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SCHOOL OF MECHANICAL ENGINEERING
DEPARTMENT OF AUTOMOBILE ENGINEERING

SAUA1303 – FUELS AND LUBRICANTS

Unit -1 - MANUFACTURE OF FUELS AND LUBRICANTS – SAUA1303

UNIT 1

MANUFACTURE OF FUELS AND LUBRICANTS.

Structure of petroleum, refining process, fuels, thermal cracking, catalytic cracking, polymerization, alkylation, isomerisation, blending, products of refining process, manufacture of lubricating oil base stocks, manufacture of finished automotive lubricants, distillation curve.

FUELS

INTRODUCTION

The engine converts the heat energy which is obtained from the chemical combination of fuel with the oxygen, into mechanical energy. Since the heat energy is derived from the fuel, the fundamental knowledge in types of fuels and their characteristics is essential in order to understand the combustion phenomenon.

Fuel is a combustible substance, containing carbon as main constituent, which on proper burninggives a large amount of heat, which can be used economically for domestic and industrial purposes. During the process of combustion of a fuel (like coal), the atoms of carbon, hydrogen, etc. combine with oxygen with the simultaneous liberation of heat at a rapid rate.

$$\textbf{FUEL} + \textbf{O}_2 \longrightarrow \textbf{PRODUCTS} + \textbf{HEAT}$$

The primary or main source of fuels are coals and petroleum oils. These are stored fuels available in earth's crust and are, generally, called 'fossil fuels'.

CLASSIFICATION OF FUELS

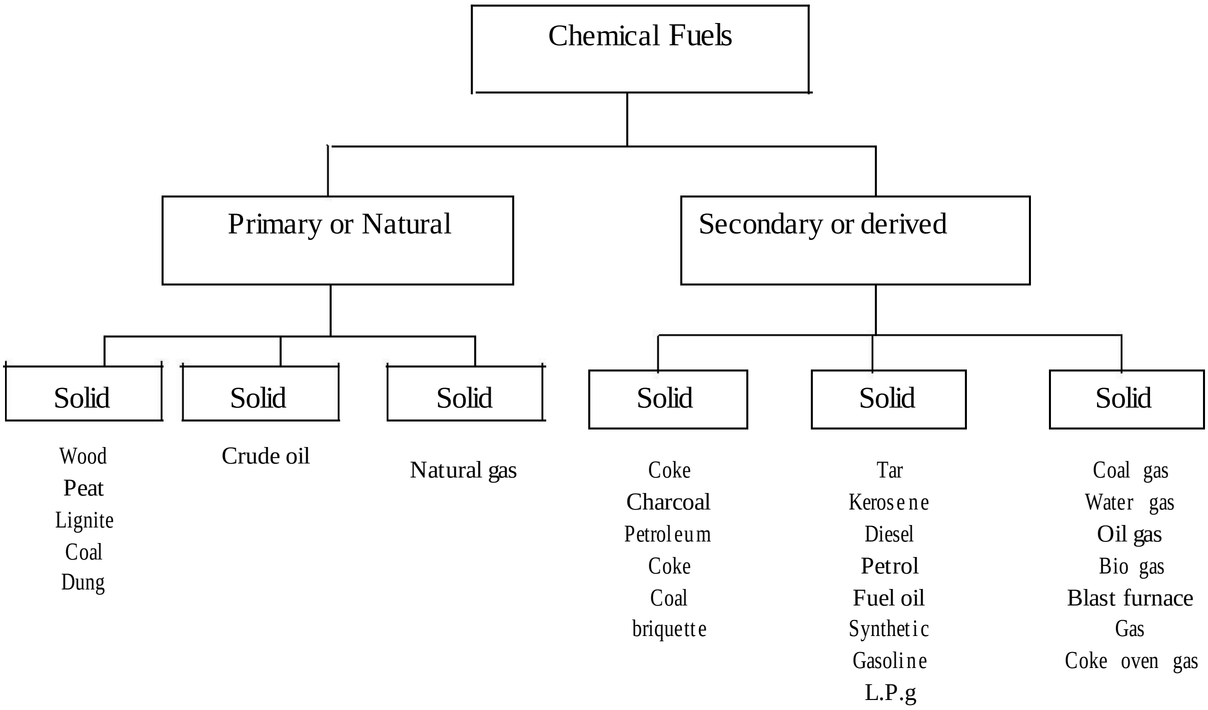


Fig. 1.1. Classifications of Fuels

The fuels may be classified mainly into two types.

- Primary or natural fuels
- Secondary or derived fuels

( ) Primary or natural fuels are found in nature such as, for e.g., wood, peat, coal, petroleum, natural gas, etc.

(a) Secondary or derived fuels are those which are prepared form the primary fuels. For example, charcoal, coke, kerosene oil, diesel oil, petrol, coal gas, oil gas, producer gas, blast furnace gas, etc.

It is further subdivided into following three types. There are

(i) Solid fuels (ii) Liquid fuels (iii) Gaseous fuels

SOLID FUELS

The natural solid fuels are wood, peat, lignite or brown coal, bituminous coal and anthracite coal. The prepared solid fuels are wood charcoal, coke, briquetted coal and pulverised coal. Some of the solid fuels are discussed below.

Wood

At one time it was extensively used as a fuel. It consists of mainly carbon and hydrogen. The wood is converted into coal when burnt in the absence of air. The average calorific value of the wood is 19700 kJ/kg

Peat

It is a spongy humid substance found in boggy land. It may be regarded as the first stage in the formation of coal. It has a large amount of water contents (upto 30%) and therefore has to be dried before use. It has a characteristic odour at the time of burning, and has a smoky flame. Its average calorific value is 23000 kJ/kg.

Lignite or brown coal

It represents the next stage of peat in the coal formation, and is an intermediate variety between bituminous coal and peat. It contains nearly 40% moisture and 60% of carbon. When dried, it crumbles and hence does not store well. Due to its brittleness, it is converted into briquettes, which can be handled easily. Its average calorific value is 25000 kJ/kg.

Bituminous coal

It represents the next stage of lignite in the coal formation and contains very little moisture (4 to 6%) and 75 % to 90% of carbon. It is weather resistant and burns with a yellow flame. The average calorific value of bituminous coal is 33500 kJ/kg.

Anthracite coal

It represents the final stage in the coal formation, and contains 90% or more carbon with a very little volatile matter. It is thus obvious, that the anthracite coal is comparative smokeless, and has very little flame. It possesses a high calorific value of about 36000 kJ/kg and therefore, very valuable for steam raising and general power purposes.

Wood charcoal

It is made by heating wood with a limited supply of air in a temperature not less than 280^0 C. It is a well prepared solid fuel, and is used for various metallurgical processes.

Coke

It is produced when coal is strongly heated continuously for 42 to 48 hours in the absence of air in a closed vessel. This process is known as carbonisation of coal. Coke is dull black in colour, porous and smokeless. It has high carbon content (85 to 90%) and has a higher calorific value than coal.

If the carbonisation of coal is carried out at 500° C to 700° C, the resulting coke is called lower temperature coke or soft coke. It is used as a domestic fuel. The coke produced by carbonisation of coal at 900° C to 1100°C, is known as hard coke. The hard coke is mostly used as a blast furnace fuel for extracting pig iron from iron ores, and to some extent as a fuel in cupola furnace for producing cast iron.

Briquetted coal

It is produced from the finely ground coal by moulding under pressure with or without a binding material. The binding materials usually used are pitch, coal tar, crude oil and clay etc.

Pulverised coal

The low grade coal with a high ash content, is powdered to produce pulverised coal. The coal is first dried and then crushed into a fine powder by pulverising machine. The pulverised coal is widely used in the cement industry and also in metallurgical processes.

LIQUID FUELS:

Almost all the commercial liquid fuels are derived from natural petroleum (or crude oil). The liquid fuel consists of hydrocarbons. The natural petroleum may be separated into petrol or gasoline, paraffin oil of kerosene, fuel oils and lubricating oils by boiling crude oil at different temperatures and subsequent fractional distillation or by a process such as cracking. Some of the liquid fuels are discussed below.

1. Petrol or gasoline.

It is the lightest and most volatile liquid fuel, mainly used for light petrol engines. It is distilled at a temperature from 65^{0} C to 220^{o} C.

2. Kerosene or paraffin oil.

It is heavier but less volatile fuel than the petrol, and is used as heating and lighting fuel. It is distilled at a temperature from 220^{o} C to 345^{o} C.

3. Heavy fuel oils.

The liquid fuels are distilled after petrol and kerosene are known as heavy fuel oils. These oils are used in diesel engines and in oil-fired boilers. These are distilled at a temperaturefrom 345^{o}C to 470 ^{o}C.

Advantages of liquid fuels over solid fuels

1. High calorific value.
2. Low storage capacity required.
3. Cleanliness and free from dust.
4. Practically no ashes.
5. Non-deterioration in storage.
6. Non-corrosion of boiler plates.

Disadvantages

1. Highly expensive.
2. High risk of fire.
3. Expensive containers are required for storage and transport.

GASEOUS FUELS:

1. Natural gas.

The natural gas is, usually, found in or near the petroleum fields, under the earth's surface. The main constituents of natural gas are methane (CH_4) and ethane (C_2H_6). It has calorificvalue nearly 21000 kJ/m^3. It is used alternately or simultaneously with oil for internal combustion engines.

2. Coal gas.

The quality of coal gas depends upon the quality of the coal used, temperature of thecarbonisationand the type of plant. It is used in domestic lighting, furnaces and for running gas engines. Its calorificvalue is about 21000 kJ/m^3 to 25000 kJ/ m^3

3. Producer gas

It isobtained by the partial combustion of coal, coke, anthracite coal charcoal in a mixed air-steam blast. Its manufacturing cost is low, and has a calorific value of about 5000 kJ/m^3 to6700 kJ/m^3.

4. Water gas.

It is a mixture of hydrogen and carbon monoxide and is made by passing steam overincandescent coke. As it burns with a blue flame, it is also known as blue water gas. The water gas is usually converted into carburetted (enriched) water gas by passing it through a carburetter into which a gas oil is sprayed.

It is, usually, mixed with coal gas to form town gas. The water gas is used in furnaces and for welding.

5. Mond gas.

It is produced by passing air and a large amount of steam over waste coal at about 650^0 C. It is used for power generation and heating. It is also suitable for use in gas engine. Its calorific value is about 5850 kJ/m^3.

6. Blast furnace gas

It is a by-product in the production of pig iron in the blast furnace. The gas serves as a fuel in steel works, for power generation in gas engines, for steam raising in boiler and for pre heating the blast for furnace.

It is extensively used as fuel for metallurgical furnaces. The gas leaving the blast furnace has a high dust content the proportion of which varies with the operation of the furnace. It has a low heating value of about 3750 kJ/m^3.

7. **Coke oven gas.**

It is a by-product from coke oven, and is obtained by the carbonisation of bituminous coal. Its calorific value varies from 14500kJ/m^3 to 18500 kJ/m^3. It is used for industrial heating and power generation.

Advantages of gaseous fuels

1. The supply of fuel gas, and hence the temperature of furnace is easily and accurate controlled.
2. The high temperature is obtained at a moderate cost by pre-heating gas and air with combustion of waste gases.
3. They are directly used in internal combustion engines.
4. They are free from solid and liquid impurities.
5. They do not produce ash or smoke.
6. They undergo complete combustion with minimum air supply.

