PRPE: UNIT-2

Petroleum Products and their specifications

- Average consumer tends to think of petroleum products as consisting of a few items such as motor gasoline, jet fuel, home heating oils, kerosine, etc.,
- American Petroleum Institute (API) identified over 2,000 products made to individual specifications. Table shows the number of individual products in 17 classes.

Table 2.1 Products Made by the U.S. Petroleum Industry

Class	Number
Fuel gas	1
Liquefied gases	13
Gasolines	40
Motor	19
Aviation	9
Other (tractor, marine, etc.)	12
Gas turbine (jet) fuels	5
Kerosines	10
Middle distillates (diesel and light fuel oils)	27
Residual fuel oil	16
Lubricating oils	1156
White oils	100
Rust preventatives	65
Transformer and cable oils	12
Greases	271
Waxes	113
Asphalts	209
Cokes	4
Carbon blacks	5
Chemicals, solvents, miscellaneous	300
Total	2347

- Very few products which dictate refinery design the basic refinery processes are based on the large-quantity products such as gasoline, diesel, jet fuel, and home heating oils.
- Storage and waste disposal are expensive, so it is necessary to sell or use all of the items produced from crude oil even if some of the materials, such as high-sulfur heavy fuel oil and fuel-grade coke, must be sold at prices less than the cost of fuel oil.
- Usually the lowest value of a hydrocarbon product is its heating value or fuel oil equivalent (FOE).
- Knowledge of the physical and chemical properties of the petroleum products is necessary for an understanding of the need for the various refinery processes.
- To provide an orderly portrayal of the refinery products, they are described in the following paragraphs in order of increasing specific gravity and decreasing volatility and API gravity.

- The petroleum industry uses a shorthand method of listing lower-boiling hydrocarbon compounds.
- For example, propane is shown as C_3 and propylene as $C_3^=$. The corresponding hydrogen atoms are assumed to be present unless otherwise indicated.

LOW-BOILING PRODUCTS

The classification low-boiling products includes the compounds which are in the gas phase at ambient temperatures and pressures: methane, ethane, propane, butane, and the corresponding olefins.

Methane (C_1 or CH_4)

1. Methane is used as *a refinery fuel*, and as a feedstock for *hydrogen* production by *pyrolytic cracking* and *reaction with steam*.
2. Its quantity is generally expressed in terms of pounds or kilograms, standard cubic feet (scf) at 60°F and 14.7 psia, normal cubic meters (Nm3) at 15.6°C and 1 bar (100 kPa), or in barrels fuel oil equivalent (FOE) .
3. Boiling point is as low as -258 ^oF.
4. Specific gravity = 0.3 at 60 ^oF and API gravity = 340

(Note: remember these values as it is the lightest product from refinery)

Ethane (C_2 or C_2H_6)

1. Ethane (C_2 or C_2H_6) is used as **refinery fuel**
2. Ethane is used as feedstock to produce hydrogen or ethylene. hydrogen or ethylene are used in petrochemical processes.
3. Sometime, Ethylene and hydrogen are recovered in the refinery and sold to petrochemical plants.

LPG

Liquefied petroleum gas or liquid petroleum gas (LPG or LP gas), also referred to as simply propane or butane, are flammable mixtures of hydrocarbon gases used as fuel in heating appliances, cooking equipment, and vehicles.

Propane (C_3 or C_3H_8)

1. Propane is sold as a **liquefied petroleum gas** (**LPG)** whose properties are specified by *the* ***Gas* Processors Association (GPA)**
2. Propane also used as a refinery fuel
3. Typical specifications include :
    a. **Maximum vapor pressure** of **210 psig** at 100°F (37.8°C)
    b. **95% boiling point of -37°F** (-38.3°C) or lower at 760 mmHg (1 bar) atmospheric pressure.
4. Sometimes, ***propylene*** is separated for sale to polypropylene manufacturers.

