AT 2305 – Automotive Fuels & Lubricants

Unit I

Introduction to Automotive Fuels:

Automobile: Suitable Engine Classification
IC Engines (A type of Heat Engine)

Heat Engine: Heat Energy \( \rightarrow \) Mechanical Energy

Fuel \( \rightarrow \) Chemical Energy

Types of Fuels

1. Solid fuels – coal, biomass etc.
2. Liquid fuels – petrol, diesel, methanol, ethanol, biodiesel etc
3. Gaseous fuels – LPG, CNG, methane etc.

1. Liquid and gaseous fuels are widely being used in IC engines.
2. Solid fuel can also be used in IC engines after suitable modifications like gasification, slurry production.

Chemical reactions are fast enough to release heat energy but the method of preparing the mixture and its introduction into the engine depends mainly upon the nature of the fuel. Hence the automotive fuels should have certain physical, chemical and combustion properties.

1. High energy density – mass basis or volume basis
2. Good combustion qualities
3. High thermal stability
4. Low deposit forming tendencies
5. Compatibility with the engine hardware
6. Good fire safety
7. Low toxicity
8. Low pollution
9. Easy transferability and onboard vehicle storage

The natural petroleum oil is the largest single source of almost all internal combustion engine fuels.
Boiling range of petrol: 30 to 200 °C
Boiling range of diesel: 200 to 375 °C
Other IC engine fuels are hydrocarbon mixtures, coal, oil shale and fermentation products such as ethyl alcohol, methanol etc. Mixture of Carbon monoxide and hydrogen if catalytically converted can form good automotive engine fuel. But these processes are very costly and technical know-how is not available.

**Structure of Petroleum**

Usually the fuels used in IC engines are complex mixtures of hydrocarbons made by refining process. In addition, it may contain small quantities of other compounds such as nitrogen, oxygen and sulphur. In some petroleum, metallic compounds such as derivatives of vanadium, nickel, iron and arsenic etc may also found.

The constituents of crude petroleum are classified in four main groups.

There are:

(i) paraffins having the general formula $C_nH_{2n+2}$,
(ii) olefins having the general formula $C_nH_{2n}$,
(iii) naphthenes having the general formula $C_nH_{2n-2}$, and
(iv) aromatics having the general formula $C_nH_{2n-6}$.

Physical properties of the individual compound vary according to the carbon and hydrogen atoms in the molecule. The physical differences even in the group influence the way in which the fuel evaporates and hence the formation of combustible mixture. The chemical differences between the hydrocarbon types, which depend on the chemical composition and hence on the crude source and the nature of refining process, affect mainly the combustion processes and hence the proportions of fuel and air required.
Refining Process

The crude oil, as it comes out from the oil wells, contains impurities such as water, solids and gases consisting mainly of ethane and methane. By simple atmospheric pressure distillation, utilizing the fact that the boiling points of various hydrocarbons increase with an increase in molecular weight, the crude oil is separated into gasoline, kerosene, fuel oil or reduced crude oil.

First of all the lightest fractions such as butane, propane, ethane etc., which were either standing above the liquid in earth or dissolved in the crude, are obtained at low temperature and form natural gas. Then comes gasoline, naphtha kerosene, and fuel and gas oils, in order of increasing molecular weight. After distillation residue of paraffin wax or asphalt depending on the base of the crude is left.

The gasoline demand is much more than that of other petroleum products. This led to the development of refinery processes to convert unwanted streams of crude into salable products and to upgrade quality of these streams, i.e. to crack the larger molecules into smaller molecules having low boiling point as in the gasoline range, and in processes to polymerize or alkylate small molecules into larger molecules into larger molecules, both having boiling points as in the gasoline range.

The main refinery processes of petroleum are as follows:

<table>
<thead>
<tr>
<th>No. of carbon atoms</th>
<th>Prefix</th>
<th>No. of carbon atoms</th>
<th>Prefix</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>meth</td>
<td>7</td>
<td>hept</td>
</tr>
<tr>
<td>2</td>
<td>eth</td>
<td>8</td>
<td>oct</td>
</tr>
<tr>
<td>3</td>
<td>prop</td>
<td>9</td>
<td>non</td>
</tr>
<tr>
<td>4</td>
<td>but</td>
<td>10</td>
<td>doc</td>
</tr>
<tr>
<td>5</td>
<td>pent</td>
<td>11</td>
<td>undec</td>
</tr>
<tr>
<td>6</td>
<td>hex</td>
<td>12</td>
<td>dodec</td>
</tr>
</tbody>
</table>
A) **Thermal cracking**

If large hydrocarbon molecules are heated to a high temperature and pressure they decompose into smaller, lower boiling point molecules. This process of thermal decomposition is called cracking. The more stable molecules form cracked gasoline and the reactive ones polymerize, forming cracked oil and petroleum coke. Gasoline is the primary final product from the cracking plant.
(ii) **Catalytic cracking.** Catalytic cracking using a catalyst is done at a lower pressure and temperature than the thermal cracking. Due to the catalysis the napthenes are cracked to olefins and paraffins, and olefins to isoparaffins, and thus forming gasoline.

