What is Petroleum?

- *The word petroleum originated from the latin words, petra, meaning rock and oleum, meaningoil.Literallyitmeans'rockoil,'andcanalsobedefinedasanon-renewablefossil fuel or oil that is foundunderground.*
- *Technically,thetermpetroleumreferstodescribeanysolid,liquidorgaseoushydrocarbons. It'salsoknownas'crudeoil'or'mineraloil.'*

Differences Between Crude Oil, Petroleum Products And Petroleum

- *Crudeoil-Mixtureofhydrocarbonsexistingasliquidinnaturalundergroundreservoirsand remain liquid duringextraction.*
- *Petroleum products- Produced from the processing of crude oil at petroleum refineries and extraction of liquid hydrocarbons at natural gas processing plants.*
- *Petroleum-referstothebroadcategorythatincludesbothcrudeoilandpetroleumproducts.*

Occurrence of Petroleum

- *Petroleumoccursintheearth'scrust,inallpossiblestatesandvariesincolorfromlight browntodarkbrownorblack,exhibitingluminescenceinsomecases.*
- *It is a mixture of various hydrocarbons, of homologous series namely Paraffins, Naphtheneand Aromatics.*

Thefinalresultisablackviscousproductofcomposition:

- *Carbon 80 to89%*
- *Hydrogen12 to14%*
- *Nitrogen 0.3 to 1%*
- *Sulphur 0.3 to3%*
- *Oxygen 2 to3%*

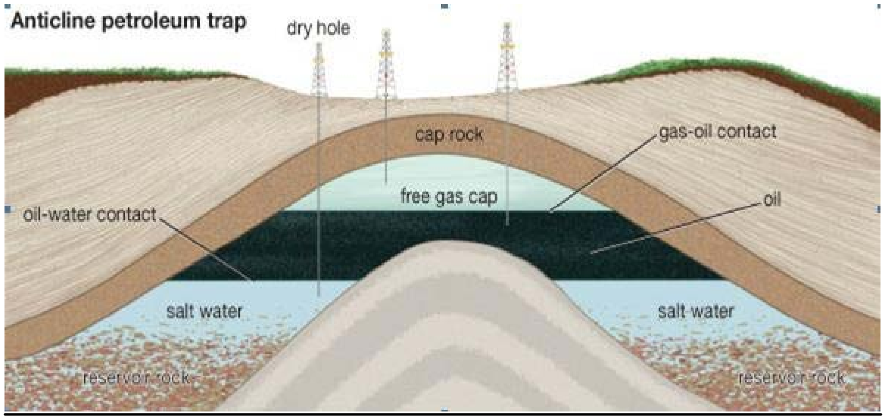
Petroleum Formation

Modern Theory

According to modern views, petroleum is believed to be formed by the decay and decomposition of:

- *Marine animals*

- *Vegetable organism of the pre-historic forests, i.e. it is of animal as well as of plant origin.*
  It is thought that due to some upheavals or earthquakes, these prehistoric forests, and sea animals got buried under the crust of earth.
- *Due to action of prolonged action of high temperature and pressure in the interior of earth for ages, the biological matter decomposed into petroleum.*



Composition of petroleum

*The principal components of petroleum a*re hydrocarbons (paraffins, naphthenes, aromatics, olefins etc.), small amounts of sulphur, nitrogen & oxygen compounds as impurities and some inorganic compounds & metals (vanadium and platinum in traces). Sulphur compounds found in petroleum are hydrogen sulphide, thiophenes, mercaptans. Oxygen occurs in combined form in alcohols, phenols, resins and organic acids present in petroleum. Nitrogen compound include pyridines, etc. Inorganic compounds present in petroleum are salt, clay and sand etc.

Atypical composition (by weight %) of is given below

Carbon = 84-87%	Hydrogen = 11-15%	Sulphur = 0.1-3%
Nitrogen = 0.1-1.5%	Oxygen = 0.3-1.8%	

Typical properties of crude oil

Specific gravity = 0.80 - 0.95, viscosity at 37.8°C = 2.3 - 23 cst
carbon/hydrogen ratio = 6 - 8, pour point = 18 - 30°C ,
wax content = 6 -12%, flash point = 15 - 27°C
water content = 0.1 - 1.5% , Salt content = 1.5 - 8%,
Ash content = 0.004 - 0.006%.

Production of Petroleum

- *Petroleum almost always occurs along with gas called natural gas. After drilling in the crust of earth both natural gas and oil flow up through pipe under pressure initially. When the oil pressure decreases, then the residual oil is either sucked by a pump or pressure is created by injecting compressed gas or high pressure water through a pipe bored by the side of oil delivery pipe so that it can flow out.*
- *When the oil well contains both oil and gas it is called (**wet well**) and if it contains only gas then it is called a **(dry well**).*
- *A sketch of typical oil pool formation inside the crust of earth is given in Fig.1. Hard cap rock and hard rock at the bottom, both are impermeable to oil and gas. Geological studies indicate that petroleum was not formed in the pools where it is found today.*

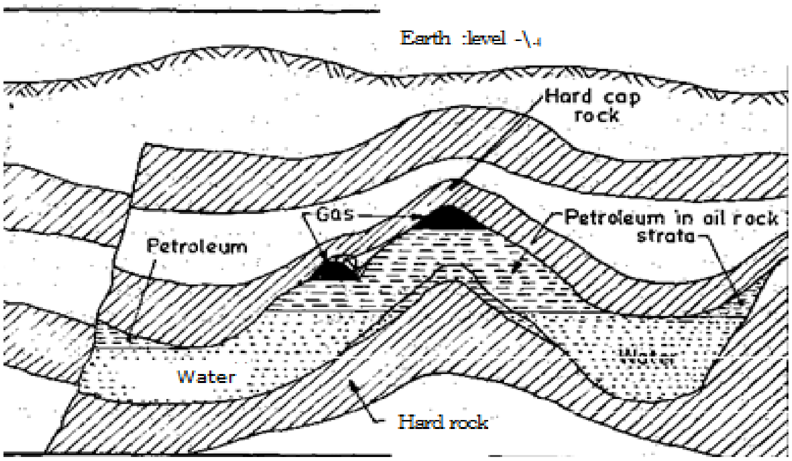


Fig.1. Typical oil-pool formations. In the centre, pool water has forced the petroleum and gas up into a dome, or anticline, in the porous oil rock layer. Hard cap rock prevents the escape of the oil. A fault, at the left, or a stratigraphic.

Pre-Treatment of Oil at Oil Field before Refining

Oil and gas when they come out of oil field are separated. The natural gas is compressed to liquefy it which is used for heating of domestic and industrial ovens. Petroleum oil is made free of:

- *Water,*
- *Sediments and*
- *Salts present in it.*

*It is then made free of some dissolved gases into it by the process called '**stabilisation**'. It is then sent to oil refinery _ for separation into various petroleum products by distillation mainly and auxiliary operations.*

Crude oil as it comes out of well may contain up to (25%) water, salts ($MgC1_2$,$CaC1_2$, NaCI etc.) up to 2000-5000 (mg/litre) and sediments up to (1-1.5%). For refining crude oil, the salt content in it should be < 50 mg/litre and Water < 03%. Excessive water in crude requires extra heat for its distillation, increases its cost of transportation, forms emulsion which absorb materials like resin (hence emulsion breakers are to be used).