Butane/n-butane (n-C_4 or n-C_4H_{10})

1. Butane is used as components of gasoline and LPG.
2. Normal butane/n-butane (nC_4) has a lower vapor pressure than isobutane (iC4). So n-butane (nC4) is usually preferred for blending into gasoline to regulate its vapor pressure.
3. n-butane promotes better starting in cold weather.
4. n-butane has a Reid vapor pressure (RVP) of 52 psi (358 kPa) as compared with the 71 psi (490 kPa) RVP of isobutane, and more nC4 can be added to gasoline without exceeding the RVP of the gasoline product.
5. n-butane has a octane rating/ octane number of 90 or more and is a low-cost octane improver of gasoline
6. Gasoline has a higher sales value than LPG. So in economic viewpoint more butane is blended with gasoline.
7. Normal butane is also used as a feedstock to isomerization units to form isobutane

Isobutane (i-C_4 or i-C_4H_{10})

1. Isobutane has its greatest value when used as a feedstock to alkylation units, In alkylation units isobutane is reacted with unsaturated materials (propenes, butenes, and pentenes) to form high-octane isoparaffin compounds in the gasoline boiling range.
2. Iso-butane is supplied mainly from fluid catalytic cracking (FCC) and hydrocracking (HC) units in the refinery and from natural gas processing plants.
3. Isobutane can be used as LPG or used as a feedstock for propylene (propene) manufacture.
4. A significant amount of isobutane is converted to isobutylene which is reacted with methanol to produce methyl tertiary butyl ether (MTBE).

GASOLINE

- Gasolines are complex mixtures of hydrocarbons having typical boiling ranges from 100 to 400°F as determined by the ASTM method.
- Components are blended to promote high antiknock quality, ease of starting, quick warm-up, low tendency to vapor lock, and low engine deposits.
- The components used in blending motor gasoline are light straight-run (LSR) gasoline or isomerate, catalytic reformate, catalytically cracked gasoline, hydrocracked gasoline, polymer gasoline, alkylate, n-butane, and such additives as MTBE (methyl tertiarybutyl ether), ETBE (ethyl tertiary butyl ether), TAME (tertiary amyl methyl ether) and ethanol. Additives such as antioxidants, metal deactivators are added.
- Light straight-run (LSR) gasoline consists of the C5-190°F (TBP or True Boiling Point) fraction of the naphtha cuts from the atmospheric crude still. (**Note:** C5-190°F fraction means that pentanes are included in the cut but that C4 and lower-boiling compounds are excluded). If higher octanes are needed, isomerization is done to achieve Posted octane number (PON) improvements of 13 to 20.
- Catalytic reformate is the $C5^+$ gasoline product of the catalytic reformer. Heavy straight-run (HSR) and coker gasolines are used as feed to the catalytic reformer, and when the octane needs require, FCC and hydrocracked gasolines of the same boiling range may also be processed by this unit to increase octane levels. The reformer increases the octane by converting low-octane paraffins to high-octane aromatics.
- The FCC and HC gasolines are generally used directly as gasoline blending Stocks. It is necessary to hydrotreat the FCC feedstock to reduce the sulfur level sufficiently to produce FCC naphthas with acceptable sulfur contents.
- Polymer gasoline is manufactured by polymerizing olefins.
- Alkylate gasoline is the product of the reaction of isobutane with propylene, butylene, or pentylene to produce branched-chain hydrocarbons in the gasoline boiling range. The blending octane (PON) of alkylate is higher.
- Normal butane is blended into gasoline to give the desired vapor pressure [Reid vapor pressure (RVP)].
- Butane has a high blending octane number and is a very desirable component of gasoline;

Gasoline specifications

- The three that have the greatest effects on engine performance are the Reid vapor pressure, boiling range, and antiknock characteristics.
- The Reid vapor pressure (RVP) and boiling range of gasoline governs ease of starting, engine warm-up, rate of acceleration, loss by crankcase dilution, mileage economy, and tendency toward vapor lock. Engine warm-up time is affected by the percent distilled at 158°F (70°C) and the 90% ASTM distillation temperature.

(Note: Warm-up is expressed in terms of the distance operated to develop full power without excessive use of the choke. A two- to four-mile (3- to 7-km) warm-up is considered satisfactory)

- Tendency to vapor lock is directly related to the RVP of the gasoline. In order to control vapor, the vapor pressure of the gasoline should not exceed the following limits:

Ambient temp.	Max. allowable RVP
°F	psia
60	12.7
70	11.0
80	9.4
90	8.0

There are 3 types of octane numbers for spark ignition engines

1. motor octane number (MON)
2. research octane number (RON)
3. posted octane number (PON)

- The RON represents the performance during city driving when acceleration is relatively frequent.
- The MON is a guide to engine performance on the highway or under heavy load conditions. The difference between the research and motor octane is an indicator of the **sensitivity** of the performance of the fuel
- Posted octane number (PON) is the arithmetic average of the research and motor octane numbers. [(RON +MON)/2]

Most refiners produce gasoline in two or three grades, **unleaded regular, premium, and super-premium, and in addition supply a regular gasoline.** The principal difference between the regular and premium fuels is the antiknock performance.