Catalytic cracking gives better anti-knock property gasoline as compared to thermal cracking.

(iii) **Polymerisation.** Polymerisation is the process of converting olefins, the unsaturated products of cracking, into heavier and stable compounds such as high octane gasoline. The typical reaction is

\[
\begin{align*}
\text{2 moles} & \quad \text{CH}_3 \\
\text{isobutylene} & \quad \text{CH}_3 \\
\text{C} = \text{CH}_2 & \rightarrow \text{CH}_3 - \text{C} - \text{CH}_2 - \text{C} = \text{CH}_2 \\
\text{CH}_3 & \\
\end{align*}
\]

1 mole di-isobutylene

(iv) **Alkylation.** Alkylation combines an olefin with an iso-paraffin to produce a branched chain isoparaffin of molecular weight equal to the sum of reactants, in the presence of a catalyst. This gives a fuel of very high octane number such as iso-octane or isopentane.

\[
\text{alkylation} \quad \text{isobutylene} + \text{isobutane} \rightarrow \text{iso-octane}
\]

(v) **Isomerisation.** Isomerisation is the process by which isomers, *i.e.* compounds having same chemical formula but different properties, are produced. Isomerisation is used:

1. to convert *n*-butane into iso-butane for alkylation.
2. to convert *n*-pentane and *n*-hexane into isoparaffins to improve knock rating of highly volatile gasolines.

Octane ratings between 93 and 107 are obtained with 95 percent pure iso-paraffins.

(vi) **Reforming.** Reforming is used to convert low anti-knock quality stocks. It does not increase the total gasoline volume as is the case in cracking polymerisation and alkylation processes.

(vii) **Blending.** Blending is the process of obtaining a product of desired quality by mixing certain products in some suitable proportion.

To meet the changing demands the volume of gasoline and distillates from the refinery is adjusted by changing the cut off points of various refinery processes.
**Products of refining process**

The important products of refining process are as follows.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Approximate boiling range °C</th>
<th>Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Fuel gas</td>
<td>-160 to -44</td>
<td>Methane, ethane and some propane used as refinery fuel</td>
</tr>
<tr>
<td>2. Propane</td>
<td>-40</td>
<td>L.P.G.</td>
</tr>
<tr>
<td>3. Butane</td>
<td>-12 to 30</td>
<td>Blended with motor gasoline to increase its volatility</td>
</tr>
<tr>
<td>4. Light Naptha</td>
<td>0 to 150</td>
<td>Motor gasoline for catalytic reforming</td>
</tr>
<tr>
<td>5. Heavy Naptha</td>
<td>150 to 200</td>
<td>Catalytic reforming fuel. Blended with light gas oil to form jet fuels</td>
</tr>
<tr>
<td>6. Kerosene</td>
<td>middle 200 to 300</td>
<td>Domestic, aviation fuels</td>
</tr>
<tr>
<td>7. Light gas oil</td>
<td>distillates 200 to 315</td>
<td>Furnace fuel oil, diesel fuels</td>
</tr>
<tr>
<td>8. Heavy gas oil</td>
<td>215 to 425</td>
<td>Feed for catalytic cracking</td>
</tr>
<tr>
<td>9. Vacuum gas oil</td>
<td>425 to 600</td>
<td>Feed for catalytic cracking</td>
</tr>
<tr>
<td>10. Pitch</td>
<td>&gt; 600</td>
<td>Heavy fuel oil, asphalts</td>
</tr>
</tbody>
</table>

**Natural Gas:**
Natural gas is found dissolved in petroleum or in huge amounts under earth surface in oil and gas bearing areas. Natural gas is made up mainly of the paraffinic compound methane, as small amount of propane, ethane, butane and other light hydrocarbons plus some nitrogen and oxygen.

**Liquified Petroleum Gas, LPG:**
Propane and butane and some other light hydrocarbons after separation from natural gas, if stored under pressure, from liquid and this is called Liquified Petroleum Gas (LPG). LPG is supplied in containers under pressure.