Disadvantages

1. They are readily inflammable.
2. Air requires large storage capacity.

STRUCTURE OF PETROLEUM

Usually the fuels used in internal combustion engines are complex mixtures of hydrocarbons made by refining petroleum. Petroleum as obtained from the oil wells is predominantly a mixture of many hydrocarbons with differing molecular structure. It also contains small amounts of sulphur, oxygen, nitrogen and impurities such as water and sand. The carbon and hydrogen atoms may be linked in different ways in a hydrocarbon molecule and this linking influences the chemical and physicalproperties of different hydrocarbongroups. The carbon to hydrogen ratio which isone of the important parameters and their nature of bonding determine the energycharacteristics of the hydrocarbon fuels. Depending upon the number of carbon and hydrogen atoms the petroleum products are classified into different groups. They are

(i) Paraffin series (C_nH_{2n+2})

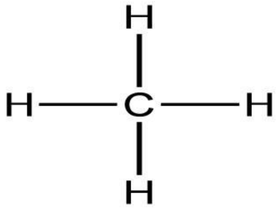
(ii) Olefin series (C_nH_{2n})

(iii) Naphthene series (C_nH_{2n})

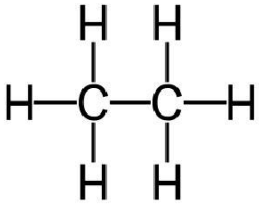
(iv) Aromatic series (C_nH_{2n-6})

(i) Paraffin series

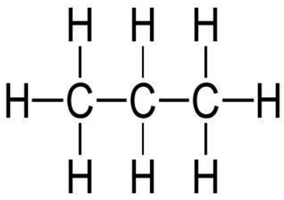
The normal paraffin hydrocarbons are of straight chain molecular structure. They are represented by a general chemical formula C_nH_{2n+2}, where n is number of carbon atoms. In these hydrocarbons the valency of all the carbon atoms is fully utilized by single bonds with hydrogen atoms. Therefore the paraffins hydrocarbons are saturated compounds and their characteristics are very stable. The name of each member ends in 'ane' as in methane, propane, hexane, etc. n-Propane means normal propane.



n =1: Methane

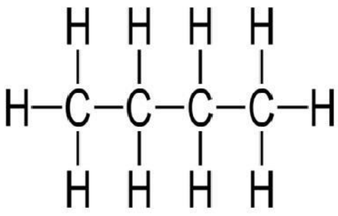


n = 2 : Ethane

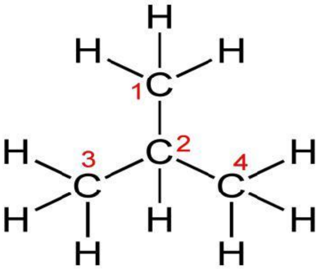


n = 3 : Propane

A variation of the paraffin family consists of an open chain structure with an attached branch and is usually termed a branched chain paraffin. The hydrocarbons which have the same chemical formulae but different structural formulae are known as isomers.



n = 4 : Butane

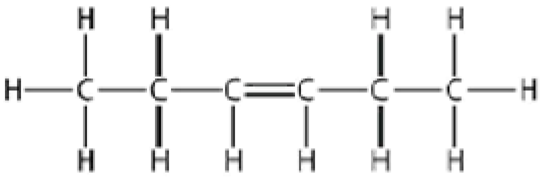


n = 4 : Iso Butane

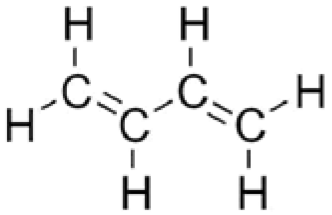
Isobutane shown above has the same general chemical formula and molecular weight as butane but a different molecular structure and physical characteristics. It is called as isomer of butane and is known as isobutane. Isoparaffins are also stable compounds. The lower paraffins are gases, the higher being liquids and still higher, solids.

(ii) Olefin series:

Olefins are also straight chain compounds similar to paraffins but are unsaturated because they contain one or more double bonds between carbon atoms.The names of hydrocarbons having one double bond end in lene' as in ethylene, butene, etc., and in `adiane' for two double bonds as in butadiene, etc.



n=6: Hexene

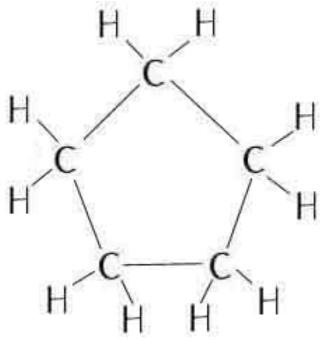


n=6:Butadiene

The general formulae are C_nH_{2n} for mono-olefins (one double-bond) and C_nH_{2n-2} for the diolefins (two double-bonds).

(iii) Naphthene series

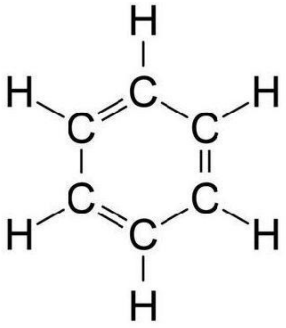
The naphthenes have the same chemical formula as the olefin series of hydrocarbons but have a ring structure and therefore often they are called as cyclo-paraffins. They are saturated and tend to be stable.



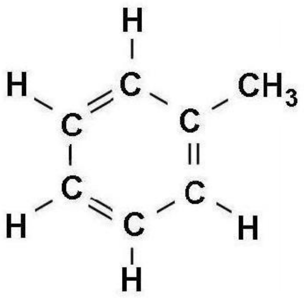
n = 5 : Cyclopentane

(iv) Aromatic Series

Aromatic compounds are ring structured having a benzene molecule as their central structure and have a general chemical formula C_nH_{2n-6}. Though the presence of double bonds indicates that they are unsaturated, a peculiar nature of these double bonds causes them to be more stable than the other unsaturated compounds.



n = 6: Benzene



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Various aromatic compounds are formed by replacing one or more of the hydrogen atoms of the benzene molecules with an organic radical such as paraffins, naphthenes and olefins. By adding a methyl group (CH_3). Benzene is converted to toluene ($C_6H_5CH_3$) the base for the preparation of Trinitrotoluene (TNT) which is a highly explosive compound.

Family of Hydrocarbons	**Chemical Formula**	**Molecular Structure**	**Saturated / Unsaturated**	**Stability**
Paraffin	C_nH_{2n+2}	Chain	Saturated	Stable
Olefin	C_nH_{2n}	Chain	Unsaturated	Unstable
Naphthene	C_nH_{2n}	Ring	Saturated	Stable
Aromatic	C_nH_{2n-6}	Ring	Highly Unsaturated	Most unstable

General characteristics of hydrocarbon due to the molecular structure:

- Normal paraffins exhibit the poor antiknock quality when used in an SI engine. But the antiknock quality improves with the increasing number of carbon atoms and the compactness of the molecular structure. The aromatics offer the best resistance to knocking in SI Engines.
- For CI engines, the order is reversed i.e., the normal paraffins are the best fuels and aromatics are the least desirable.
- As the number of atoms in the molecular structure increases, the boiling temperature increases. Thus fuels with fewer atoms in the molecule tend to be more volatile.
- The heating value generally increases as the proportion of hydrogen atoms to carbon atoms in the molecule increases due to the higher heating value of hydrogen than carbon. Thus paraffin’s have the highest heating value and the aromatics the least.

REFINING OF PETROLEUM

The process of (i) removing impurities and (ii) separating petroleum into more useful fractions with different boiling point range is known as refining of petroleum.

(i) Removal of impurities:

Step 1: Separation of Water (Cottrell’sProcess)

The crude oil from the oil well is an extremely stable emulsion of oil and salt water. The process of freeing oil from water consists in allowing the crude to flow between two highly charged electrodes. The colloidal water droplets coalesce to form large drops, which separate out from the oil.

Step2: Removal of harmful sulphur compounds

It involves in treating oil with copper oxide. A reaction occurs with sulphur compounds, which results in the formation of copper sulphide, which is then removed by filtration.

(ii) Fractional distillation

The crude oil is separated into gasoline, kerosene, fuel oil etc. by the process of fractional distillation. In the first step, the petroleum is passed through a separator in which the gases are removed and a product known as natural gasoline is obtained. The liquid petroleum is then vapourized in a still, at temperatures of 600 ^{0}C and the vapour is admitted at the bottom of the fractionating tower. The vapour is forced to pass upwards along a labyrinth like arrangement of plates which direct the vapour through trays of liquid fuel maintained at different temperatures. The compounds with higher boiling points get condensed out at lower levels while those with lower boiling points move up to higher levels where they get condensed in trays at appropriate temperature. Generally the top fraction is called the straight run gasoline and the other fractions, kerosene, diesel oil, fuel oil etc., are obtained in the increasing range of boiling temperatures.

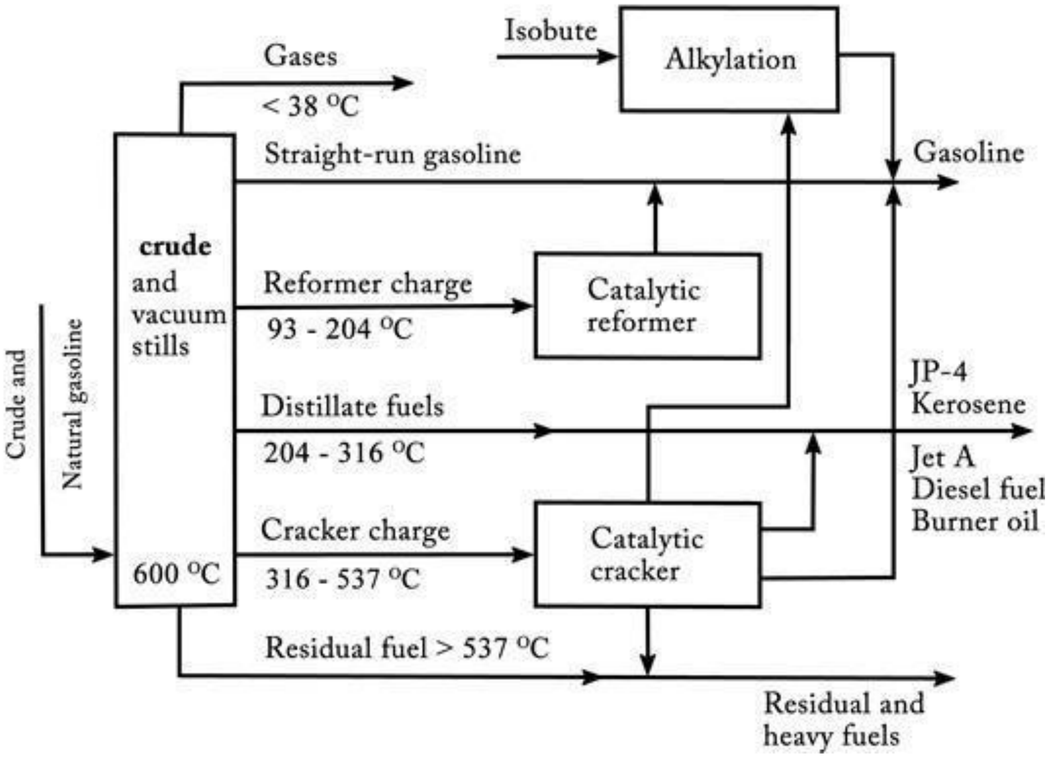

Fig. 1.2. Refinining process

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. Many processes can be used to convert some of these fractions to compounds for which there is a greater demand.