Salt in crude oil causes:

- *scaling*
- *corrosion*
- *reduces heat transfer co-efficient during its processing.*

Sediments present in crude causes:

- *erosion*
- *scaling.*

In mechanical method of separation of impurities from crude oil, it is subjected to centrifuging, filtration and settling after heating it to 120-160°C at 6-8 atm. pressure. In physico-chemical method, emulsion breakers are added. But they are costly and cause corrosion & sludge formation.

Stabillsation of Crude Oil

Removal of dissolved gases from crude oil by heating it is called its stabilisation. Gas accompanied with crude oil must be removed to avoid breathing loss (loss of gasoline, if gas is not removed from oil during prerefining). Breathing loss occurs due to changes of humidity of ambient air and day and night temperature change also during emptying and filling of crude tanker.

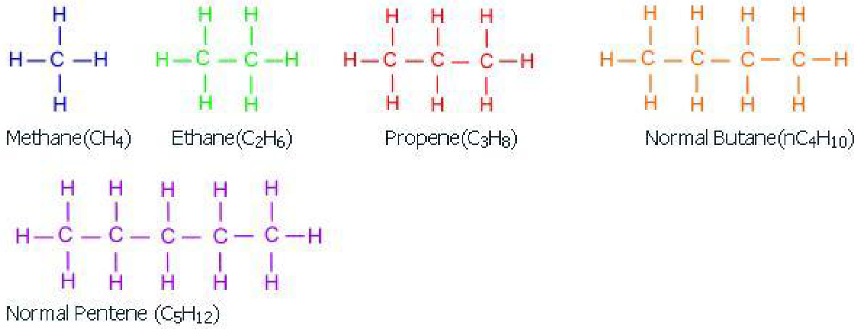
Classification of Petroleum

Depending on the nature of hydrocarbons present in it, crude petroleum oil is classified as

- *paraffin base,*
- *naphthene base,*
- *asphalt base,*
- *mixed base.*

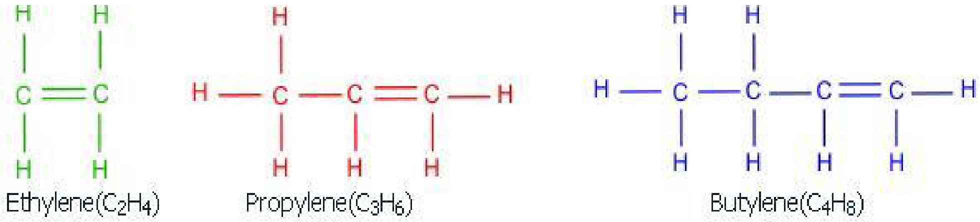
Paraffins

Paraffins refer to alkanes such as methane, ethane, propane, n and iso butane, n and iso pentane. These compounds are primarily obtained as a gas fraction from the crude distillation unit.



Olefins

Alkenes such as ethylene, propylene and butylenes are highly chemically reactive.

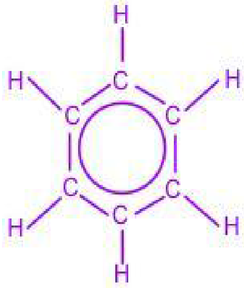


Naphthenes

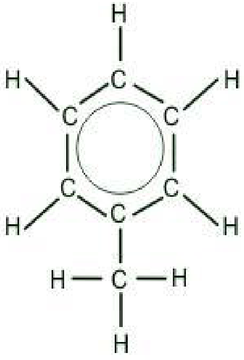
Naphthenes or cycloalkanes such as cyclopropane, methyl cyclohexane are also present in the crude oil. These compounds are not aromatic and hence do not contribute much to the octane number. Therefore, in the reforming reaction, these compounds are targeted to generate aromatics which have higher octane numbers than the naphthenes.

Aromatics

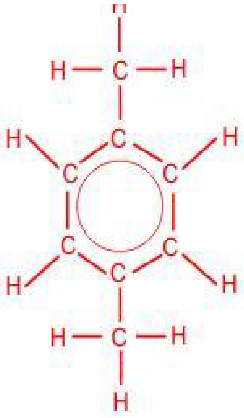
Aromatics such as benzene, toluene o/m/p-xylene are also available in the crude oil. These contribute towards higher octane number products and the target is to maximize their quantity in a refinery process.



Benzene(C_6H_6)



Tolune(C_7H_8)



Para-X ylene(C_8H_{10})

Organic sulphur compounds

Not all compounds in the crude are hydrocarbons consisting of hydrogen and carbon only. Organic sulphur compounds such as thiophene, pyridine also exist in the crude oil. The basic difficulty of these organic sulphur compounds is the additional hydrogen requirements in the hydrotreaters to meet the euro III standards.

Oxygen containing compounds

These compounds do not exist 2 % by weight in the crude oil. Typical examples are acetic and benzoic acids. These compounds cause corrosion and therefore needs to be effectively handled.

Resins

Resins are polynuclear aromatic structures supported with side chains of paraffins and small ring aromatics. Their molecular weights vary between 500 – 1500. These compounds also contain sulphur, nitrogen, oxygen, vanadium and nickel.

Asphaltenes

Asphaltenes are polynuclear aromatic structures consisting of 20 or more aromatic rings along with paraffinic and naphthenic chains. a crude with high quantities of resins and asphaltenes (heavy crude) is usually targeted for coke production.

Crude Oil Properties (Petroleum Assay)

Important Characterization Properties

Numerous important feed and product characterization properties in refinery engineering include:

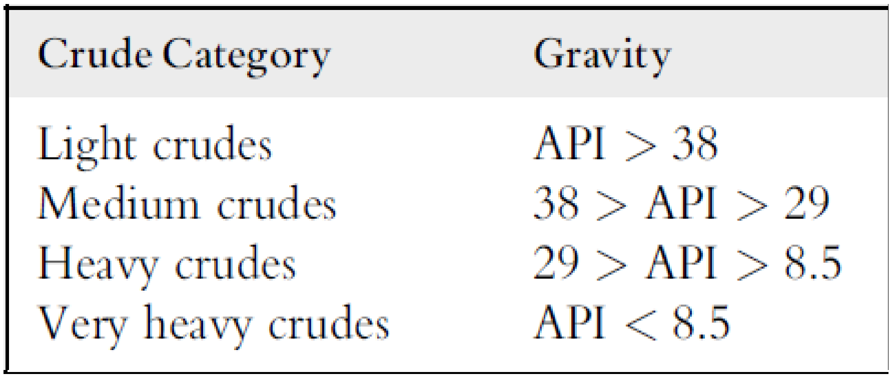
- *API gravity*
- *Watson Characterization factor*
- *Viscosity*
- *Sulfur content*
- *True boiling point (TBP) curve*
- *Pour point*
- *Flash and fire point*
- *ASTM distillation curve*
- *Octane number*

1. ***API gravity*** *API gravity of petroleum fractions is a measure of density of the stream. Usually measured at 60 ^{o}F, the API gravity is expressed as:*

API^{o} = 141.5/specific gravity – 131.5
where specific gravity is measured at 60 ^{o}F.

lighter API gravity value is desired as more amount of gas fraction, naphtha and gas oils can be produced from the lighter crude oil than with the heavier crude oil. Therefore, crude oil with high values of API gravity is expensive to procure due to their quality.

Table 2.: Classification of crude oils



Crude Category	Gravity
Light crudes	API > 38
Medium crudes	38 > API > 29
Heavy crudes	29 > API > 8.5
Very heavy crudes	API < 8.5

2. Watson characterization factor

The Watson characterization factor is usually expressed as:

K = (TB)1/3/specific gravity

Where TB is the average boiling point in degrees R taken from five temperatures corresponding to 10, 30, 50, 70 and 90 volume % vaporized.