**Gasoline:**
Gasoline is the lightest liquid petroleum fraction. All material boiling up to 200 °C is generally considered as gasoline. This is mixture of a number of
hydrocarbons (more than 40). The composition depends upon the crude oil and refining process. Gasoline lies in specific gravity range 0.70 to 0.78. This covers most of the fuels used for spark-ignition engines.

**Kerosene:**

The kerosene is a fraction heavier than gasoline. Its boiling range is 150 to 300 °C and the specific gravity range is 0.78 to 0.85. Kerosenes are used in aviation gas turbines, as jet fuel and in lamps and stoves.

**Distillate:**

The distillate is slightly heavier than kerosene. These are used as tractor fuels and domestic fuels.

**Diesel Oils:**

Diesel oils are fuels which lie between kerosene and lubricating oils. These cover a wide range of specific gravity and boiling point. Boiling range is 200 to 370 °C. These form the fuels for compression ignition engines.

**Fuel Oils:**

Fuel oils are similar to diesel fuel in specific gravity and distillation range but their composition varies in a range wider than those of diesel fuels. These are used as industrial fuels.

**Lubricating Oils:**

Lubricating oils are made up of heavy distillate of petroleum and residual oil. These are used for lubricating purposes.

**Tar and Asphalt:**

Tar and asphalt are solid or semi-solid undistilled products of petroleum.

**Petroleum Coke:**

Petroleum coke is used as solid industrial fuel.
**Lubricating Oil Base Stocks**

Base oil, also called base stock, is the name given to the main liquid component (or components) of a lubricant. Base oils may be mineral oil based (mineral refers to the fact it was extracted from rocks in the form of crude oil), vegetable, or synthetic in origin. Synthetics may be petroleum-based or chemical-based. The base stock provides the basic lubricating requirements of a lubricant i.e. the "oiliness". In most modern lubricants, a base oil mixture alone is insufficient to deliver the technical performance characteristics required. Therefore, the base oils are mixed with a variety of different additives, each chosen to impart additional performance benefits to the finished oil.

There are two types of conventional mineral base oil – naphthenic and paraffinic – depending on the composition of the crude oil from which they are produced. All oils are composed of various ratios of these types of oil.

<table>
<thead>
<tr>
<th></th>
<th>Naphthenic</th>
<th>Solvent Refined</th>
<th>Hydro-Cracked</th>
</tr>
</thead>
<tbody>
<tr>
<td>n and Iso-paraffin</td>
<td>12</td>
<td>18</td>
<td>33</td>
</tr>
<tr>
<td>Cycloparaffins</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1, 2 Rings</td>
<td>29</td>
<td>39</td>
<td>50</td>
</tr>
<tr>
<td>3+ Rings</td>
<td>17</td>
<td>27</td>
<td>17</td>
</tr>
<tr>
<td>Aromatics</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1, 2 Rings</td>
<td>25</td>
<td>13</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>3+ Rings</td>
<td>6</td>
<td>1.3</td>
<td>Nil</td>
</tr>
<tr>
<td>Thiophenes</td>
<td>9</td>
<td>0.2</td>
<td>Nil</td>
</tr>
<tr>
<td>Polars</td>
<td>1.6</td>
<td>1.3</td>
<td>Nil</td>
</tr>
</tbody>
</table>

Fig. Base Oil Chemical Composition

Paraffinic base oils have higher viscosity index (generally >95) and a high pour point. They are produced from feed stocks rich in paraffins, and are used for lubricants for which VI and oxidation stability are important. Paraffinic base oils are not very good at dissolving additives and they do not emulsify easily. Because of their structure - long chains - they have high film strength and excellent lubricating properties. That is why paraffinics are used as the base fluid in engine oils, hydraulics and industrial lubes.

Naphthenic base oils have low viscosity index (VI) (generally 0-40) and a low pour point. They are produced from feed stocks rich in naphthenes and low in wax content. They are used mainly for lubricants in which color and color stability are important, and VI and oxidation stability are of secondary
importance. Naphthenic oils also have a greater propensity to solublize additives. Their structure does not lend them to the film strength and lubricating properties of the paraffinics but they are still good. They are therefore used extensively in the formulation of oil-based metalworking fluids.

Each of these types of oil has several grades, according to its viscosity. The American Petroleum Institute has developed a classification system for base oils in order to facilitate engine oil interchange guidelines.

The five groups are:

*Group I:* base stocks contain less than 90 percent saturates and/or greater than 0.03 percent sulfur and have viscosity index greater than or equal to 80 and less than 120.