Some of the main refinery processes are as follows

(i) Cracking consists of breaking down large and complex hydrocarbon molecules intosimplercompounds. Thermal cracking subjects the large hydrocarbon molecules to high temperature and pressure and they are decomposed into smaller, lower boiling point molecules.

(ii) Catalytic cracking using catalysts is done at a relatively lower pressure and temperature than the thermal cracking. Due to catalysis, the naphthenes are cracked to olefins, paraffins and olefins toisoparaffins needed for gasoline. Catalytic cracking gives better antiknock property for gasoline as compared to thermal cracking.

(iii) Hydrogenation consists of the addition of hydrogen atoms to certain hydrocarbonsunder high pressure and temperature to produce more desirable compounds. It is often used to convert unstable compound to stable ones.

(iv) Polymerization is the process of converting olefins, the unsaturated products of cracking, into heavier and stable compounds.

(v) Alkylation combines an olefin with an isoparaffin to produce a branched chain isoparaffin in the presence of a catalyst.

Example: isobutylene + isobutane $\xleftrightarrow{\text{Alkylation}}$ iso-octane

(vi) Isomerization changes the relative position of the atoms within themolecule of a hydrocarbon without changing its molecular formula. For example, isomerization is used for the conversion of n-butane into isobutane for alkylation. Conversion of n-pentane and n-hexane intoisoparaffins to improve knock rating of highly volatile gasoline is another example.

(vii) Cyclization joins together the ends of a straight chain molecule to form a ring compound of the naphthene family.

(vii) Aromatization is similar to cyclization, the exception being that the product is an aromatic compound.

(viii) Reformation is a type of cracking process which is used to convert the low antiknock quality stocks into gasoline of higher octane rating. It does not increase the total gasoline volume.

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

PRODUCTS OF REFINING PROCESS:

(i) 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, a small amount of propane, ethane, butane and other light hydrocarbons plus some nitrogen and oxygen. When natural gas occurs along with petroleum in oil wells, it is called wet gas. On the other hand, when the gas is associated with crude oil, it is called dry gas.

Uses:

- It is an excellent domestic fuel and can be conveyed over very large distances in pipelines.
- It has been recently used in the manufacture of a number of chemicals by synthetic processes

(ii) LPG:

Liquefied petroleum gas (LPG) or bottled gas or refinery gas is obtained as a by-product, during the cracking of heavy oils or from natural gas. It is stored in liquid form in special cylinders at a pressure of about 100psi (700 kpa) and the engine is provided with a special fuel system. Its calorific value is about 27800 kcal/m^3.

The main constituents of LPG are n-butane, isobutane, butylene and propane, with little or no propylene and ethane.

Advantages:

- Better mixing with air and improved distribution, which means lesser emissions.
- No need of a fuel pump.
- No carbon deposits.
- No crank case dilution because of vapour form. This means lesser oil consumption.
- High octane rating.
- Less engine wear.

Disadvantages:

- Special fuel system has to be provided.

- Heavy pressure cylinders increase the vehicle weight unnecessarily.
- Hard to start in winter.

(iii) 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 fuels used for spark-ignition engines. Its calorific value is about 47102 kJ/kg

(iv) Kerosene.

The kerosene has heavy fraction than gasoline. Its boiling range is 150°C to 300°C and the specific gravity range is 0.78 to 0.85.Its calorific value is about 46474 kJ/kg

(v) Distillate.

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

(vi) 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.

(vii) Fuel Oils.

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

(viii) Lubricating Oils.

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

(ix) Tar and Asphalt.

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

(x) Petroleum Coke.

Petroleum coke is used as solid industrial fuel.

MANUFACTURING OF LUBRICATING OIL BASE STOCK PROCESSES

The manufacture of lubricant base oils consists of five basic steps: 1) distillation and 2) deasphalting to prepare the feedstocks, 3) solvent or hydrogen refining to improve viscosity index and remove undesirable constituents, 4) solvent or catalytic dewaxing to remove wax and improve the low temperature properties of paraffinic base oils and 5) clay or hydrogen finishing to improve the colour, stability and quality of the lubricant base stocks.

Distillation

In a lubricant base oil and wax manufacturing plant, crude oil is first distilled in an atmospheric distillation unit (ADU) to remove gases, gasoline, naphtha's, kerosene and light gas oil. The atmospheric residuum (reduced crude) is then fractionated in a vacuum distillation unit (VDU) into fractions of the desired viscosity and flash for further processing.

Deasphalting

The vacuum residuum contains recoverable lubricant stock of high viscosity mixed with asphalt and resins. This oil is separated from the asphalt and resins using propane deasphalting, an extractive precipitation process.

Refining

The deasphalted oil and the distillates usually contain undesirable constituents such as aromatics and naphthenes and these must be removed to yield an oil of high viscosity index and high lubricating quality. These undesirable constituents are removed by treating the stocks separately with a solvent (furfural, phenol, N-methyl-2-pyrrolidone or liquid sulphur dioxide) which selectively removes (extracts) these constituents from the oil. The extract, containing the undesirable materials which have been removed, may be used as fluid catalytic cracking unit (FCCU) or coker feedstock, blended into fuel oil, hydrocracked or used as rubber extender oil.

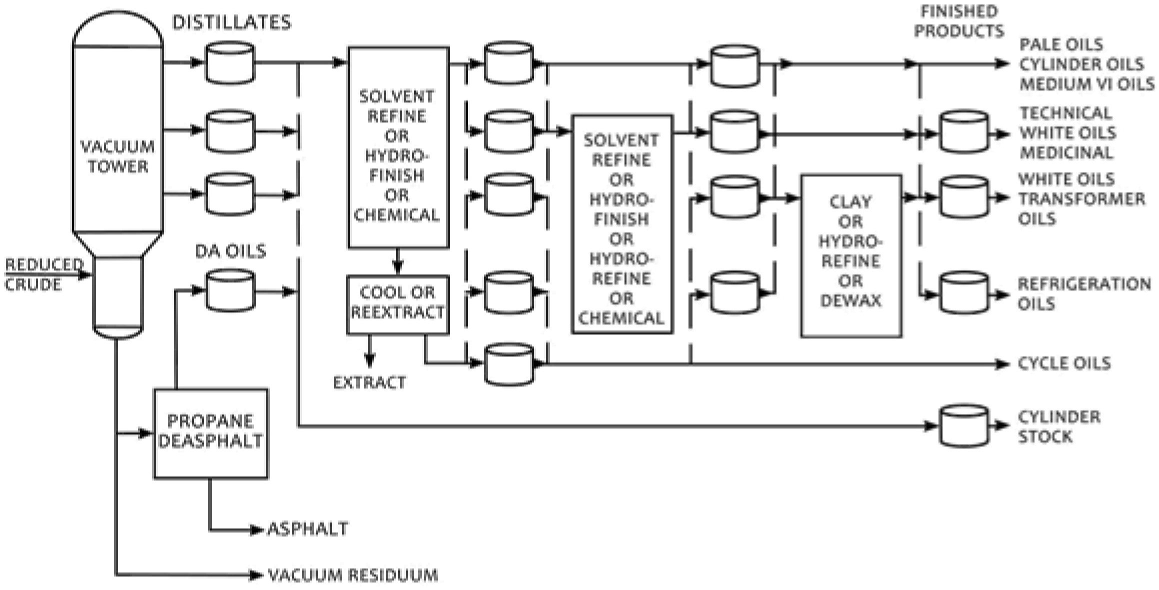

Fig. 1.3. Manufacture of lubricating base oils

Hydro extraction, a mild solvent extraction of distillates and deasphalted oils followed by moderate severity hydro treating (mild hydrocracking) is conducted by some refiners for the purpose of decreasing hydrogen consumption and increasing refined oil yields.

Hydrocracking followed by distillation is sometimes used as an alternative to solvent refining. The stabilization of hydrocracked base oils is usually done using a high pressure-low temperature hydrogenation called high severity hydro finishing, speciality products hydrogenation or hydro refining. Solvent extraction is also used to stabilize hydrocracked base oils.

Hystarting or the removal of sulphur, nitrogen and oxygen by hydrogenation prior to solvent extraction is used for some feedstocks by some refiners. When conducted at sufficiently high temperature and pressure this process will also saturate some of the aromatics.

Dewaxing

The refined paraffinic oils contain waxes which crystallize out at low temperatures, thus reducing the fluidity of these oils which have a high pour point. In order to produce lubricating oil which is not a solid at low temperatures, the wax is removed by solvent dewaxing (a crystallization-filtration process). The slack waxes from the dewaxing process are used as FCCU feed or deoiled using a warm-up or recrystallization process to produce a hard wax and a soft wax. The soft wax or foots oil is frequently used as a seal oil or as FCCU feedstock.

A selective hydrocracking process called catalytic dewaxing is used as an alternative to solvent dewaxing and hydrogen finishing for the removal of wax and finishing of lubricant base oils. No wax is produced from catalytic dewaxing unless the desired wax is removed by solvent dewaxing prior to catalytic dewaxing.

Finishing

Both the dewaxed oil and the product wax are normally hydrofinished or treated with adsorbent clay to meet the colour and oxidation stability requirements of a marketable product. A severe hydrogen finishing process, hydrorefining, is used to remove large amounts of sulphur and nitrogen and trace impurities in the manufacture of food grade wax and pharmaceutical grade white oils or to stabilize base oils produced by hydrocracking. Solvent refining is also used to stabilize hydrocracked base oils.

Product Formulation

The finished base oils are then blended with one another and with additives to produce the desired high grade lubricants. Speciality oils such as refrigeration oils and white oils are manufactured using the conventional processes in conjunction with acid and clay treating or hydrorefining processes.

DISTILLATION CURVE:

A distillation curve is essentially a plot of boiling temperature vs. cumulative percent volume evaporated from the sample during heating. This type of plot can be used to distinguish quickly between one or several product types. The distillation curve for SI engine fuel and CI engine fuels are discussed below in detail.

SI ENGINE FUELS:

Volatility is one of the main characteristic properties of gasoline which determines its suitability for use in an SI engine. Since gasoline is a mixture of different hydrocarbons, volatility depends on the fractional composition of the fuel. The usual practice of measuring the fuel volatility is the distillation of the fuel in a special device at atmospheric pressure and in the presence of its own vapour. The fraction that boils off at a definite temperature is measured. The characteristic points are the temperatures which 10, 40, 50 and 90% of the volume evaporates as well as the temperature at which boiling of the fuel terminates.

A certain part of the gasoline should vapourize at the room temperature for easy starting of the engine. Hence, the portion of the distillation curve between about 0 and 10% boiled off have relatively low boiling temperatures. As the engine warms up, the temperature will gradually increase to the operating temperature. Low distillation temperatures are desirable throughout the range of the distillation curve for best warm-up.