- *Typically Watson characterization factor varies between 10.5 and 13 for various crude streams.*
- *A highly paraffinic crude typically possesses a K factor of 13. On the other hand, a highly naphthenic crude possesses a K factor of 10.5.*
- *Therefore, Watson characterization factor can be used to judge upon the quality of the crude oil in terms of the dominance of the paraffinic or naphthenic components.*

3. Sulfur content

- *sulphur is present in the crude oil. crude oils with high sulphur content are termed as sour crude. On the other hand, crude oils with low sulphur content are termed as sweet crude.*
- *Typically, crude oil sulphur content consists of 0.5 – 5 wt % of sulphur. Crudes with sulphur content lower than 0.5 wt % are termed as sweet crudes. It is estimated that about 80 % of world crude oil reserves are sour.*

4. Viscosity

- *Viscosity is a measure of the flow properties of the refinery stream. Typically in the refining industry, viscosity is measured in terms of centistokes (termed as cst) or saybolt seconds or redwood seconds.*
- *Viscosity is a very important property for the heavy products obtained from the crude oil. The viscosity acts as an important characterization.*

5. Flash and fire point

- *Flash and fire point are important properties that are relevant to the safety and transmission of refinery products. Flash point is the temperature above which the product flashes forming a mixture capable of inducing ignition with air.*
- *Fire point is the temperature well above the flash point where the product could catch fire. These two important properties are always taken care in the day to day operation of a refinery.*

6. Pour point

- *When a petroleum product is cooled, first a cloudy appearance of the product occurs at a certain temperature. This temperature is termed as the cloud point.*
- *Upon further cooling, the product will ceases to flow at a temperature. This temperature is termed as the pour point. Both pour and cloud points are important properties of the product streams as far as heavier products are concerned.*

7. TBP/ASTM distillation curves

- *The most important characterization properties of the crude/intermediate/product streams are the TBP/ASTM distillation curves. Both these distillation curves are measured at 1 atm pressure. In both these cases, the boiling points of various volume fractions are being measured.*
- *The basic difference between TBP curve and ASTM distillation curve is that while TBP curve is measured using batch distillation apparatus consisting of no less than 100 trays and very high reflux ratio, the ASTM distillation is measured in a single stage apparatus without any reflux. Therefore, the ASTM does not indicate a good separation of various components and indicates the operation of the laboratory setup far away from the equilibrium.*

8. Octane number

Octane number expresses the anti-knocking characteristics of petrol. Normal heptane (s constituent of petrol) when burnt in a petrol. Engine knocks it very badly i.e. the anti-knocking value of n-heptane is very poor and it is assigned an octane number equal to zero. On the other hand, iso-octane (also a constituent of petrol) has got a very good anti-knock characteristic;hence it is assigned on octane number of 100.

- ***Definition of octane number.** Octane number of petrol is the percentage by volume of iso-octane in a mixture of iso-octane and normal heptane with the same knocking tendency as the petrol in question.*

If the octane number of a petrol is 80 then it means that this petrol gives as much knocking as a mixture of 80% iso-octane and 20% normal heptane.

- ***Significance of octane number.*** *Higher octane number of petrol means higher efficiency and higher power output by the engine. Hence, higher the octane number, better the petrol,*

- ***Means to improve octane number.*** *Octane number of petrol is increased by adding some additive compounds in it. The most important additive is Tetra Ethyl Lead (TEL). Quantity added is 3.6 ccl /gallon of motor petrol and, 5.6 cc/gallon of aviation petrol.*

TEL is extremely poisonous, hence petrol containing TEL is always coloured for identification and safety.

Petroleum Fuel Processing, and Product Applications

The bulk of hydrocarbon-type fuels are derived from crude oil, coal, and other fossil deposits. In rare cases, crude oil can be used directly from the wellhead, comparable to the burningofrun-of-minecoal,butingeneralitissubjectedtoavarietyofrefiningandblending processesbeforetheresultingproductsaresuitableforuse.

Oil-refining

Followingtheremovalofgases,dirtandwater,freshlywoncrudepetroleumistransportedto therefinerywhereitbecomesthefeedstockforthemainrefineryprocesses. Thesearedesignedtoproduce'fractions',orbatchesofdifferenthydrocarbonsboiling within certainrangesoftemperature.Theseproductsareobtainedbythefollowingtypesofprocess:

(a) separation,
(b) conversion(bymolecularsplitting,combinationortypechange)and
(c) Treatment.

Representative processes are shown in simplified form in the figure:

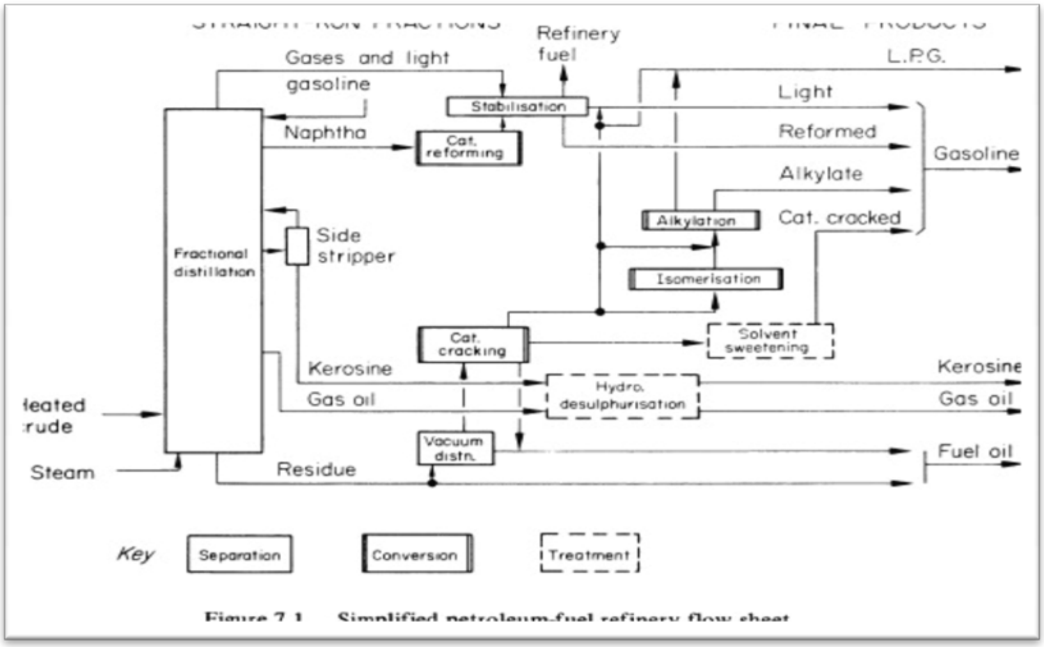


Figure 7.1 Simplified petroleum-fuel refinery flow sheet

Natural Gas

It is a mixture of paraffinic hydrocarbons, in which methane is the main constituent. It occurs:

- in the gas field (under the crust of earth) .
- in association with crude petroleum in oil fields.

After delivery from wells, natural gas is processed to remove the solids. It is then treated for recovery of gasoline and liquified natural gas (LNG).

- When natural gas contains very less recoverable condensate ($<15gm/ m^3$), it is known as **dry natural gas**.
- while it is termed as **wet natual gas** if recoverable condensate is more ($>50gm/ m^3$).

This condensate is recovered and is known as (**natural gasoline**) which is used as a blending agent for motor fuel.

The condensate (**natural gasoline**) recovery from gas is done by compressing& cooling or adsorption on a porous solid.