*Group II:* base stocks contain greater than or equal to 90 percent saturates and less than or equal to 0.03 percent sulfur and have viscosity index greater than or equal to 80 and less than 120.

*Group III:* base stocks contain greater than or equal to 90 percent saturates and less than or equal to 0.03 percent sulfur and have viscosity index greater than or equal to 120.

*Group IV:* base stocks are polyalphaolefins (PAO).

*Group V:* base stocks include all other base stocks not included in groups I, II, III or IV. Naphthenic oils are considered Group V.

<table>
<thead>
<tr>
<th>Base Oil Category</th>
<th>% Saturates</th>
<th>% Sulfur</th>
<th>Viscosity Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>Group I</td>
<td>&lt; 90</td>
<td>and/or &gt; 0.03</td>
<td>80 - 119</td>
</tr>
<tr>
<td>Group II</td>
<td>≥ 90</td>
<td>and ≤ 0.03</td>
<td>80 - 119</td>
</tr>
<tr>
<td>Group III</td>
<td>≥ 90</td>
<td>and ≤ 0.03</td>
<td>≥ 120</td>
</tr>
<tr>
<td>Group IV</td>
<td>All Polyalphaolefins (PAO’s)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Group V</td>
<td>Anything Not Covered in Groups 1-IV</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. API Base Oil Classification System

Group II base oils are differentiated from Group I base oils because they contain significantly lower levels of impurities. They also look different. Group II and Group III oils made using modern hydroisomerization technology are so pure that they have almost no color at all. From a performance standpoint, improved purity means that the base oil and the additives in the finished
product can last much longer. Some refiners sell intermediate grades labeled as Group 1+ or Group II +.

Historically, PAOs have had superior lubricating performance characteristics such as VI, pour point, volatility, and oxidation stability that could not be achieved with conventional mineral oils. Now, in modern base oil manufacturing, VI, pour point, volatility, and oxidation stability can be independently controlled. Modern Group III oils today can be designed and manufactured so that their performance closely matches PAOs in most commercially significant finished lube applications. From a processing standpoint, modern Group III base oils are manufactured by essentially the same processing route as modern Group II base oils. Higher VI Is achieved by increasing the temperature or time in the hydro cracker.

Base Oil Properties

Certain properties are very important in determining the usefulness and application for a particular base oil:

**Viscosity** - The viscosity of an oil is a measure of its resistance to flow, and depends on the temperature at which the measurement is made. It has high values at low temperatures, and low values at high temperatures. A viscosity measurement has no value unless it is associated with a temperature. In the past, viscosity was expressed in Engler (Europe), Redwood (UK) and Saybolt (USA). Nowadays, centistoke (kinematic viscosity) and centipoise (dynamic viscosity) are commonly used units.

**Viscosity index** - As viscosity depends on temperature, a measure of its sensitivity to temperature is expressed by its viscosity index (VI) value. VI is determined by comparing the change of viscosity with temperature to two reference oils - one of which changes very little with temperature and is given a VI = 100, and another which changes a lot and is given a VI = 0.

**Oxidation stability** - Most oils, when exposed to air over time, react with oxygen. The Turbine Oil Stability Test (TOST) and the resulting TOST life are measures of the oxidation stability, i.e. how much it degrades in the presence of air. Oils used to blend lubricants must have high oxidation stability; otherwise, they become discolored during storage. When base oils with poor oxidation stability are used in engines, the high temperature causes them to form corrosive acids and insoluble sludge. This can hamper the engine's performance by forming a hard layer in the grooves of the piston rings.

**Aniline Point** - Aniline point is defined as the minimum temperature at which equal volumes of anhydrous aniline and oil mix together. Its main use is determining the quality of fuels. Since aniline is an aromatic compound, it freely
mixes with other aromatics so a low aniline point indicates low diesel index (because of high percentage of aromatics). High aniline point indicates that the fuel is highly paraffinic and hence has a high diesel index and very good ignition quality. In case of aromatics the aniline point is low and the ignition quality is poor.

In the metalworking industry, the aniline point is useful in determining the solvency power of your base oil. The lower the aniline point, the better the base oil will be at solubilizing and holding onto additives and emulsifiers.

**Pour point and cloud point** - The cloud point of an oil is the temperature at which the first trace of wax starts to separate out, causing it to become turbid or cloudy. If the temperature is reduced further, more wax will crystallize out until a point is reached when the oil and wax crystallize together as a whole, and will not flow when poured. The temperature at which this just happens is the pour point of the oil. Oils used for lubricants must have a low pour point so that in areas where the temperature is very low, they remain as fluids. A low cloud point ensures that they remain clear and bright in such areas.