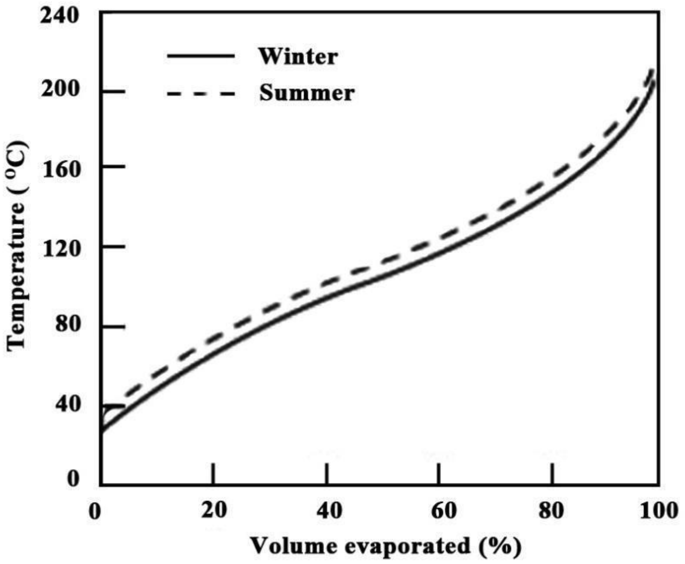

Fig. 1.4. Distillation curve for SI engine fuels

In order to obtain good vapourization of the gasoline, low distillation temperatures are preferable in the engine operating range. Better vapourization tends to produce both more uniform distribution of fuel to the cylinders as well as better acceleration characteristics by reducing the quantity of liquid droplets in the intake manifold.

Liquid fuel in the cylinder causes loss of lubricating oil (by washing away oil from cylinder walls) which deteriorates the quality of lubrication and tends to cause damage to the engine through increased friction. The liquid gasoline may also dilute the lubricating oil and weaken the oil film between rubbing surfaces. To prevent these possibilities, the upper portion of the distillation curve should exhibit sufficiently low distillation temperatures to insure that all gasoline in the cylinder is vapourized by the time the combustion starts.

High rate of vapourization of gasoline can upset the carburettor metering or even stop the fuel flow to the engine by setting up a vapour lock in the fuel passages. This characteristic, demands the presence of relatively high boiling temperature hydrocarbons throughout the distillation range.

CI ENGINE FUELS:

The fuel should be sufficiently volatile in the operating range of temperature to produce good mixing and combustion. The fuel should help in starting the engine easily. This requirement demands high enough volatility to form a combustible mixture readily and a high cetane rating in order that the self-ignition temperature is low.

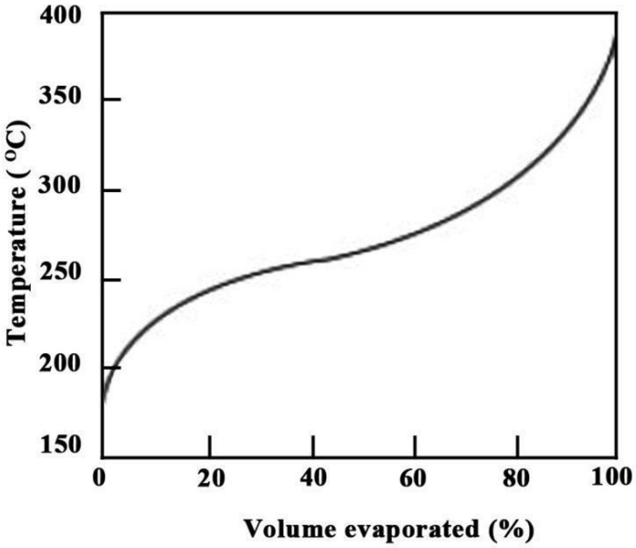

Fig. 1.5. Distillation curve for CI engine fuels

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SCHOOL OF MECHANICAL ENGINEERING

DEPARTMENT OF AUTOMOBILE ENGINEERING

Unit - 2 - FUELS FOR I C ENGINES – SAUA1303

UNIT-II

FUELS FOR I C ENGINES

Types of fuels, liquid and gaseous fuels, heating value of fuels, higher and lower heating values, chemical structure of hydro-carbons SI engine fuels, volatility characteristics, desirable characteristics of SI engine fuels, knock rating and additives, alternate fuels for SI engines, CI engine fuels, desirable characteristics, Cetane rating and additives

Types of Fuels

Since the heat energy is derived from the fuel, a fundamental knowledge of the types of fuels and their characteristics is essential to understand the combustion phenomenon.
The characteristic of fuel has a considerable influence on the design, efficiency, output and particularly the reliability and durability of the engine. Further, the fuel characteristics play an important role in the atmospheric pollution caused by the automobile engines.

Internal combustion engines can be operated on different types of fuels such as

- Solid fuels
- Liquid fuels
- Gaseous fuels

The design of the engine usually depends upon the type of fuel used.

Solid fuels

This type of fuel was used in early engines. During the initial stages of engine development, solid fuels (such as finely powdered coal) were used. However, due to the problem of handling the fuel as well as in disposing off the solid residue or ash (after combustion), solid fuels find little practical application today.

- Further, there are storage and feeding problems associated with solid fuels as compared to gaseous and liquid fuels.
- However, attempts are being made to produce gaseous or liquid fuels from charcoal for their use in engines.

Liquid fuels

The liquid fuels are mostly used in modern internal combustion engines. Basically, they are the derivatives of liquid petroleum. The commercial types are:

- Benzyl
- Alcohol
- Petroleum products

Petroleum (obtained from crude oil) is a mixture of many hydrocarbons with varying molecular structure. It also contains small amounts of

- Sulphur
- Oxygen
- Nitrogen
- Impurities (such as water, sand etc.)

Advantages of liquid fuels over solid fuels

- 1. High calorific value.
- 2. Low storage capacity required.

- 3. Cleanliness and free from dust.
- 4. Practically no ashes.
- 5. Non-deterioration in storage.
- 6. Non-corrosion of boiler plates.

Disadvantages

- 1. Highly expensive.
- 2. High risk of fire.
- 3. Expensive containers are required for storage and transport

Gaseous fuels

Gaseous fuels are ideal for internal combustion engines. They mix more homogeneously with air. However, their use is restricted in automobiles due their storage and handling problems. Gaseous fuels are suitable for stationary power plants near the source of availability of the fuel. They can be liquefied under pressure to reduce the storage volume, but this process is very expensive and risky.

Advantages of gaseous fuels

1. The supply of fuel gas, and hence the temperature of furnace is easily and accurate Controlled.
2. The high temperature is obtained at a moderate cost by pre-heating gas and air with Combustion of waste gases.
3. They are directly used in internal combustion engines.
4. They are free from solid and liquid impurities.
5. They do not produce ash or smoke.
6. They undergo complete combustion with minimum air supply.

Disadvantages

1. They are readily inflammable.
2. Air requires large storage capacity.

Heating value

For fuels where the precise fuel composition is not known, the enthalpy of the reactants cannot be determined from the enthalpies of formation of the reactant species. The ***heating value*** of the fuel is then measured directly.

The heating value QHv or calorific value of a fuel is the magnitude of the heat of reaction at constant pressure or at constant volume at a standard temperature [usually 25°C **(77"F)** for the complete combustion of unit mass of fuel.

Complete combustion means that all carbon is converted to CO, all hydrogen is converted to H and O, and slny sulfur present is converted to SO,. The heating value is usually expressed in joules per kilogram or joules per kilomole of fuel.

The term ***higher heating value*** QHHv (gross heating value) is used when the H,O formed is all condensed to the liquid phase; the term ***lower heating value*** QLHv (or net heating value) is used when the H,O formed is all in the vapor Phase.

Heating value of fuels are measured in calorimeters. For gaseous fuels, it is most convenient and accurate to use a continuous-flow atmosphere pressure calorimeter.

CHEMICAL STRUCTURE OF PETROLEUM

Depending upon the number of carbon and hydrogen atoms the petroleum products are classified into different groups. They are

(i) Paraffin series (C_nH_{2n+2})

(ii) Olefin series (C_nH_{2n})

(iii) Naphthene series (C_nH_{2n})
(iv) Aromatic series (C_nH_{2n-6})

Various aromatic compounds are formed by replacing one or more of the hydrogen atoms of the benzene molecules with an organic radical such as paraffins, naphthenes and olefins. By adding a methyl group (CH_3). Benzene is converted to toluene ($C_6H_5CH_3$) the base for the preparation of Trinitrotoluene (TNT) which is a highly explosive compound.

Family of Hydrocarbons	**Chemical Formula**	**Molecular Structure**	**Saturated / Unsaturated**	**Stability**
Paraffin	$\mathbf{C_nH_{2n+2}}$	Chain	Saturated	Stable
Olefin	$\mathbf{C_nH_{2n}}$	Chain	Unsaturated	Unstable
Naphthene	$\mathbf{C_nH_{2n}}$	Ring	Saturated	Stable
Aromatic	C_nH_{2n-6}	Ring	Highly Unsaturated	Most unstable

SI engine fuels

Gasoline which is mostly used in the present day SI engines is usually a blend of several low boiling paraffin, naphthenes and aromatics in varying proportions. Some of the important qualities of gasoline are discussed below.

- ❖ Volatility
- ❖ Starting and warm up
- ❖ Operating Range Performance
- ❖ Crank case dilution
- ❖ Vapour lock characteristics
- ❖ Antiknock quality
- ❖ Gum Deposits
- ❖ Sulphur Contents.

Volatility

It is the most important characteristics of a SI engine fuel. Volatility is a physical concept that loosely defined as the tendency to evaporate at a temperature lower than their boiling temperature. It is the most dominant factor that controls the air-fuel ratio inside the combustion chamber.

One of the most important requirements for proper and smooth combustion is the availability of a highly combustible air-fuel mixture at the moment of the start of the ignition inside the combustion chamber.

A highly volatile (of low molecular weight) fuel generates a rich fuel air ratio at low starting temperature, to satisfy the criteria at the starting of the ignition. But, it will create another problem during running operation; it creates vapour bubble which choked the fuel pump delivery system. This phenomenon is known as vapour lock.

A vapour lock thus created restricts the fuel supply due to excessive rapid formation of vapour in the fuel supply system of the carburetor. High volatility of fuel can also result in excessive evaporation during storage in a tank which will also pose a fire hazards.Low volatile fuel like kerosene and distillates can be used for SI engines for tractors.

Starting and warm up

A certain part of the gasoline should vapourize at the room temperature for easy starting of the engine. Hence the portion of the distillation curve between 0 and 10% boiled off have relatively low boiling temperature. As the engine warms up, the temperature will gradually increase to the operating temperature.

Operating Range Performance

In order to obtain good vaporization of the gasoline, low distillation temperature are preferable in the engine operating range. Better vaporization tends to produce both more uniform distribution of fuel to the cylinder as well as better acceleration characteristics by reducing the quantity of liquid droplets in the intake manifold.

Crank case dilution

Liquid fuel in the cylinder causes loss of lubricating oil(by washing away oil from the cylinder walls) which deteriorates the quality of lubrication and tends to cause damage to the engine through increased friction. The liquid gasoline may also dilute the lubricating oil and weaken the oil film between rubbing surfaces. To prevent this situation, the upper portion of the distillation curve should exhibit sufficiently low distillation temperatures to ensure that all gasoline in the cylinder is vapourized by the time the combustion starts.

Vapour lock characteristics

High rate of vapourisation of fuel can upset the carburetor metering or even stop the fuel flow to the engine by setting up a vapour lock in the fuel passages. This characteristic demands the presence of relatively high boiling temperature throughout the distillation range.

Antiknock quality

Abnormal burning or detonation in an SI engine combustion chamber causes a very high rate of energy release, excessive temperature and pressure inside the cylinder adversely effects its thermal efficiency. Therefore, the characteristic of fuel should be such that it reduces the tendency to detonation and this property is called its antiknock property. The antiknock property of a fuel depends on the self-ignition characteristics of its mixture and varies largely with the chemical composition and molecular structure of fuel. In general, the best SI engine fuel will be that having the highest antiknock property, since this permits the use of higher compression ratios and thus the engine thermal efficiency and the power output can be greatly increased.