Typical composition and properties of natural gas are given in Table.1.

Table (1). Composition and Properties of Natural' Gas

Parameters	Dry and sweet gas	Wet and sweet gas
Composition (volume%)		
CH_4	96.91	77.22
C_2H_6	1.33	11.18
C_3H_8	0.19	5.83
C_4H_{10}	0.05	2.34
C_5H_{12}	0.02	1.18
CO_2	0.82	0.80
N_2	0.68	1.39
Gross C.V., kcal/Vm^3(dry)	9000	11200
Sp. g^{r}avity (Air = 1)	0.574	0.741

Natural gas of some localities contains large quantity of N_2 and CO plus recoverable amount of helium. Sometimes H_2S are also present in the gas which is recovered as elemental sulphur. H_2S free gas is called a sweet gas.

Natural gas is used as a fuel for:

- cooking, domestic
- industrial heating,
- process furnace and boilers
- fertiliser production
- a source of carbon and hydrogen in chemical industries.

Refinery Gases

Gases obtained during distillation, cracking and other processing of petroleum and its fractions which contain paraffins (e.g. methane, ethane, propane and butane), olefins (e.g. ethylene, propane and butane), hydrogen sulphide and hydrogen are called refinery gases. A possible range of volumetric composition and properties of refinery gases is given in Table 3.

Table (3) Composition and Properties of Refinery Gas

Pro pone + Propane	40-55%
Butene + Butane	upto30%
Ethylene + Ethane	8-12%
Methane	8-10%
Hydrogen	6-8`%
Hydrogen sulphide	6-8%
Calorific value, kcal/Nm^3	20500
Specific gravity (Air = 1)	1.35

Table (4) Yield of refinery gases in the form of LPG in various refinery processes

Refinery process	**Feedstock**	**Main products**	**Yield of LPG (weight% on feed)**
Visbreaking/coking	Residuum, heavy gas	Coke	5-10
Catalytic reforming	Light virgin naphtha	Aromatics, gasoline	5-10
Alkylation/Polymerisation	Butane-unsaturated	Gasoline	10-15
Catalytic cracking	Gas oil	Ethylene, propylene petrochemicals)	15-20

Liquefied petroleum gas

Liquefied Petroleum Gas

known as LPG or LP gas, is the term applied to a mixture of certain light hydrocarbons derived from petroleum which are gaseous at normal ambient temperature and atmospheric pressure but condensed to the liquid state at ambient temperature by application of moderate pressure. Although they are normally used as gases, they are stored and transported as liquids under pressure.

Composition of LPG

- Liquefied petroleum gases are usually mixtures of saturated and unsaturated hydrocarbons in the C3 and C4 range.
- LPG consists of one or more of the following hydrocarbons:
- Propane **(C_3H_8)**
- Propylene **(C_3H_6)**
- n-butane **(C_4H_{10})**
- Iso-butane **(C_4H_{10})**
- Butylene **(C_4H_8)**
- Traces to small quantities of one or more of the following hydrocarbons may also be present:

1. Ethane (C_2H_6)
2. Ethylene (C_2H_4)
3. Pentane (C_5H_{12})
4. Pentene (C_5H_{10})

- LPG separated from heavier hydrocarbons by a straight distillation process contains only the saturated hydrocarbons.

- LPG obtained from conversion processes such as thermal/catalytic cracking, reforming and hydrocracking contains unsaturated hydrocarbons as well.

Properties of LPG

1. LPGs are characterized by their high calorific values and a high degree of purity.
2. Vapour pressure is one of the most important characteristics of LPG.
3. It determines the pressure that will be exerted by the gas at ambient temperature and therefore affects the requirements for handling and the designed working pressures of storage vessels.
4. LPG has a very low sulphur content.
5. The density of LPG in its liquid form is about half that of water.
6. The limits of flammability for LPG are much narrower than most other gaseous fuels.
7. LPG is odourless.
8. However, a distinctive odour is addedmercaptane to aid in detection in the case of leakage.
9. LPG when vaporised leaves little or no residue.

Production of LPG

- There are two main sources of LPG. These are:

(a) Extraction of LPG from natural gas at well head; and
(b) Refining of crude oil.

- Extraction of LPG from natural gas
- There are several processes by which LPG can be extracted from natural gas.
- These are:

1. Compression and cooling.
2. Adsorption.

3. Absorption.
4. Cryogenic processes.

LPG Treatment

- Most of straight-run LPG produced from crudes requires only caustic wash as the mercaptan level is below 50 ppm.
- Merox treatment (extractive type) is necessary Odourisation.
- Since LPG is used as domestic fuel the chances of fire in confined locations become large in the case of accidental leakage

Uses of LPG

- LPG is used as a domestic fuel,
- a fuel for internal combustion engine and
- a feedstock for the manufacture of various chemicals and olefins (by pyrolysis).

NAPHTHAS

Naphtha is a generic name given to

- Light hydrocarbons boiling in the gasoline range.
- It is a light distillate obtained from refining of crude oil.
- The boiling ranges of various types of naphthas produced include:

- C5 - 85°C
- C5 - 110°C
- C5 - 140°C
- C5 - 160°C
- C5 - 175°C and
- C5 - 200°C.

In these initial boiling point (IBP) is constant. Other boiling ranges can be

- 60 - 85°C
- 85 - 110°C and
- 110 - 140°C

Naphtha are usually classified as

- light, If the naphtha fraction boils below 100°C.
- intermediate the boiling range lies between 100 and 150°C .
- and heavy naphthas boils above 150°C .

Methods of Manufacture of Naphthas

Naphtha is produced

1. by atmospheric distillation of crude oil. This is called straight-run naphtha.
2. Several conversion processes such as visbreaking, fluid catalytic cracking, hydrocracking, coking also produce naphthas. These are called cracked naphthas.

Composition of Naphthas

• Naphtha is a complex mixture of hydrocarbons. Its composition depends on

the crude oil processed and the conversion process employed.

For the composition of naphthas, two types of analyses are usually carried out.

• hydrocarbon type analysis; determines the percentage of paraffins, olefins, naphthenes and aromatics.

Uses of Naphthas

- Naphtha finds an extensive use as fertilizer feedstock
- In petrochemical industry,
- straight-run naphtha used as a steam-cracker feedstock.
- The use of naphtha as gasoline requires its high antiknock value or octane number

GASOLIN

The gasolines are

- colourless blends of volatile liquid-petroleum fractions .
- which boil within the temperature range of about 30 to 200 °C.
- In general, motor gasolines (mogas).

For aviation gasolines (Avgas),

• the distillation range is limited to about 50 to 170 °C, in view of the more stringent requirements for vapour control at altitude, and for uniform distribution of mixture to the engine cylinders.

• Avgas blending components are also restricted, and the relative density is about 0.72.

Overall average properties,

1. gasolines can be considered as roughly equivalent to **octane** (C_8H_{18}), but their components range from about C5 to C12.
2. Thus they have some of the volatility properties of **pentane** for ease of starting in the cold.

• The narrow cuts of C5 /C6 boiling from 20 to 60 °C, and of C6/C7 boiling from 60 to 100 °C, known, respectively, as petroleum ether and naphtha also distil with the gasolines but are used more commonly as solvents, paint thinners and feedstock than as fuels.

1. The net calorific values of gasolines lie at about 43.9 MJ/Kg and 31.8 MJ/Kg.
2. but the most important property is the anti-knock rating.

– since this determines the proportion of energy that can be extracted from the fuel when used in its main application - the spark-ignition engine.

