocarbons are also cyclic, but are derivatives of Benzene. The rings are characterized by alternating double bonds and in contrast to Olefins, are quite stable, though not as stable as Paraffins. Crude oils are complex mixtures of these hydrocarbons. Oils containing primarily Paraffin hydrocarbons are called Paraffin-Based or Paraffinic. Traditional examples are Pennsylvania grade crude oils. Naphthenic-Based crudes contain a large percentage of Cycloparaffins in the heavy components. Examples of this type of crude come from the US midcontinental region. Highly aromatic crudes are less common but are still found.
around the world. Crude oils tend to be a mixture of Paraffins-Naphthenes-Aromatics, with Paraffins and Naphthenes the predominant species.

**Major Products**

Petroleum products are usually grouped into three categories:

1. Light distillates (LPG, Gasoline, Naphtha)
2. Middle distillates (Kerosene, Diesel)
3. Heavy distillates and residuum (Heavy Fuel Oil, Lubricating Oils, Wax, Asphalt).

This classification is based on the way Crude Oil is distilled and separated into fractions (called distillates and residuum) as in the below drawing.

- Liquified Petroleum Gas (LPG)
- Gasoline (also known as Petrol)
- Naphtha
- Diesel Fuel
- Fuel Oils
- Lubricating Oils
- Paraffin Wax
- Asphalt and Tar
- Petroleum Coke
- Sulfur
Oil refineries also produce various intermediate products such as Hydrogen, Light Hydrocarbons, Reformate and Pyrolysis Gasoline. These are not usually transported but instead are blended or processed further on-site. Chemical plants are thus often adjacent to oil refineries. For example, light hydrocarbons are steam-cracked in an Ethylene plant, and the produced ethylene is polymerized to produce Polyethylene.

**Common Processing Units Found in a Refinery**

- Desaltering Unit: washes out salt from the crude oil before it enters the atmospheric distillation unit.
- Atmospheric Distillation Unit: distills crude oil into fractions.
- Vacuum Distillation Unit: further distills residual bottoms after atmospheric distillation.
- Naphtha Hydrotreater Unit: uses hydrogen to desulfurize naphtha from atmospheric distillation. Must hydrotreat the naphtha before sending to a catalytic reformer unit.
- Catalytic Reformer Unit: used to convert the Naphtha-Boiling range molecules into higher octane reformate (reformer product). The reformate has higher content of aromatics and cyclic Hydrocarbons. An important by product of a reformer is Hydrogen released during the catalytic reaction. The Hydrogen is used either in the Hydrotreaters or the Hydrocracker.
- Distillate Hydrotreater: desulfurizes distillates (such as Diesel) after atmospheric distillation.
- Fluid Catalytic Cracker (FCC) Unit: upgrades heavier fractions into lighter, more valuable products.
- Hydrocracker Unit: uses hydrogen to upgrade heavier fractions into lighter, more valuable products.
- Merox Unit: treats LPG, kerosene or Jet Fuel by oxidizing mercaptans to organic disulfides.
- Alternative processes for removing Mercaptans are known, e.g. Doctor sweetening process and caustic washing.
- Coking Units (delayed coking, fluid coker): process very heavy residual oils into Gasoline and Diesel Fuel, leaving petroleum coke as a residual product.
- Alkylation Unit: uses Sulfuric acid or Hydrofluoric acid to produce high-octane components for Gasoline blending.
- Dimerization Unit: converts Olefins into higher-octane Gasoline blending components. For example, Butenes can be dimerized into Isooctene which may subsequently be hydrogenated to form Isooctane. There are also other uses for dimerization. Gasoline produced through dimerization is highly unsaturated and very reactive. It tends spontaneously to form gums. For this reason the effluent from the dimerization need to be blended into the finished Gasoline pool immediately or hydrogenated.
- Isomerization Unit: converts linear molecules to higher-octane branched molecules for blending into gasoline or feed to alkylation units.
- Steam Reforming Unit: produces hydrogen for the hydrotreaters or hydrocracker.
- Liquified Gas Storage Vessels: store propane and similar gaseous fuels at pressure sufficient to maintain them in liquid form. These are usually spherical vessels or "bullets" (i.e. horizontal vessels with rounded ends).
- Storage Tanks Store: crude oil and finished products, usually cylindrical, with some sort of vapor emission control and surrounded by an earthen berm to contain spills.
- Amine Gas Treater, Claus Unit and Tail Gas Treatment: convert hydrogen sulfide from hydro desulfurization into elemental sulfur.
- Utility Units: such as cooling towers circulate cooling water, boiler plants generates steam and instrument air systems include pneumatically operated control valves and an electrical substation.
- Wastewater Collection and Treating System: consist of API(American Petroleum Institute) separators, dissolved air flotation (DAF) units and further treatment units such as an activated sludge biotreater to make water suitable for reusing or for disposal.
- Solvent Refining Units: use solvent such as Furfural to remove unwanted, mainly aromatics from lubricating oil stock or diesel stock.
- Solvent Dewaxing Units: remove the heavy waxy constituents petrolatum from vacuum distillation products.

**Flow Diagram of Typical Refinery**

The image on the following page is a schematic flow diagram of a typical oil refinery that depicts the various unit processes and the flow of intermediate product streams that occurs between the inlet crude oil feedstock and the final end products. The diagram depicts only one of the literally hundreds of different oil refinery configurations. The diagram also does not include any of the usual refinery facilities providing utilities such as steam, cooling water, and electric power as well as storage tanks for crude oil feedstock and for intermediate products and end products.