Gum deposits

Reactive hydrocarbons and the impurities in the fuel have a tendency to oxidize and form liquid and solid gummy substances. Unsaturated hydrocarbons are more prone to form gum deposits. Gum deposits may lead to clogging of carburetor jets and enlarging of the valve stems, cylinders and pistons.

Sulphur content

Hydrocarbon fuels may contain free sulphur, hydrogen sulphide and other sulphur compounds which are objectionable for several reasons. The sulphur is the corrosive element of the fuel that can corrode fuel lines, carburetors and injection pumps and it will unite with oxygen to form sulphur dioxide that, in presence of water at low temperatures, may form sulphurous acid. Since sulphur has a low ignition temperature, the presence of sulphur can reduce the self-ignition temperature, then promoting knock in the SI engine.

Important characteristics of SI engine fuels

Every SI engines are designed for a particular fuel having some desired qualities. For a good performance of a SI engine the fuel used must have the proper characteristics.The followings are requirements of a good SI engine fuels or Gasolines.

- It should readily mix with air to make a uniform mixture at inlet, ie. it must be volatile
- It must be knock resistant
- It should not pre-ignite easily
- It should not tend to decrease the volumetric efficiency of the engine.
- It should not form **gum** and **varnish**
- Its Sulphur content should be low as it is corrosive
- It must have a high calorific value

Rating of SI engine fuels:-

The knock resistance is the most important characteristic of the fuel for SI engine. The fuels differ widely in their ability to resist knock depending on their chemical composition. In addition to the chemical properties of the hydrocarbons in the fuel other operating parameters such as fuel-air ratio, ignition timing, dilution, engine speed, shape of combustion chamber, ambient conditions, compression ratio etc. affect the tendency to knock in the engine cylinder. Therefore, in order to determine the knock resistance characteristic of the fuel, the engine and its operating variables must be fixed at standard values.

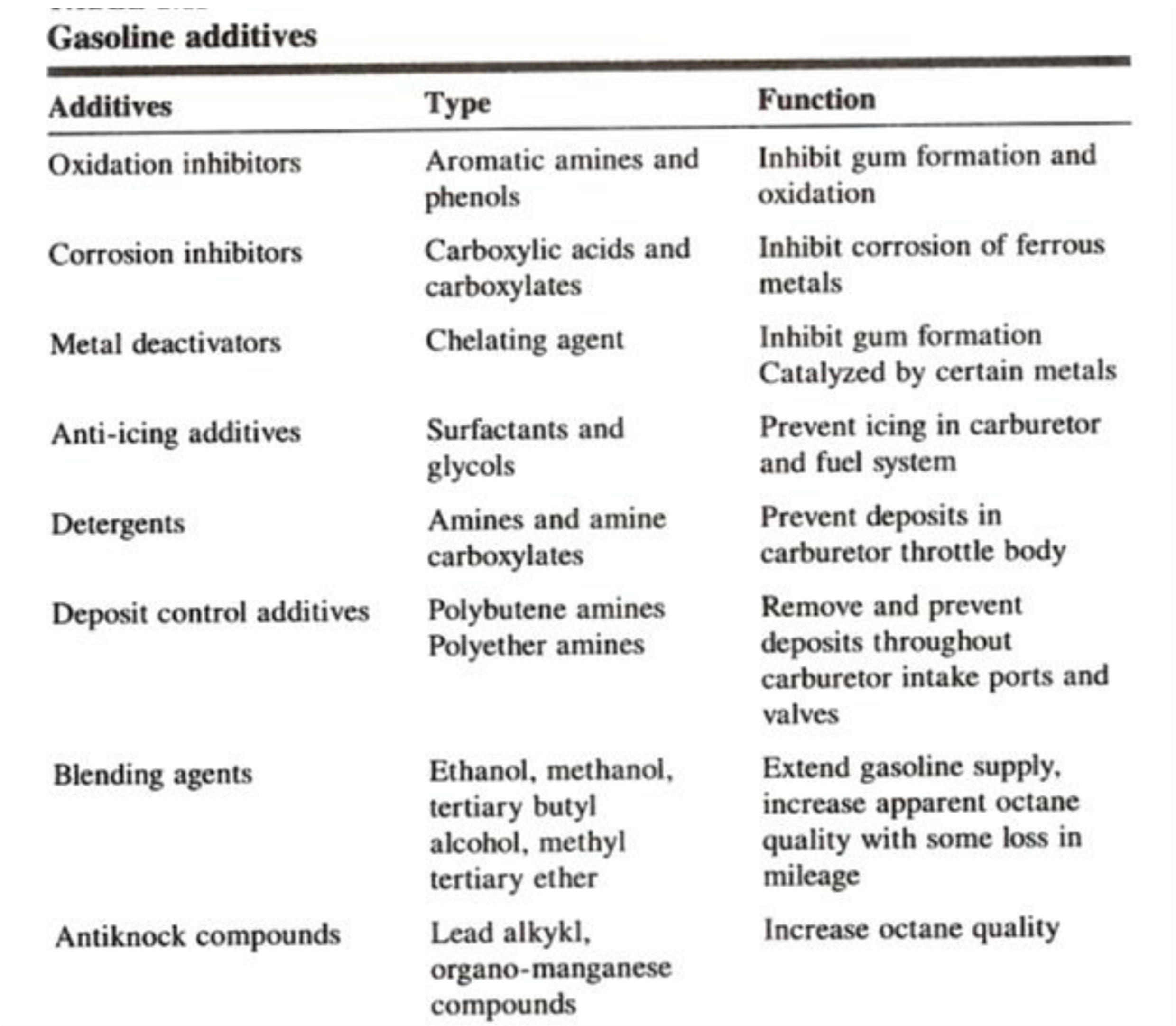
Here also there are two reference fuels viz. iso-octane (C_8H_{18}) chemically being a very god antiknock fuel, has been assigned an octane number of 100 and normal heptane (C_7H_{16}), it has very poor antiknock qualities and is assigned an octane number of 0.

Def. The octane number of a fuel is defined as the percentage, by volume, of iso-octane in a mixture of iso-octane and normal heptanes, which exactly matches the knocking intensity of the fuel in standard engine under a set of standard operating conditions.

The octane number at the higher range of scale will produce greater antiknock effect compared to the same unit at the lower end of the scale e.g. octane number increase from 90 to 91 produces greater antiknock effect than a similar increase from 30 to 31. The addition of some chemicals like tetra ethyl lead(TEL) to iso-octane produces fuels of greater antiknock qualities.

Antiknock Quality

Abnormal burning/detonation in SI engine causes a very high rate of energy release, temperature and pressure. This adversely affects the thermal efficiency. The fuel characteristics should resist this tendency. This property of fuel is called its antiknock quality. With no self-ignition, the pressure force on piston follows a smooth curve, resulting in smooth engine operation. When self-ignition occurs, pressure forces on piston are not smooth and engine knock occurs.



Gasoline additives

Additives	Type	Function
Oxidation inhibitors	Aromatic amines and phenols	Inhibit gum formation and oxidation
Corrosion inhibitors	Carboxylic acids and carboxylates	Inhibit corrosion of ferrous metals
Metal deactivators	Chelating agent	Inhibit gum formation Catalyzed by certain metals
Anti-icing additives	Surfactants and glycols	Prevent icing in carburetor and fuel system
Detergents	Amines and amine carboxylates	Prevent deposits in carburetor throttle body
Deposit control additives	Polybutene amines Polyether amines	Remove and prevent deposits throughout carburetor intake ports and valves
Blending agents	Ethanol, methanol, tertiary butyl alcohol, methyl tertiary ether	Extend gasoline supply, increase apparent octane quality with some loss in mileage
Antiknock compounds	Lead alkykl, organo-manganese compounds	Increase octane quality

CI Engine Fuels

Knock characteristics

Knock in the CI engine occurs because of an ignition lag in the combustion of the fuel between the time of injection and the time of actual burning. As the ignition lag increases, the amount of fuel accumulated in the combustion chamber increases and when combustion actually takes place, abnormal amount of energy is suddenly released causes an excessive rate of pressure rise which results in an audible knock. Hence, a good CI engine fuel should have a short ignition lag and will ignite more readily. Furthermore, ignition lag affects the starting, warm up, and leads to the production of exhaust smoke in CI engine. The present day measure in the cetane rating, the best fuel in general, will have a Cetane rating sufficiently high to avoid objectionable knock.

Volatility

The fuel should be sufficiently volatile in the operating range of temperature to produce good mixing and combustion.

Starting Characteristics

The fuel should help in starting the engine easily. This requirement demands high enough volatility to form a combustible mixture readily and a high cetane rating in order that the self-ignition temperature is low.

Smoking and odor

The fuel should not promote either smoke or odour in the engine exhaust. Generally, good volatility is the first prerequisite to ensure good mixing and therefore complete combustion.

Viscosity

CI engine fuel should be able to flow through the fuel system and the strainers under the lowest operating temperatures to which the engine is subjected to.

Corrosion and Wear

The fuel should not cause corrosion and wear of the engine components before or after combustion. These requirements are directly related to the presence of sulphur, ash and residue in the fuel.

Handling Ease

The fuel should be a liquid that will readily flow under all conditions that are encountered in actual case. This requirement is measured by the pour point and the viscosity of the fuel. The fuel should also have a high flash point and a high fire point

Rating of fuels:-

Rating of fuels is normally done for their antiknock qualities. The rating of fuels is done by defining two parameters cetane number and octane number for diesel and gasoline respectively. Here the detailed description of the rating is given.

Rating of CI engine fuels:-

The knock resistance depends on chemical properties as well as on the operating and design conditions of the engine. So the knock rating of a diesel fuel is found by comparing the fuel at a specific condition with primary reference fuels. The reference fuels are normal cetane $C_{16}H_{34}$, which has been assigned a cetane number of 100 and alpha methyl naphthalene, $C_{11}H_{10}$, with a cetane number of 0.