Anti-knock quality

1. is a fuel-engine relationship, and cannot be represented completely by any standard test of the fuel alone.
2. However, the Research octane number (R.O.N.) is considered to give the closest approximation to the anti-knock quality of motor gaszolines in current vehicle applications.
3. In order to attain such levels of quality,
4. straight-run gasolines are blended with high quality stocks such as :

- catalytically reformed aromatics,
- catalytically cracked or polymerized olefins,
- and isomerizes or
- alkylate paraffins.

Absolute vapour pressures range from

- 5.5 lbf/in.2 (37.9 kPa) minimum for aviation gasoline,
- to about 13 lbf/in.2 (90 kPa) maximum for winter-grade motor gasolines.
- Hence gasolines must be vented in storage to prevent pressure build-up and, since the flash points are well below ambient (approximately —40 °C),
- all potential sources of ignition are excluded from the vicinity of gasoline storage tanks where the over-rich vented vapour—air mixture is brought through the flammable mixture zone by progressive dilution with atmospheric air.
- The **freezing point of motor gasoline** lies at about -70 °C, but its specification is unnecessary.
- Prior to **stabilization in the refinery**, gasolines may contain unstable materials capable of oxidizing or polymerizing to form gums
- under low-temperature conditions during storage or
- Under high-temperature conditions, the formation of lacquer leads to valve and piston-ring sticking, with serious damage to the engine.
- Refinery stabilization may therefore be augmented by additives of the anti-oxidant and copper-deactivating types.

- The **sulphur content** of gasoline must be limited to about 0.05 per cent mass to prevent Corrosion.
- and avoid inhibiting the response to T.E.L. addition.
- The odour of a gasoline may also have to be treated.

The well-known major **application of gasoline** is

- the spark-ignition reciprocating-piston engine widely used for powered transport.
- and for certain portable or static equipment where modest power is required from small lightweight units.
- One minor application is as fuel for flameless catalytic- type heaters.

Wide-cut gasoline (Avtag):.

- Its relative density is about 0.77,
- net calorific values 43.4 MJ/kg and 33.9 MJ/1,
- and absolute vapour pressure between 2 and 3 lbf/in.2 (about 14 and 20 kPa).
- Its overall average properties are roughly equivalent to decane.

Kerosines

The kerosines are

– colourless blends of relatively involatile petroleum fractions.

– which boil between about 150 and 250 °C.

– and have a relative density in the region of 0.8.

– The net calorific values lie at about 43.3 MJ/kg and 34.6 MJ/l.

– The vapour pressure is too low to be specified, but volatility can be determined indirectly in terms of flash point.

More recent applications include:

1. domestic heating-systems,
2. blow lamps,
3. cookers

twokerosine types of burner fuel are classified as C1 and C2.

– with minimum smoke-points of 35 and 25 mm, respectively,

– and maximum char values of 10 and 20 mg/kg, respectively.

Commercial grades of kerosine are

– sometimescoloured and/or

– perfumed

Aviation gas-Turbine kerosine’ (Avtur), is

– basically similar to lamp kerosine but particular care is taken over such properties

• as viscosity and

• distillation characteristics

– to control

1. atomisation and
2. combustion efficiency,
3. aromatic content to restrict product deposition and
4. smoke, and freezing point for satisfactory fuel-system operation under winter conditions and at altitude.

and for supersonic flight kerosines must be

For aircraft-carrier operations,

– where space for the storage of aviation fuels is limited

– increased storage safety

– This has a minimum flash-point 140 °F (60 °C)

- The relative density is about 0.82,
- and the calorific values are about 43.1 MJ/kg and 35.8 MJ/1.

•

The overall average properties of kerosine and high-flash kerosine are very roughly equivalent to dodecane, $C_{12} H_{26}$, and tridecane, $C_{13} H_{28}$, respectively.

Manufacture of Kerosines

• Straight-run kerosine cut obtained from crude

– aromatics content.

The main disadvantage of high aromatics content isthat kerosine burns with a smoky flame.

• In order, therefore, to produce a superior quality of kerosinewhich will burn with a flame height without smoke,

– the straight-run kerosine is treated with liquid sulphur dioxide to reduce the aromatics content.

Liquid sulphur dioxide process is also known as Edeleanu process.

– aromatic and unsaturated hydrocarbons are completely miscible with liquid SO_2

– but the paraffins and naphthenes are not.

– SO_2 also extracts cyclic sulphur compounds and nitrogen compounds.

• abehaviour that makes the process useful in handling certain high sulphurkerosines.

• Another process to treat kerosines from either sweet or sour crudes ishydrofining.

• Hydrofining of kerosines is especially attractive in refineries where sweet crude e is not available.

It affects improvements in

1. sulphur content,
2. odour,
3. colour and
4. burning qualities (as measured by wick فتيلة char).
5. By hydrotreatment of a kerosine fraction,

– Aromatics can be converted into naphthenes,

– there by producing an improvement in burning characteristics.

• The smoke point of kerosine is an important burning characteristic.

– The tendency of kerosine to smoke is mainly dependent on the types of hydrocarbons present.

• The greater percentage of elemental carbon in aromatics, compared with paraffins,

– means that high aromatic fuels will smoke more readily

– and hence aromatics may have to be removed during the manufacture of kerosines.

• The tendency of kerosines to smoke decreases in the order:

Aromatics >Naphthenes>Isoparaffins>Paraffins

• The tendency of paraffins to smoke increases with

– increase in molecular weight.

– Branching and olefin linkage in paraffins increases the tendency to smoke.

• The tendency of naphthenes to smoke decreases with

– increasing molecular weight and increases on addition of double bond.

– With increase in molecular weight, the tendency of aromatics to smoke decreases

Uses of Kerosines

Kerosine is used as

1. domestic fuel.
2. It is used for cooking and lighting.

3. Kerosine is also used to manufacture insecticides*مبيدحشري* , herbicides *مبيدالاعشاب* and fungicides *مبيدالفطريات* .
4. These are used to control pests*الحشرات* , weeds*اعشابضارة* and fungi *فطريات* .
5. Normal paraffins in the range of C10 - C13 are extracted from kerosine employing selective adsorption into synthetic zeolites (molecular sieves).
6. A range of highly aromatic white spirits and kerosine solvents may be manufactured from the kerosine extracts.

AVIATION TURBINE FUELS (ATF)

AVIATION TURBINE FUELS (ATF)

- A potential fuel for the gas turbine engines used in aircraft requires

– high thermal stability,
– high heat content,
– lowvapour pressure,
– good combustion characteristics,
– good viscosity- temperature relationship,
– high density,
– high specific heat,
– uniformity
– and good handling characteristics.

- The combustion properties of aviation turbine fuel (ATF) are generally controlled using several of the following five tests:

– smoke point,
– luminometer number,
– aromatics content,
– aniline point
– and gravity.

- The heat of combustion is normally calculated from the aniline point and gravity.
- Only two basic types of ATFs,

– thekerosine type and
– the wide-cut gasoline type,

- are in general used worldwide.
- High heat content per unit volume is required in high speed aircraft

– while weight is more important in low speed aircraft.
– Naphthenes have high heat content per unit volume and paraffins per unit weight.
– Low vapour pressure is needed to minimize evaporation losses.

- A fuel with a dense molecular structure permits more energy to be packed in a given tank space.
- Fuels capacity as a coolant depends on

– specific heat
– and heat of vaporization.

- Fuels should

– possess high smoke points, high luminometer number to minimize the temperature rise in combustion zone from flame radiation.