**Flash point** - The flash point of oil is the temperature at which its vapor ignites when exposed to a flame. A minimum flash point is normally specified for safety reasons.

**What is a lubricant?**

A lubricant is made from base oil and additives. The quality of a lubricant, therefore, depends on the quality of the base oil and additives used in the formulation. Additives, although used in relatively small quantities, play a very important role in the performance and composition of the lubricants. Many types of additives are used including:

1. Pour-point depressants to decrease the pour point of the oil.
2. VI improvers to increase the viscosity index, i.e. to reduce the viscosity at low temperatures
3. Anti-wear additives to decrease the engine/unit wear
4. Anti-oxidants to extend lubricant life by reducing degradation by oxygen from the air
5. Corrosion inhibitors and detergents to prevent the corrosion of various metals

6. Ash less dispersants to keep particles or deposits in suspension
7. Extreme-pressure load-carrying additives for gear oils
8. Various other additives such as anti-foams and friction modifiers
**Why are additives used in lubricating oil?**

Additives are used in lubricating oil to change, alter, or enhance its properties. Base oil as such cannot be used in most of the present-day lubricating applications. Their properties - like resistance to heat, oxygen, wear etc - have to be increased. This improvement is done with the use of these additives. To increase the resistance to oxidation, we add antioxidants; to increase resistance to wear, we add anti-wear additives, etc.

**Lubricating Oil Refining Process**

![Lubricating Oil Refining Process Diagram]

**Vacuum distillation unit**

The first step in the processing of lubricating oils is separation in the distillation units of the individual fractions according to viscosity and boiling range specifications. The heavier lube oil raw stocks are included in the vacuum fractionating tower bottoms with asphaltenes, resins and other undesirable materials. The raw lube oil fractions from most crude oils contain components which have undesirable characteristics for finished lubricating oils. These must be removed or reconstituted by processes such as extraction, crystallization, hydro cracking and hydrogenation. Vacuum distillation separates raw lube oil into two or three streams with increasing viscosity. The heavier stream is derived by removing asphalt from the residue in a de-asphalting unit. The lighter feed stocks are sent directly to a solvent extraction. This first stage determines the final base oil viscosity grades. The further process sequence is usually in the order of deasphalting, solvent extraction, dewaxing and finishing.

**De-asphalting**

Propane is usually used as the solvent in de-asphalting but it may also be used with ethane or butane in order to obtain the desired solvent properties.
Propane has unusual solvent properties in temperatures from 40°C (104°F) to 60°C (140°F). Paraffins are very soluble in propane but the solubility decreases with an increase in temperature until at the critical temperature of propane (96.8°C/206.2°F) all hydrocarbons become insoluble. In the range of 40°C (104°F) to 96.8°C (206°F) the higher molecular weight asphaltenes and resins are largely insoluble in propane. Separation by distillation is generally by molecular weight of the components and solvent extraction by type of molecule structure.

Solvent extraction

There are three solvents used for the extraction of aromatics from lube oil feedstock’s and the solvent recovery portions of the systems are different for each. The solvents are furfural, phenol and N-methyl-2-pyrrolidione (NMP). The purpose of solvent extraction is to improve the viscosity index (VI), oxidation resistance, and colour of the lube oil base stock and to reduce the carbon- and sludge-forming tendencies of the lubricants by separating the aromatic portion from the naphthenic and paraffinic portion of the feed stock.

Furfural extraction

The process flow through the furfural extraction unit is similar to that of the propane de-asphalting unit except for the solvent recovery section which is more complex. The oil feedstock is introduced into a continuous countercurrent extractor at a temperature which is a function of the viscosity of the feed; the greater the viscosity the higher temperature is used.

Phenol extraction

The process flow for the phenol extraction unit is somewhat similar to that of the furfural extraction unit but differs markedly in the solvent recovery section because phenol is easier to recover than furfural.

NMP extraction

NMP extraction uses N-methyl-2-pyrrolidione as the solvent to remove the condensed ring aromatics and polar components from the lubricating oil distillate bright stocks. This process was developed as a replacement for phenol extraction because of the safety, health, and environmental problems associated with the use of phenol.

De-waxing

All lube oil stocks, except those from a relatively few highly naphthenic crude oils, must be de-waxed or they will not flow properly at ambient temperatures.
Dewaxing is one of the most important and most difficult processes in lubricating oil manufacture.

**Hydro finishing**

Hydro treating of de-waxed lube oil stocks is needed to remove chemically active compounds that affect the color and color stability of lube oils.