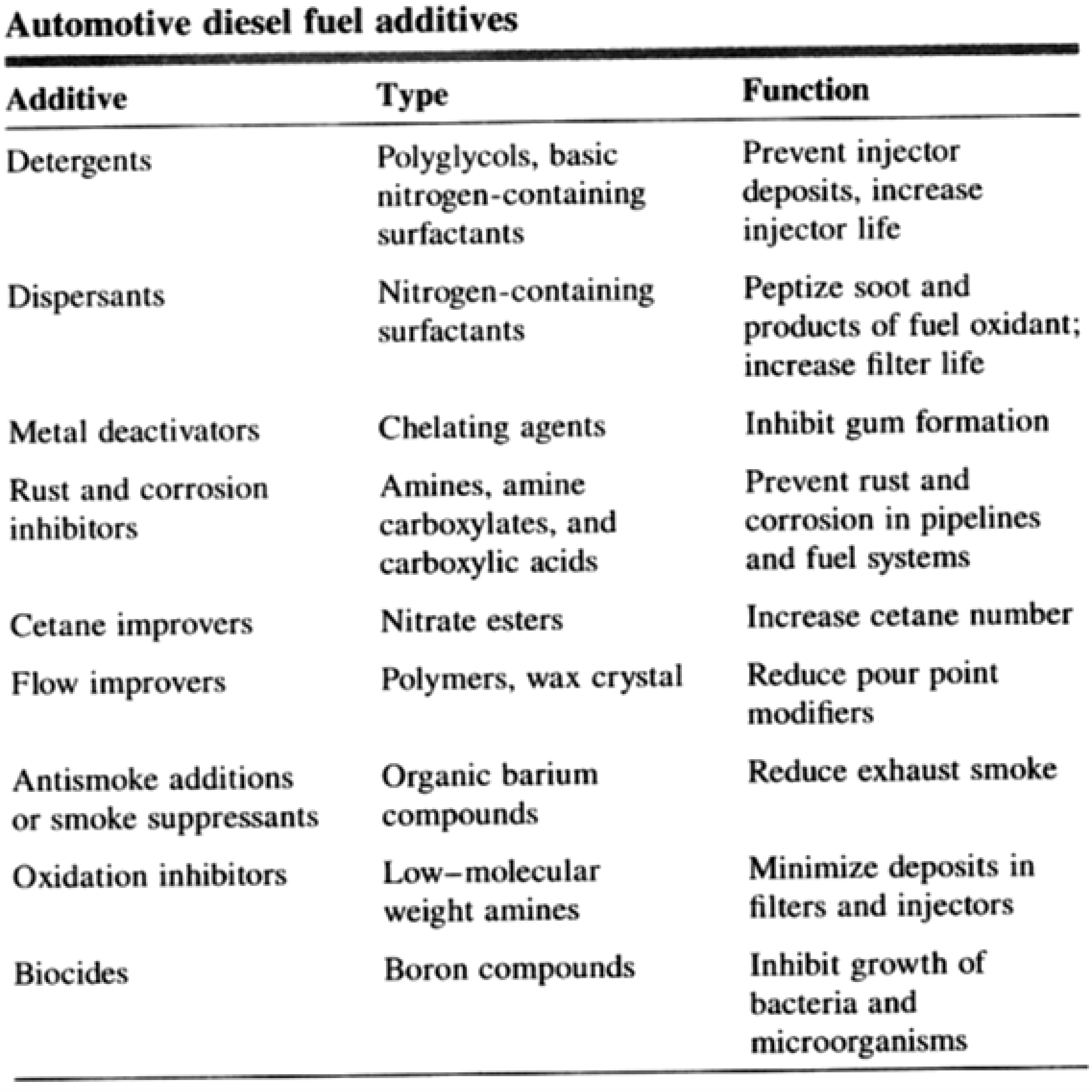
Def. Cetane number of a fuel is defined as the percentage by volume of normal cetane in a mixture of normal cetane and alpha methyl naphthalene which has the same ignition characteristics (ignition delay) as the test fuel when combustion is carried out in a standard engine under specified operating conditions.

The knock should be directly related to the ignition delay as it is the major factor in controlling of the autoignition in the CI engine. Knock resistance property of a diesel oil can be improved by adding small quantities of compounds like amyl nitrate, ethyl nitrate or ether.

Additives

Some compounds called additives or dopes are used to improve the combustion properties of fuels. The main combustion problems that arise when the operating conditions become severe are knocking and surface ignition. That can be tackled by a lot of ways of which one is using additives.

- For an additive to be acceptable, it must satisfy some basic requirements. These are as follows:-
- It must be affective in desired reaction that is knock resistance or surface ignition or both.
- It should be soluble in fuel under all conditions.
- It should be stable in storage and have no adverse effect on fuel stability.
- It should be in the liquid phase at normal temperature, and volatile to give rapid vaporization in the manifold.
- It must not produce harmful deposits.
- Its water solubility must be minimum to minimize handling loses.



Automotive diesel fuel additives

Additive	Type	Function
Detergents	Polyglycols, basic nitrogen-containing surfactants	Prevent injector deposits, increase injector life
Dispersants	Nitrogen-containing surfactants	Peptize soot and products of fuel oxidant; increase filter life
Metal deactivators	Chelating agents	Inhibit gum formation
Rust and corrosion inhibitors	Amines, amine carboxylates, and carboxylic acids	Prevent rust and corrosion in pipelines and fuel systems
Cetane improvers	Nitrate esters	Increase cetane number
Flow improvers	Polymers, wax crystal	Reduce pour point modifiers
Antismoke additions or smoke suppressants	Organic barium compounds	Reduce exhaust smoke
Oxidation inhibitors	Low–molecular weight amines	Minimize deposits in filters and injectors
Biocides	Boron compounds	Inhibit growth of bacteria and microorganisms

TEXT / REFERENCE BOOKS

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SCHOOL OF MECHANICAL ENGINEERING

DEPARTMENT OF AUTOMOBILE ENGINEERING

Unit - 3 - COMBUSTION OF FUELS – SAUA1303

UNIT -3

COMBUSTION OF FUELS

Stoichiometry - calculation of theoretically correct air required for combustion of liquid and gaseous fuels, volumetric and gravimetric analysis of the dry products of combustion, mass of dry gas per kg of fuel burnt, mass of carbon in the exhaust gas, mass of carbon burnt to carbon-monoxide per kg of fuel, heat loss due to incomplete combustion, exhaust gas analysis by Orsat apparatus.

STOICHIOMETRY

This section develops relations between the composition of the reactants (fuel and air) of a combustible mixture and the composition of the products. Since these relations depend only on the conservation of mass of each chemical element in the reactants, only the relative elemental composition of the fuel and the relative proportions of fuel and air are needed.

Complete oxidation of simple hydrocarbon fuels forms carbon dioxide (C02) from all of the carbon and water (H_20) from the hydrogen, that is, for a hydrocarbon fuel with the general composition *CnHm,*

$$C_nH_m + \left(n + \frac{m}{4}\right)O_2 \longrightarrow nCO_2 + \frac{m}{2}H_2O$$

Even in the idealized case of complete combustion, the accounting of all species present in combustion exhaust involves more than simply measuring the CO2 and H20. Since fuels are burned in air rather than in pure oxygen, the nitrogen in the air may participate in the combustion process to produce nitrogen oxides. Also, many fuels contain elements other than carbon, and these elements may be transformed during combustion. Finally, combustion is not always complete, and the effluent gases contain unburned and partially burned products in addition to CO2 and H20. Air is composed of oxygen, nitrogen, and small amounts of carbon dioxide, argon, and other trace species. Since the vast majority of the diluent in air is nitrogen, for our purposes it is perfectly reasonable to consider air as a mixture of 20.9% (mole basis) O2 and 79.1 % (mole basis) N2 • Thus for every mole of oxygen required for combustion, 3.78 mol of nitrogen must be introduced as well. Although nitrogen may not significantly alter the oxygen balance, it does have a major impact on the thermodynamics, chemical kinetics, and formation of pollutants in combustion systems. For this reason it is useful to carry the "inert" species along in the combustion calculations. The stoichiometric relation for complete oxidation of a hydrocarbon fuel, CnHm, becomes

$$C_nH_m + \left(n + \frac{m}{4}\right)(O_2 + 3.78N_2) \longrightarrow nCO_2 + \frac{m}{2}H_2O + 3.78\left(n + \frac{m}{4}\right)N_2$$

Thus for every mole of fuel burned, 4.78(*n* + *m14)* mol of air are required and 4. 78(*n* + *m14)* + *m14* mol of combustion products are generated. The molar *fuel/air* ratio for stoichiometric combustion is 1*I* [4. 78(*n* + *m14)*].

Gas compositions are generally reported in terms of mole fractions since the mole fraction does not vary with temperature or pressure as does the concentration (moles/ unit volume). The product mole fractions for complete combustion of this hydrocarbon fuel are

$$y_{CO_2} = \frac{n}{4.78(n + m/4) + m/4}$$

$$y_{H_2O} = \frac{m/2}{4.78(n + m/4) + m/4}$$

$$y_{N_2} = \frac{3.78(n + m/4)}{4.78(n + m/4) + m/4}$$

Calculation of theoretically correct air required for combustion of liquid Fuels

Air is a mixture of about 21% oxygen, 78% nitrogen, and 1% other constituents by volume. For combustion calculations it is usually satisfactory to represent air as a 21% oxygen, 79% nitrogen mixture, by volume. Thus for every 21 moles of oxygen that react when air oxidizes a fuel, there are also 79 moles of nitrogen involved. Therefore, 79/21 = 3.76 moles of nitrogen are present for every mole of oxygen in the air. At room temperature both oxygen and nitrogen exist as diatomic molecules, O2 and N2, respectively. It is usually assumed that the nitrogen in the air is non reacting at combustion temperatures; that is, there are as many moles of pure nitrogen in the products as there were in the reactants. At very high temperatures small amounts of nitrogen react with oxygen to form oxides of nitrogen, usually termed NOx. These small quantities are important in pollution analysis because of the major role of even small traces of NOx in the formation of smog. However, since these NOx levels are insignificant in energy analysis applications, nitrogen is treated as inert here. The molecular weight of a compound or mixture is the mass of 1 mole of the substance. The average molecular weight, M, of a mixture, as seen earlier, is the linear combination of the products of the mole fractions of the components and their respective molecular weights. Thus the molecular weight for air, Mair, is given by the sum of the products of the molecular weights of oxygen and nitrogen and their respective mole fractions in air. Expressed in words:

M_{air} = Mass of air/Mole of air = (Moles of N_2 /Mole of air)(Mass of N_2 /Mole of N_2) + (Moles of O_2/Mole of air) (Mass of O_2 /Mole of O_2)

Or $M_{air} = 0.79\ M_{nitrogen} + 0.21\ M_{oxygen} = 0.79(28) + 0.21(32) = 28.84$

The mass fractions of oxygen and nitrogen in air are then $mf_{oxygen} = (0.21)(32)/28.84 = 0.233$, or 23.3%

and $mf_{nitrogen} = (0.79)(28)/28.84 = 0.767$, or 76.7%

Theoretical Air and Air-Fuel Ratio -The minimum amount of air which will allow the complete combustion of the fuel is called the Theoretical Air (also referred to as Stoichiometric Air). In this case the products do not contain any oxygen. If we supply less than theoretical air then the products could include carbon monoxide (CO), thus it is normal practice to supply more than theoretical air to prevent this occurrence. This **Excess Air** will result in oxygen appearing in the products.

The standard measure of the amount of air used in a combustion process is the Air-Fuel Ratio (AF), defined as follows:

$$AF = \frac{m_{air}}{m_{fuel}}$$

Thus considering only the reactants of the methane combustion with theoretical air presented above, we obtain:

$$\underset{\text{fuel}}{CH_4} + \underset{\text{2 kmol air}}{2(O_2 + 3.76N_2)} \leftrightarrow \text{ Reactants}$$

$$AF = \frac{m_{air}}{m_{fuel}} = \frac{2(4.76)\ [\text{kmol}]\ 29\left[{}^{kg}/_{kmol}\right]}{1\ [\text{kmol}]\ (12+4)\left[{}^{kg}/_{kmol}\right]}$$

$$AF = 17.3\,\frac{\text{kg - air}}{\text{kg - fuel}}$$

Analysis of the Products of Combustion - Combustion always occurs at elevated temperatures and we assume that all the products of combustion (including the water vapor) behave as ideal gases. Since they have different gas constants, it is convenient to use the ideal gas equation of state in terms of the universal gas constant as follows:

$$P.V = m.R.T = \frac{m}{M}R.M.T$$

where: m is mass [kg], V is volume [m^3], P is pressure [kPa] and T is temperature [K]

$R\left[\frac{kJ}{kg.K}\right]$ is the gas constant

$M\left[\frac{kg}{kmol}\right]$ is the molar mass of the substance

thus: $P.V = N.R_u.T$

where: $R_u = R.M = 8.314\left[\frac{kJ}{kmol.K}\right]$ is the Universal Gas Constant

$N = \frac{m}{M}$ is the number of kmols

Volumetric and gravimetric analysis

Fuels are generally comprised of a number of different elements in a vast array of molecular forms. The main elements in flammable materials are Carbon C, Hydrogen, H, Oxygen, O, Nitrogen, N, and Sulphur with other trace elements to boot.