- Normal paraffins are the best from luminosity and smoke point of view.
- Specific heat as related to density is the highest for paraffin, lowest for aromatics and intermediate for naphthenes

Composition of ATFs

- Aviation turbine fuels are

– distillate fractions of crude oil in the boiling range of 150 - 270°C,
– and consist predominantly of hydrocarbons.
– The minor constituents of ATFs consist of
• sulphur,
• nitrogen and oxygen compounds
• and traces of particulate matter
• and water as contaminants.
– Paraffins and naphthenes are the major compounds in ATFs and their ratio varies with crude source.
• On a weight basis, the heat of combustion is the
– highest for paraffins,
– lowest for aromatics and
– intermediate for naphthenes.

Properties of ATFs

• Physical properties such as
– density,
– viscosity,
– volatility,
– auto-ignition temperature
• are of considerable importance with regard to engine and fuel system design.
• These properties also affect storage and handling facilities.
– Density is an important parameter in the design of fuel tanks in aircraft.
– Fuels of a considerable density range can readily satisfy the essential quality requirements of ATF.
• However, it is usually necessary to limit the density of a particular type of fuel, e.g. kerosine type to get satisfactory engine control.
• The specific energy of the fuel on a volume basis
– increases with increasing density,
– and it decreases on a weight basis.
• Hence, the density of the fuel is important in respect of total heat (energy) content.
• Depending on
– route structures,
– traffic density and
– a balance between payload and fuel weight, one can decide the aircraft to be weight limited or volume limited.
• ATF specifications set minimum values for the net (or lower) calorific value per unit weight.
• For maximum energy, therefore, in a volume-limited situation, a high density fuel is required.

Viscosity is specified to maintain fuel line pressure losses at low-temperature operation at acceptable levels and to ensure the fuel injection nozzles and fuel system controls at or near to design conditions.
• For ATFs (kerosine type),

– Indian specification requires a maximum viscosity of 15 cSt at - 34.4°C and 6 cSt at - 17.8°C.

– The volatility of ATFs is controlled to minimize the loss of fuel from unpressurised aircraft tanks due to boiling-off at high altitudes.

- For this reason the low volatility of kerosine type ATF is desirable.
- Distillation specification requires

– at least 20 vol.% recovery up to 200°C.

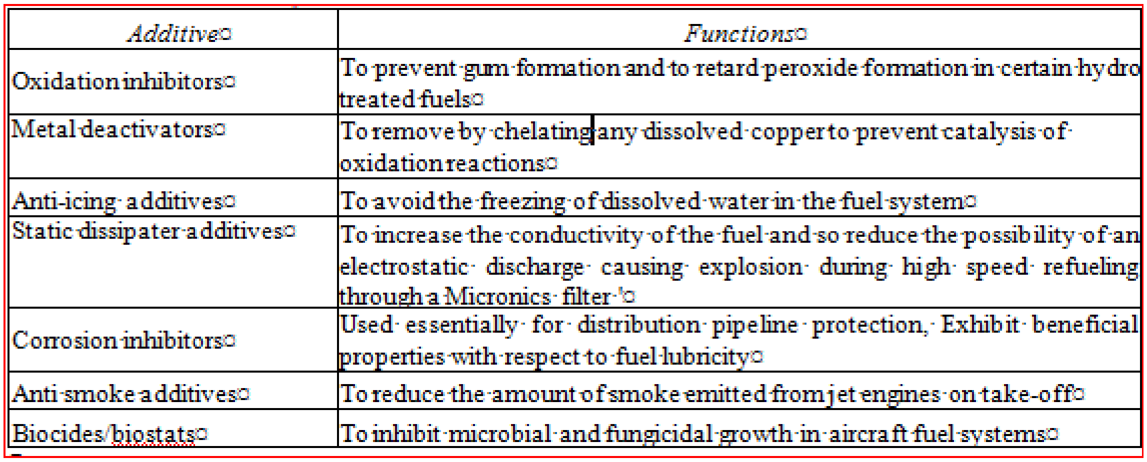
– The 20 percent point controls front-end volatility,

– and ensures that the fuel will readily vaporize for cold starting

– and limit evaporation losses at high altitudes.

- Auto-ignition of ATF can happen with a slight leak of fuel from the engine shortly after shutdown, or from a fuel line fracture during operation.
- The temperature for auto-ignition increases with increase in vapour pressure.
- As the atmospheric pressure is reduced the vapour pressure of the fuel increases, and so the auto-ignition temperature increases

ATF Additives

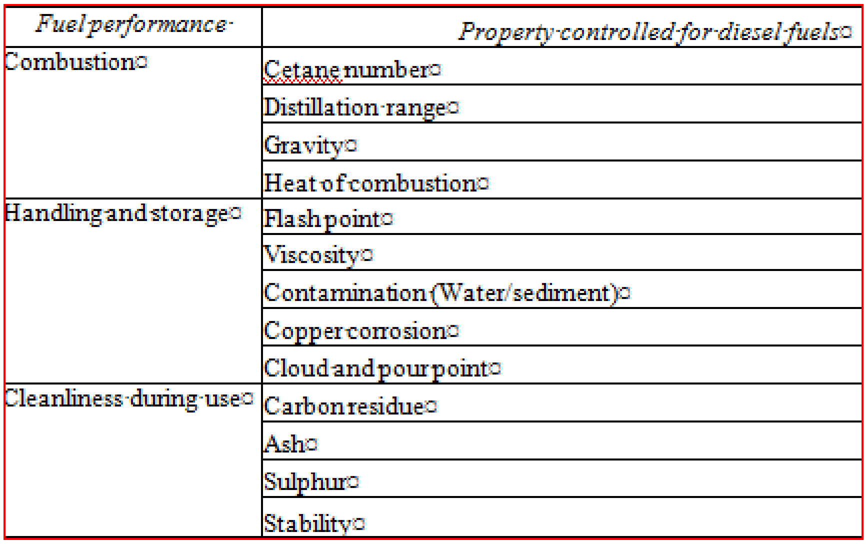


Additive	*Functions*
Oxidation inhibitors	To prevent gum formation and to retard peroxide formation in certain hydro treated fuels
Metal deactivators	To remove by chelating any dissolved copper to prevent catalysis of oxidation reactions
Anti-icing additives	To avoid the freezing of dissolved water in the fuel system
Static dissipater additives	To increase the conductivity of the fuel and so reduce the possibility of an electrostatic discharge causing explosion during high speed refueling through a Micronics filter
Corrosion inhibitors	Used essentially for distribution pipeline protection, Exhibit beneficial properties with respect to fuel lubricity
Anti smoke additives	To reduce the amount of smoke emitted from jet engines on take-off
Biocides/biostats	To inhibit microbial and fungicidal growth in aircraft fuel systems

DIESEL FUELS

• Combustion quality of diesel fuels relates those properties which directly affect the ability of a fuel to ignite properly.
– Diesel fuels must be suitable for handling by the injection equipment.
• The handling and storage characteristic is a function of
– volatility,
– fluidity,
– contamination during refinement
– and product shipment or movement.
• The characteristic of cleanliness during use is related to
– composition,
– trace contamination,
– and the degree of inherent stability of the particular fuel.
• Diesel fuels for automotive use need good ignition quality
– to ensure easy starting and smooth running.
• Sulphur content must be critically controlled
– to minimize environmental pollution, corrosion, wear and tear.
• The diesel fuels are
– darkish-brown petroleum fractions comprising distillate and/or residual components,
– with a relative density of about 0.87.
– The net calorific values are typically 41.9 MJ/kg and 36.5 MJ/1.
– Diesel fuels are used in
• the heavier, larger diesel engines employed in marine and
• stationary electricity-generating installations, which operate at relatively low rotational speeds and are less critical of fuel quality.
– Class E fuel is for burner use in industrial heating, hot-water boilers and drying processes, and has a maximum viscosity of 12.5 cSt at 180 °F (82.2 °C).
– Its minimum temperature for satisfactory handling is about 10 °C. The maximum viscosity of class B2 fuel is 14 cSt at 100 °F (37.8 °C).
– The maximum pour-points of B1 and B2 fuels are 0 and 3 °C, respectively,
– and the minimum flash-point of both fuels has recently been reduced to 60 °C.