Posted method octane number (PON) of **unleaded regular gasolines was about 87** and that of premium gasolines ranged from **89 to 93.**

DISTILLATE FUELS

Distillate fuels can be divided into three types: jet or turbine fuels, diesel fuels, and heating oils.

JET AND TURBINE FUELS

1. Jet and Turbine Fuels are used by both commercial aviation and military aircraft.
2. The primary source of jet fuel blending stocks is the ***straight-run kerosine fraction*** from the atmospheric crude unit.
3. Stringent aromatic and naphthalene content and ***smoke point specifications*** limit the amount of cracked stocks for blending into jet fuels.
4. Kerosine boiling range hydrocarbons from ***hydrocracker unit*** can also meet jet fuel specifications and is a major contributor to jet fuel production.
5. Usually jet fuels sell at higher prices than diesel fuels and No. 1 and No. 2 heating oils, and it is more profitable for the refiner to blend the kerosine fractions from the atmospheric crude unit and the hydrocracker into jet fuel rather than other products.
6. Two of the critical specifications relate to its clean burning requirements and limit the total aromatics as well as the content of double ring aromatic compounds. These are the ***smoke point, expressed in mm of flame height*** at which smoking is detected, and the volume percent total aromatics and naphthalenes.
7. Specifications ***limit total aromatic concentration to 20% and the naphthalene content to 3% or 3.0%*** depending upon the specific specifications.
8. The freeze point specification is very low from-40 to -58°F max.
9. Hydrocracking normally produces a very low (14 to 16mm) smoke point jet fuel.
10. Jet fuel is blended from low sulfur or desulfurized kerosine, hydrotreated light coker gas oil, and hydrocracked blending stocks.
11. The two basic types of jet fuels are naphtha and kerosine.
12. Naphtha jet fuel is produced primarily for the military and is a wide-boiling-range stock.It is more volatile and has more safety problems in handling.

13. Other is commercial jet fuels to the narrower-boiling range product [350–550°F] which is sold as Jet A, Jet A-1, JP-5 etc.
14. The principal differences among these are freezing points.
15. Other limiting specifications are flash point [110 to 150°F (43 to 66°C)], distillation, smoke point, and aromatics content.

AUTOMOTIVE DIESEL FUELS

1. Volatility, ignition quality (expressed as cetane number or cetane index), viscosity, sulfur content, percent aromatics, and cloud point are the important properties of automotive diesel fuels.
2. No. 1 diesel fuel (sometimes called super-diesel) is generally made from virgin or hydrocracked stocks having cetane numbers above 45. It is has a boiling range from 360 to 600°F (182 to 316°C) and is used in high-speed engines in automobiles, trucks, and buses.
3. No. 2 diesel fuel is very similar to No. 2 fuel oil, and has a wider boiling range than No. 1. It usually contains cracked stocks and may be blended from naphtha, kerosine, and light cracked oils from the coker and the fluid catalytic cracking unit.
4. Limiting specifications are flash point [125°F (52°C)], sulfur content (0.05% max.), distillation range, cetane number or cetane index (40 min.), percent aromatics, and cloud point.
5. The ignition properties of diesel fuels are expressed in terms of cetane number or cetane index. The cetane number expresses the volume percent of cetane ($C_{16}H_{34}$, high-ignition quality) in a mixture with alpha-methyl-naphthalene ($C_{11}H_{10}$, low ignition quality). The fuel is used to operate a standard diesel test engine according to ASTM test method D-613. Since many refineries do not have cetane test engines, a mathematical expression developed to estimate the cetane number is used. The number derived is called the cetane index and is calculated from the mid–boiling point and gravity of the sample.
6. The higher the H/C ratio, the better the burning characteristics (i.e., the higher the smoke point and the higher the cetane index).
7. The cetane index is an indicator of the H/C ratio and is also an indirect indicator of the aromatic content of the diesel fuel.

Lube oils

1. A lubricant is usually an organic substance used to reduce friction between surfaces in mutual contact.
2. It reduces the heat generated when the surfaces move.

3. The property of reducing friction is known as lubricity.
4. the volatility of lubricant oils are lower than gas oils.
5. they constitute only 2-4% of crude oil.
6. The bottoms (heavier compounds) of vaccum distillation unit are the feed stocks for lube base production. Sometimes atmospheric bottoms are also used as feed stocks.