The components of a mixture (whether liquid, solid or gas) can take be expressed in many ways: volumetric, gravimetric, dry, wet, ash free, as supplied etc. etc. It is important right from the start to know exactly what these mean so that, when combustion calculations are carried out, we have the right numbers.

Gravimetric and Volumetric Ratios

The two fundamental methods of defining the quantities of mixture are by weight (gravimetric) or by volume (molar). For clarity, the following symbols are often (but not exclusively) used.

c i = the gravimetric fraction (mass fraction) of element / molecule i

y i =the volumetric fraction (molar fraction) of element / molecule i

Of course, the sum of mass or mole fractions for all species in a mixture will be unity:

$$\sum_N \psi_i = \sum_N \chi_i = 1$$

To convert from mole fraction to mass fraction we must know the molecular weight, M (kg/kmol), of the individual chemical species. We then calculate the mass of all species by multiplying the volume fraction by the molecular weight. Then we divide the mass of the individual element/molecule by the total mass.

$$\chi_i = \frac{\psi_i M_i}{\sum_N \psi_i M_i} \quad \text{- Molar to mass}$$

$$\psi_i = \frac{\chi_i / M_i}{\sum_N \chi_i / M_i} \quad \text{- Mass to molar}$$

So, if we are given a coal of composition C 95%, H 4%, Cl 0.5%, S 0.5% by weight. Then the molar composition is calculated thus:

Element	χ_i (mass)	χ_i / M_i	ψ_i (volumetric)
C	95	7.917	66.25

H	4	4.0	33.47
Cl	0.5	0.014286	0.195
S	0.5	0.015625	0.131
Total	100	11.95	100.046

Mass of dry gas per kg of fuel

Mass of carbon in the exhaust gas

The mass emission of pollutants are calculated by means of the following equation :

$$M_i = \frac{V_{mix} * Q_i * k_H * C_i * 10^{-6}}{d}$$

M_i = Mass emission of the pollutant i in g/km
V_{mix} = Volume of the diluted exhaust gas expressed in m^3/test and corrected to standard conditions 293 K and 101.33 kPa
Q_i = Density of the pollutant i in kg/m^3 at normal temperature and pressure (293 K and 101.33 kPa)
k_H = Humidity correction factor used for the calculation of the mass emissions of oxides of nitrogen. There is no humidity correction for HC and CO.
C_i = Concentration of the pollutant i in the diluted exhaust gas expressed in ppm and corrected by the amount of the pollutant i contained in the dilution air.
d = distance covered in km

Mass of carbon burnt to carbon-monoxide

Carbon monoxide (CO) is a byproduct of incomplete combustion and is essentially partially burned fuel. If the air/fuel mixture does not have enough oxygen present during combustion, it will not burn completely. When combustion takes place in an oxygen starved environment, there is insufficient oxygen present to fully oxidize the carbon atoms into carbon dioxide (CO2). When carbon atoms bond with only one oxygen atom carbon monoxide (CO) forms.

An oxygen starved combustion environment occurs as a result of air/fuel ratios which are richer than stoichiometry (14.7 to 1). There are several engine operating conditions when this occurs normally. For example, during cold operation, warm-up, and power enrichment. It is, therefore, normal for higher concentrations of carbon monoxide to be produced under these operating conditions. Causes of excessive carbon monoxide includes leaky injectors, high fuel pressure, improper closed loop control, etc

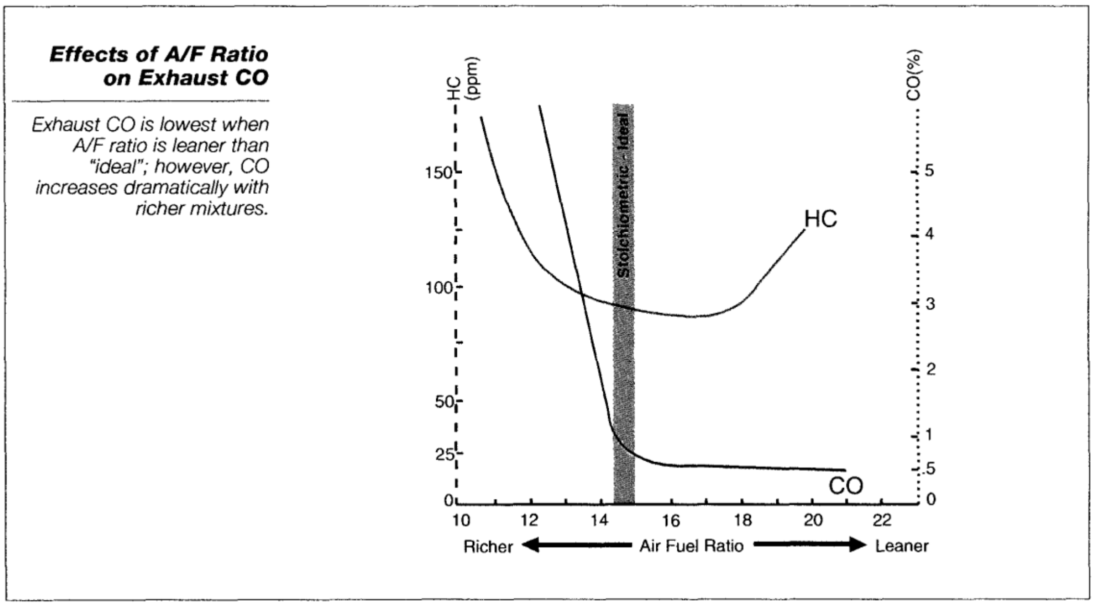
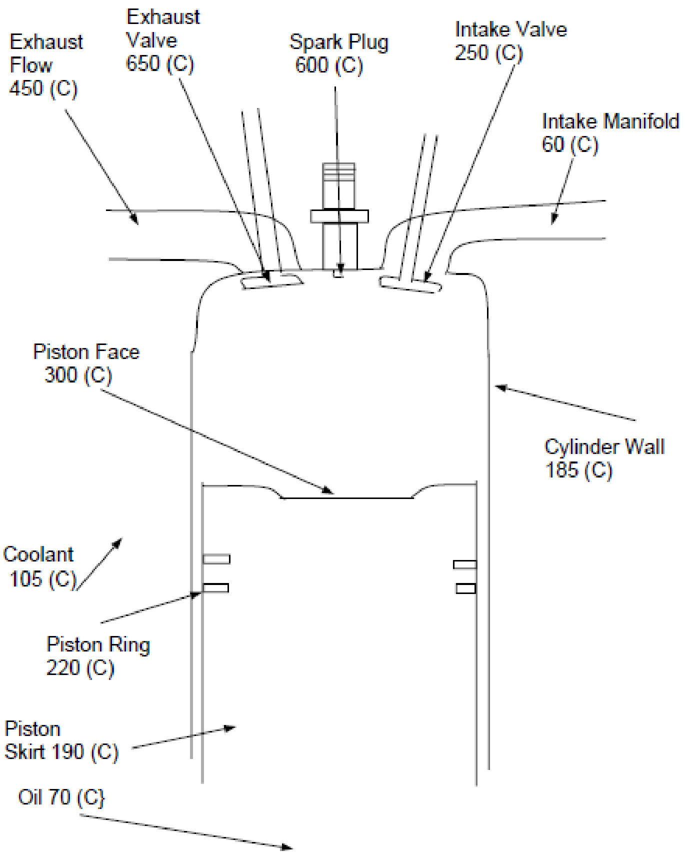


Fig. 3.1 Effect of A/F Ratio on Exhaust CO

Heat loss due to incomplete combustion

The gasoline-powered internal combustion engine takes air from the atmosphere and gasoline, a hydrocarbon fuel, and through the process of combustion releases the chemical energy stored in the fuel. Of the total energy released by the combustion process, about 20% is used to propel the vehicle, the remaining 80% is lost to friction, aerodynamic drag, accessory operation, or simply wasted as heat transferred to the cooling system.

The heat transfer from cycle to cycle varies for different points in an engine. Below figure shows the heat transfer at three different locations in the combustion chamber for a single cylinder during one cycle. There is significant variation in the heat transfer for these points.



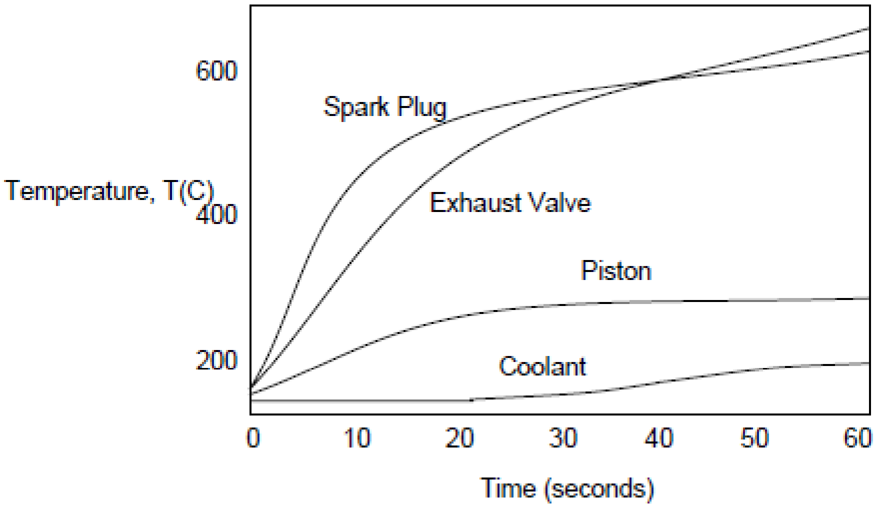


Fig: Temperarure vs. time

- **Areas where heat transfer is important**

- Intake system: manifold, port, valves

- In-cylinder: cylinder head, piston, valves, liner
- Exhaust system: valves, port, manifold, exhaust pipe
- Coolant system: head, block, radiator
- Oil system: head, piston, crank, oil cooler, sump
- **Information of interest**
- Heat transfer per unit time (rate)
- Heat transfer per cycle (often normalized by fuel heating value)
- Variation with time and location of heat flux (heat transfer rate per unit area)
- Heat transfer mostly from hot burned gas
- That from unburned gas is relatively small
- Flame geometry and charge motion/turbulence level affects heat transfer rate
- Order of Magnitude
- SI engine peak heat flux ~ 1-3 MW/m2
- Diesel engine peak heat flux ~ 10 MW/m2

For SI engine at part load, a reduction in heat losses by 10% results in an improvement in fuel consumption by 3%

– Effect substantially less at high load

ORSAT APPARATUS.

An Orsat gas analyser is a piece of laboratory equipment used to analyse a gas sample (typically fossil fuel flue gas) for its oxygen, carbon monoxide and carbon dioxide content. Although largely replaced by instrumental techniques, the Orsat remains a reliable method of measurement and is relatively simple to use.