- **Fuel Properties Needed for Acceptable Performance**



Fuel performance	*Property controlled for diesel fuels*
Combustion	Cetane number
	Distillation range
	Gravity
	Heat of combustion
Handling and storage	Flash point
	Viscosity
	Contamination (Water/sediment)
	Copper corrosion
	Cloud and pour point
Cleanliness during use	Carbon residue
	Ash
	Sulphur
	Stability

Composition of Diesel Fuel

- It is a general property of hydrocarbons that the autoignition temperature is higher for more volatile hydrocarbons.

– Therefore, the less volatile middle distillate fractions of crude oil boiling in the range of 150 - 400°C are suitable as diesel fuels.

- The hydrocarbons present in the diesel fuels include

– paraffins,

– naphthenes,

– olefins,

– and aromatics.

- Carbon number of these fuels ranges from 12 to 18.
- Diesel fuels can contain both

– saturated

– and straight or unbranched chain unsaturated hydrocarbons,

– but the latter are not present in large enough amounts to make fuel oxidation a problem.

- The aromatics that are present generally are oxidation resistant.

Properties of Diesel Fuels

- Ignition quality is important in high speed automotive diesel engines.

– It is less relevant in low speed engines used in large stationary and marine applications.

- The most universally accepted measure of the ignition quality of diesel fuels is cetane number.

– Cetane index which provides a measure of ignition quality very close to cetanenumber, is commonly used.

– It is calculated based on 10%, 50%, 90% distillation temperatures and specific gravity.

- Diesel index which is determined from

– aniline point

– and API gravity,

- provides a measure of ignition quality less close to cetane number than cetane index.
- When ignition quality improvers are added to fuels,

– the ignition quality cannot be indicated either by cetane index or diesel index.

- Fuels of poor ignition quality can lead to

– extended ignition delay and

– result in the phenomenon of ‘diesel knock’.

– This leads to decrease in
• efficiency,
• smoky exhaust,
• crankcase oil dilution
• and carbonaceous deposits in piston ring grooves.
• In general the cetane number seems to be associated with the thermal stability of the fuel hydrocarbons.
• Thus, higher molecular weight normal alkanes have high cetane numbers.
• Generally, high performance diesel oils are required to have a cetane number higher than 45.
• Volatility is the major determinant of the tendency of a hydrocarbon to produce potentially explosive vapours.
– It also is critically important to an engine's start and warm-up.
• The presence of high-boiling point components in fuels can significantly affect
– the degree of formation of solid combustion deposits.
• Proper operation of an engine depends on
– the proper viscosity of the liquid fuel.
• The viscosity of the liquid fuel is important to its flow through
– pipelines,
– injector nozzles,
– and orifices,
– and for atomization of the fuel in the cylinder.
• Diesel fuels should not creates any operational problems during its use.
– For example, diesel fuels should not cause deposits to occur in fuel injector systems or critical piston ring areas.

The carbon residue value of diesel fuel correlates with the amount of carbonaceous deposits which are formed in the combustion chamber of the engine.
– The higher carbon deposits in the combustion chamber are expected with the diesel fuels of higher carbon residues

Additives for Diesel Fuels

• Diesel fuel additives are used to enhance fuel quality and are often cost-effective.
• **Cetane improvers.**
– These are used to increase cetane number of diesel fuels.
• Straight- chain paraffins ignite readily tinder compression,
• but branched-chain paraffins and aromatics react more slowly.
– Since diesel fuel's ignition delay characteristic, and subsequent complete versus incomplete fuel burning, directly influence overall engine performance.
– Cetane number of a diesel fuel reflects the ease with which it undergoes compression ignition and is an indicator of performance related properties which include
• cold starting,
• smoke emissions during warm-up,
• noise,
• power,
• exhaust emissions,
• fuel consumption
• and engine durability.
– Cetane improvers are compounds which
• readily decompose to give free radicals and
• thus enhance the rate of chain initiation for hydrocarbon oxidation in diesel combustion.
• They promote fast oxidation of fuels and
• thus improve their ignition characteristics.
– Cetane improvers are mainly alkyl nitrates.

– Depending on the base fuel’s cetane number and additive treat rate, it is possible to obtain very cost-effective improvements between three and six cetane numbers with the isooctyl nitrate.
– One cetane number increase requires about 100 pounds per thousand barrels (ptb) cetane improver.
– Cetane improvers provide refineries with a simple and effective means of achieving operational flexibility on a day to day basis.
- Detergents.
- These are used as cleaners to
– remove carbonaceous and gummy deposits from fuel injectors

and to prevent further formations.
- Fuel gums cause

moving parts in the fuel system to stick, especially close-tolerance components like injector needles and plunger pistons.
- Lacquer and carbon
– deposited on injector needles restrict fuel flow,
– distort the fuel spray and often totally block one or more holes in a multihole injector.
- Modem detergent additives are composed mainly of
– ashless amines and amides.
– Older-style imidazones are still used.
- The detergent must be added to the base diesel fuel at a minimum dose of 40 to 50 ptb to effect optimum engine cleanup and prevent further deposits.
- Stabilizers.
- These retard the natural degradation of diesel fuels during long-term storage.
- Because diesel fuels are organic in nature,
– they will degrade from the time of manufacture until the time of use.
- The harmful effects of fuel oxidation include
– free-carbon particulate fallout
– and sedimentation sludge buildup in the fuel delivery system and fuel storage tanks.
- The following stabilizer additives are needed:
– De-emulsifier to improve anti-haze and minimize fuel/water suspension.
– Sludge retardant to limit deposit buildup.
– Dispersant to break up fuel droplets, reduce surface tension and provide buffer barrier to prevent further deposits.
– Rust-corrosion inhibitor to prevent pitting and erosion of metallic surfaces.
– Metal deactivator to inhibit deterioration by trace metals.
– Anti-oxidant to retard formation of gums and deposits.
- Dispersant
– restricts the size of fuel particles
– and reduce the fuel’s surface tension.
- By lowering the fuel’s surface tension, dispersant modifier additives such as
– polyamides,
– polyisobutane and
- cause the fuel droplets to break up and atomize more easily.
- Because they are surfactants, they
– also are adsorbed onto metallic surfaces
– and provide a huffier barrier to prevent future deposits
– and keep the surfaces of the combustion chambers
– and injection nozzles clean.
- Dispersants provide adequate performance when added to diesel fuels at doses of only 20 to 25 ptb.
- Anti-corrosion and rust-inhibitor additives

– are used to protect pipelines through which diesel fuels are transported.
– These form oily coaling over metal surfaces as protection against corrosive attack.