The feed stock (vaccum residue) is

1. Solvent deasphalted to reduce carbon- and sludge-forming tendencies
2. Solvent extracted and hydrocracked to improve viscosity index
3. Solvent dewaxed and selective hydrocracked to lower cloud and pour points
4. Hydrotreated and clay treated to improve color and oxygen stability

Critical parameter: The viscosity index (VI) measure of the change of viscosity with temperature. It is used to characterize the viscosity-temperature behavior of lubricating oils. The lower the VI, the more the viscosity is affected by changes in temperature.

Lube oil stocks are classified as

1. low Viscosity index (VI <30 & rich in aromatics)
2. medium Viscosity index (VI =30 to 85 & have aromatics and paraffins) and
3. high Viscosity index (VI > 85 & rich in paraffins)

WAX

1. Petroleum wax contains paraffins (normal and iso paraffins) and alkylated naphthenes in the range of C_{15}-C_{70}
2. Petroleum waxes are classified into
    i. paraffin wax,
    ii. micro-crystalline wax and
    iii. petrolactum.
3. Paraffin wax is produced from paraffin base or mixed base crude oil with high pour point.
4. Micro-crystalline wax produced from distillation residue,waxy sludge deposited on storage tanks etc.
5. Petrolactum is popularly known as Vaseline.
6. Production of wax from crude depends on the presence of wax in the crude oil.

7. Crudes present in india are suitable for production of paraffin and microcrystalline wax.
8. Some of the important specifications for waxes are melting point (45 ^{o}C to 75 ^{o}C), viscosity, colour and odour etc.
9. Uses: chemical products, paper waxing, tarpaulin, textilies, candles etc.

Asphalt

1. Asphalt, also known as bitumen is a sticky, highly viscous liquid or semi-solid form of petroleum.
2. Asphalt is a mixture of bitumen and minerals in any proportion. It is non volatile and softens while heating.
3. It is black or black-brown in colour.
4. There are different classes of bitumen. Some of them are penetration bitumen, viscosity graded-asphalts, oxidized bitumens etc.
5. Bitumens contain 82-85% carbon, 12-15% hydrogen and 2-3% Sulphur with oxygen.
6. They have highly aromatic in nature. Bitumens have very complex high molecular weight compounds such as asphaltenes, resins, cyclics and saturates.
7. They have specific gravities of approximately 0.99.
8. softening point is one of the critical property and it ranges from 30-65 ^{o}C.
9. The average molecular weight of these compounds range from 500-900.
10. The primary use (70%) of asphalt is in road construction, bituminous waterproofing products, including production of roofing felt and for sealing flat roofs.

HEATING OILS

1. Heating oil is a low viscosity, liquid petroleum product used as a fuel oil for furnaces or boilers in buildings.
2. Heating oil consists of a mixture of petroleum-derived hydrocarbons in the 14- to 20-carbon atom range that condense between 250 and 350 °C (482 and 662 °F) during oil refining.
3. Heating oil condenses at a lower temperature than petroleum jelly, bitumen, candle wax, and lubricating oil, but at a higher temperature than kerosene.
4. Heating Oil Specifications are given by ASTM D-396
5. Most heating oil products are chemically very similar to diesel fuel used as motor fuel.

6. The principal distillate fuel oils consist of No. 1 and No. 2 fuel oils. No. 1 fuel oil is very similar to kerosine, but generally has a higher pour point and end point. Limiting specifications are distillation, pour point, flash point, and sulfur content.
7. No. 2 fuel oil is very similar to No. 2 diesel fuel, contains cracked stock, and is blended from naphtha, kerosine, diesel, and cracked gas oils. Limiting specifications are sulfur content, pour point, distillation, and flash point.

RESIDUAL FUEL OILS

1. Residual Fuel Oil (RFO) is a low grade of fuel oil which contains the undistilled residue from atmospheric or vacuum distillation of crude oil. It may be called Bunker Fuel Oil.
2. Residual fuel oil is less useful because it is so viscous that it has to be heated with a special heating system before use and it may contain relatively high amounts of pollutants, particularly sulfur, which forms sulfur dioxide upon combustion.
3. It is composed of the heaviest parts of the crude and is generally the fractionating tower bottoms from vacuum distillation. It is sold for a very low price (historically about 70% of the price of crude from which it is produced) and is considered a by-product.
4. Critical specifications are viscosity and sulfur content.
5. Sulfur content specifications are generally set by the locality in which it is burned. Currently only low sulfur fuel oils can be burned in some areas and this trend will continue to expand. Heavy fuel oils with very low sulfur contents are much in demand and sell at prices near those of the crude oils from which they are derived.