Usually the protection of fuel system from corrosion and rust requires only 3 to 5 ptb.
• Anti-oxidants
– retard the formation of fuel gums, sludges, sedimentation deposits and oxidation byproducts.
– One notable effect of fuel degradation during long-term storage of hydrotreated or hydrocracked low-sulphur diesels is peroxides formation.
– The anti-oxidant additive is to be added to the diesel fuel as soon after the manufacture as possible.
– The peroxide inhibitors are cost-effective at a treat rate of 3 to 5 ptb
• Pour point depressants
• Paraffins exist in all diesels and vary in amount depending on the crude oil refined.
– In cold temperatures, paraffins crystallize into wax.
– Without flow modifier additives, this wax generally creates large, flat platelets crystals that tend to clump together and clog fuel filters by adhering to the screen grids.
– The resulting engine starvation can cause poor starting and engine shutdown.
– Pour point depressants, flow improvers and cloud point reducers are three basic types of cold-flow modifiers.
– Wax (paraffin) content and the type of fuel will affect each of these parameters as well as an additive’s response when treated.
– Wax content in a finished fuel is mainly a function
• of boiling range of the diesel fuel and
• the composition of the crude oil.
– Fuels with a wide boiling range usually form
• somewhat smaller, more consistently shaped wax crystals that are more responsive to additive treatments.
– The narrow boiling range diesel fuels tend to form
• larger, more dense wax crystals that do not respond well to traditional cold-flow additives.
– Pour point depressants are chemicals that lower the pour point temperature.
• Today’s pour point depressants work by changing the attraction of wax crystals and modifying the wax crystal’s shape and size as they form.
• These additives reduce the crystal formation rate effectively.
• Flow improvers primarily improve cold filterability, but they can also lower the pour point of the fuel**.**
– These chemicals change wax crystal formation by forming nuclei and arresting growth.
– As the fuel’s temperature drops below the cloud point,
• small wax crystals begin to grow on the nuclei.
– A flow improver’s molecules attach to crystal surfaces and block further growth.
– This results in smaller crystals.
– By virtue of their small size and multi-axial needle arrangement, these wax crystals pass more easily through fuel filters.
• Anti-wax settling additives (AWSA)

are flow improvers that disperse wax crystals uniformly.
– Normally, small, compact wax crystals tend to settle in tank bottoms, especially in unagitated storage tanks.
– These compounds create more porous (less dense) wax crystals with repelling charges that tend to prevent wax agglomerations into the larger/heavier wax crystal matrix.
– These additives work more efficiently in lower wax-content fuels and total wax content will affect performance of all AWSA.
– Most distillate fuels can be effectively treated with AWSAs at doses between 40 to 60 ptb.
– Cloud point reducers lower the temperature at which fuel paraffins present in the diesel fuels begin to haze or cloud.

– Generally, a reduction of approximately 2 to 3°C in the cloud point can be achieved by the use of olefin-ester copolymer.

– typical levels of cloud point depressant additives are 50 to 170 pt

• **De-emulsifier and deicer agents**

– break any fuel/water mixtures and prevent water from freezing in cold temperatures.

– De-emulsifier additives can be of different chemical makeup.

– The only effective deicer additives are chemicals of glycol-ether type.

– These additives chemically combine with water droplets (and dissolved water accumulations), break the surface connection with the fuel and lower the freezing point temperature in direct relation to the amount of de-emulsifier and deicer present.

– These additives should be used in combination at dose rates of 10 to 20 ptb.

FUEL OILS

• The fuel oils are
– brownish-black petroleum fractions
– consisting largely of the distillation residues from asphaltic-type crude oils,
– with a relative density of about 0.95.
– The net calorific values are typically 40.0 MJ/kg and 38.0 MJ/1.
– The most important property is viscosity, have maximum viscosities at 180 °F (82.2 °C) specified as 30, 70 and 115 cSt, respectively .
– Preheating is necessary, therefore, and minimum temperatures must be set for storage and handling, of 25 and 30 °C for class F fuels, and 35 and 45 °C for class G fuels, which represent a maximum viscosity of approximately 500 cSt.
– For atomization, a maximum viscosity of about 24 cSt at the burner tip is commonly adopted. The minimum flash-points are common at 66 °C.
– Sulphur content may reach about 3.5 per cent mass, and must be limited to restrict corrosion problems.
– The maximum water-content is specified as 1 per cent by volume.
– The mineral matter retained in petroleum residues appears as ash during combustion, and may contain harmful materials.
– Hence a maximum ash-content of about 0.2 per cent is also specified.
– Fuel oils are used for heating and steam-raising in ships and in industry generally.
– The heavy carbon-rich coal tar fuels range in relative density from about 1.0 to 1.2, and are classified according to the temperature (in °F) at which the viscosity reaches 100 Redwood I seconds (24.1 cSt), hence CTF 50 and CTF 250.
– They show advantages over petroleum-based fuels for furnace applications due to high luminosity and relative freedom from sulphur and vanadium contamination, despite their lower gravimetric calorific values and greater difficulties of atomisation.
–

Nature and Composition of Fuel Oils
– Fuel oils are essentially made up of residues remaining from
• atmospheric and
• vacuum distillation and
• conversion processes after the removal of the lighter hydrocarbons.
– These are sometimes cut back with high boiling distillate
• to meet the finished product specification requirements such as the viscosity.
– The viscosity of residues can also be reduced by visbreaking process.
– The finished blend of fuel oil may contain
• a number of components obtained from different sources.
– Residues from crudes differ considerably in
• sulphur and
• heavy metal contents,
– and specification requirements of fuel oil must be met by blending.

Fuel oils are blended usually in

10-20000 tonne tank sized lots**.**
– The components are introduced in the appropriate order into
- a large tank held,
- heated and blended,
- usually by jet or in-line blending.

– The fuel oil blend shall remain
- homogeneous.

– Viscosity or density samples are taken at various levels in the tank blending process
- to establish homogeneity.

– The chemical nature of fuel oils is
- most complex.

– The fuel oils are predominantly composed of
- higher molecular weight compounds known
- as asphaltic bitumens.
- These oils should not show any tendency to deposit asphaltic material during
- prolonged storage or
- on mixing with blends made from different crudes.

– Fuel oils used in industrial furnaces and boilers have
- a significant amount of metallic constituents which concentrate in the ash in the form of oxides of these metals.

– These oxides have
- deleterious effect on the refractories and
- often decrease the strength.

– Additives have been successfully used to combat this effect by modifying the nature of the residual ash.

Properties of Fuel Oils

– Important physical and chemical properties of fuel oils are:
- (a) viscosity and viscosity- temperature relationship,
- (b) pour point,
- (c) sludge and sediment formation,
- *(d)* carbon/hydrogen ratio,
- (e) sulphur content and
- (f) ash content.

– Combustion of Fuel Oils
– The reaction between
- fuel oil and
- oxygen (or air)

– releases the chemical energy into heat.
– This heat is then employed in industry to
- impart energy by radiation
- and convection to different pieces of equipment.

– For maximum overall efficiency, a good oil firing practice demands
- complete combustion and
- the most suitable type of flame

Handling and preparation of fuel oil.
- Essential pre-requisites for transfer of fuel oil from the main storage tank to the burners are the following:

– Fuel oil should be sufficiently fluid to flow at the desired rate from the main storage tank to the transfer pump.
– Pressure and horse power required for pumping the fuel oil must be

- within economic and
- physical limits.
- Fuel oil must be delivered to the burner at

– a sufficiently low viscosity to ensure satisfactory atomization.

- Fuel oils of low viscosity can be
- easily pumped at ordinary temperatures
- but it is not so with heavy viscous fuel oils.

– Since the viscosity of oil

- decreases with increase in temperature,

– more viscous grades of fuel oil have to be heated in order to

- make them fluid enough.