The apparatus consists essentially of a calibrated water-jacketed gas burette connected by glass capillary tubing to two or three absorption pipettes containing chemical solutions that absorb the gasses it is required to measure. For safety and portability, the apparatus is usually encased in a wooden box.

The absorbents are:

Potassium Hydroxide (Caustic Potash)

Alkaline pyrogallol

Ammoniacal Cuprous chloride

The base of the gas burette is connected to a levelling bottle to enable readings to be taken at constant pressure and to transfer the gas to and from the absorption media. The burette contains slightly acidulated water with a trace of chemical indicator (typically methyl orange) for coloration.

By means of a rubber tubing arrangement, the gas to be analyzed is drawn into the burette and flushed through several times. Typically, 100ml is withdrawn for ease of calculation. Using the stopcocks that isolate the absorption burettes, the level .

The gas is then passed into the caustic potash burette, left to stand for about two minutes and then withdrawn, isolating the remaining gas via the stopcock arrangements. The process is repeated to ensure full absorption. After leveling the liquid in the bottle and burette, the remaining volume of gas in the burette indicates the percentage of carbon dioxide absorbed.

The same technique is repeated for oxygen, using the pyrogallol, and carbon monoxide using the ammoniacal cuprous chloride.

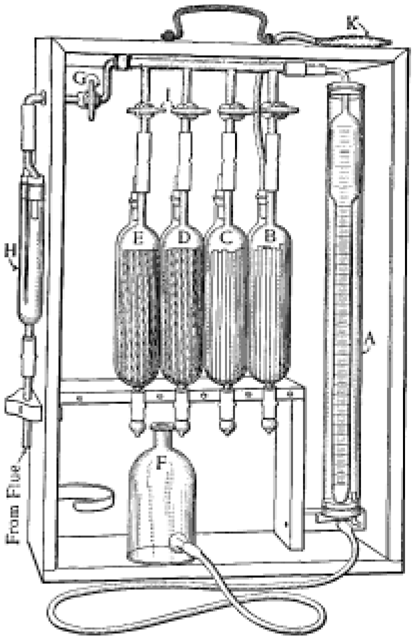


Fig: ORSAT APPARATUS

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SCHOOL OF MECHANICAL ENGINEERING

DEPARTMENT OF AUTOMOBILE ENGINEERING

Unit - 4 - LUBRICANTS – SAUA1303

UNIT IV- LUBRICANTS

Theory of Lubrication, Effect of engine variables on friction, Types of Lubrications-Hydrodynamic and Hydrostatic lubrication. Requirements for automotive lubricants and types, Viscosity index, oxidation deterioration and degradation of lubricants, additives of lubricants and synthetic lubricants, classification of lubricating oils, tests on lubricants. Grease, classification, properties, testing of grease

THEORY OF LUBRICATION

INTRODUCTION OF FRICTION

Friction generally refers to forces acting between surfaces in relative motion. In engines, frictional losses are mainly due to sliding as well as rotating parts. Normally, engine friction, in its broader sense, is taken as the difference between the indicated power (power at piston top as produced by the combustion gases) and the brake power (useful power). Usually engine friction is expressed in terms of frictional power f_p. Frictional loss is mainly attributed to the following mechanical losses.

Friction power = Indicated power – Brake power

TOTAL ENGINE FRICTION

Total engine friction, defined as the difference between indicated horse power and brake horse power, includes the power required to drive the compressor or a scavenging pump and the power required to drive engine auxiliaries such as oil pump, coolant pump and fan, etc.

Total engine friction can be divided into five main components. There are

1. Crankcase mechanical friction.
2. Blowby losses (compression-expansion pumping loss).
3. Exhaust and inlet system throttling losses.
4. Combustion chamber pumping loop losses.
5. Piston mechanical friction.

Crankcase Mechanical Friction

Crankcase mechanical friction can further be sub-divided into three types

- ✓ Bearing friction
- ✓ Valve gear friction
- ✓ Pump and miscellaneous friction.

The bearing friction includes the friction due to main bearing, connecting rod bearing and other bearings. Bearing friction is viscous in nature and depends upon the oil viscosity, the speed, size and geometry of the journal. All crankcase friction losses other than bearing and valve gear losses vary roughly in proportion to engine displacement and speed. The bearing losses are affected very little by the loading of the bearing but they rise rapidly with increase in speed because these losses are primarily the result of continuous shear of the oil film in the bearing clearance. Crankcase mechanical friction is about 15 to 20 percent of total engine friction. Since, there are a number of moving parts, the frictional losses are comparatively higher in reciprocating engines.

Blowby Losses.

Blowby is the phenomenon of leakage of combustion products past the piston and piston rings from the cylinder to the crankcase. These losses depend upon the inlet pressure and compression ratio. These losses vary as the square root of inlet pressure, and increase as the compression ratio is increased. Blowby losses are reduced as the engine speed is increased.

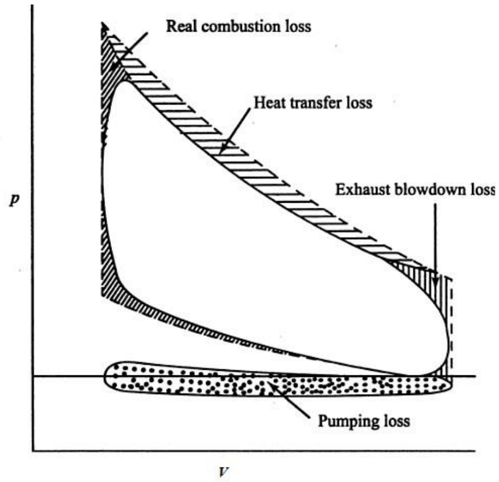


Fig. 4.1. Blowby losses

Exhaust and Inlet Throttling Loss.

The standard practice for sizing the exhaust valve is to make them a certain percentage smaller than inlet valves. This usually results in an insufficiently sized exhaust valve and hence, results in exhaust pumping loss.

Combustion Chamber Pumping Loop Losses.

In the case of pre-combustion chamber engines an additional loss occurs. This is the loss occurring due to the pumping work required to pump gases into and out of the precombustion chamber. The exact value of this would depend upon the orifice size connecting the precombustion chamber and the main chamber, and the speed. Higher the speed greater is the loss and smaller the orifice size greater is the loss

Piston Mechanical Friction.

Piston Mechanical Friction sub-divided into two types.

1. Viscous friction
2. Non-viscous friction

Non-viscous friction further divided into

(a) Friction due to ring tension, (b) Friction due to gas pressure forces behind the ring.

The viscous friction depends upon the viscosity of the oil and the temperature of the various parts of the piston. The degree to which the upper part of the piston can be lubricated also affects the viscous friction. The oil film thickness between piston and the cylinder is also affected by the piston side thrust and the resulting vibrations.

The cylinder gas pressure behind the top rings. Because of the ring tension the ring presses against the cylinder wall and results in frictional losses. In addition to the ring tension, the gas pressure behind the ring also causes friction losses. The pressure behind the top piston ring is as high as the pressure of the combustion chamber. For other piston rings it is much lower.

EFFECT OF ENGINE VARIABLES ON ENGINE FRICTION

Effect of stroke to bore ratio

The effect of stroke to bore ratio on engine friction and economy is very small. High stroke to bore ratio engines have equally good friction mep values as that for low stroke to bore ratio engine. At high speeds the higher stroke to bore ratio engine may have some disadvantages.

Effect of cylinder size and number of cylinders

The friction and economy improve as a smaller number of larger cylinders are used. This is because the proportion between the working piston area and its friction producing area, i.e. circumference, is reduced. Thus, there seems to be some justification for the layman's notion that four and six-cylinder engines are more efficient than eight cylinders.

Effect of number of piston rings

The effect of number of piston ring is not very critical and this number is usually chosen on the basis of cost, size and other requirements rather than on the basis of their effect on friction.

Effect of compression ratio

Friction mean effective pressure increases as the compression ratio is increased. But the mechanical efficiency either remains constant or improves as the compression ratio is increased. If the displacement is varied to keep the maximum engine torque constant, this results in better part load friction characteristics.

Effect of engine speed

Engine friction increases rapidly as the speed increases. The best way to improve mechanical efficiency at high speed is to increase the number of cylinders.

Effect of oil viscosity

Higher the oil viscosity greater is the friction loss. The temperature of the oil in the crankcase significantly affects the friction losses, wear and service life of an engine. As the oil temperature increases, the viscosity decreases and friction losses are reduced during a certain temperature range. If the temperature goes higher than at a certain value the local oil film is destroyed resulting in metal to metal contact.

Effect of cooling water temperature

A rise in cooling water temperature reduces engine friction through its effect on oil viscosity. During starting operation, the temperature of both the oil and the water is low. Hence, the viscosity is high. This results in high starting friction losses and rapid engine wear.

Effect of engine load

As the load increases the maximum pressure in the cylinder has a tendency to increase slightly. This results in slightly higher friction values. However, this increase in friction loss is more than compensated by the decrease in oil viscosity due to higher temperatures resulting from increased load. Further in case of petrol engines the throttling losses reduce as the throttle is opened more and more to supply more fuel for allowing an increase in engine load. Both these effects combine to reduce frictional losses of a petrol engine as engine load is increased. However, for diesel engines the frictional losses are more or less independent of engine load.

LUBRICATION

Lubrication is the admittance of oil between two surfaces having relative motion. The purpose of lubrication may be one or more of the following:

1. Reduce friction and wear between the parts having relative motion.

2. Cool the surfaces by carrying away heat generated due to friction.

3. Seal a space adjoining the surfaces such as piston rings and cylinder liner.

4. Clean the surface by carrying away the carbon and metal particles caused by wear.

5. Absorb shock between bearings and other parts and consequently reduce noise.

MECHANISM OF LUBRICATION

There are mainly three types of mechanism by which lubrication is done.

(a) Fluid-film or thick-film or hydrodynamic lubrication

In this, the moving or sliding Surfaces are separated from each other by a thick-film of fluid, so that direct surface-to surface contact and welding of junctions rarely occurs. The lubricant film covers or fills the irregularities of the sliding or moving surfaces and forms a thick layer in between them, so that there is no direct contact between the material surfaces. This consequently reduces wear. The resistance to movement of sliding or moving parts is only due to the internal resistance between the particles of the lubricant moving over each other. Therefore, the lubricant chosen should have the minimum viscosity.

For example, consider a block resting on a flat surface covered with a layer of lubricating oil. If the weight of the block is very high or the oil is thin, the oil will squeeze out. In other words, thick oil can support a higher load than that supported by a thin oil. When this block is moved over the surface, a wedge-shaped oil film is built up between the moving block and the surface. This wedge-shaped film is thicker at the leading edge than at the rear.

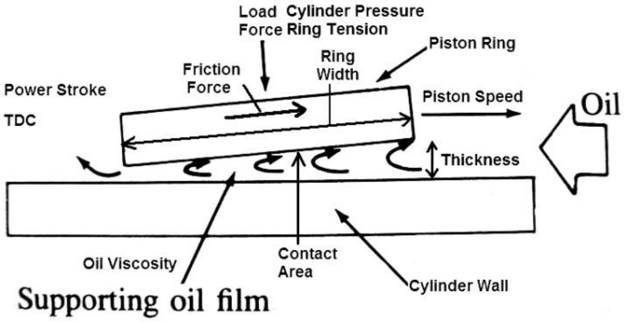


Fig. 4.2. Hydrodynamic lubrication

In other words the moving block acts as a pump to force oil into clearance that narrows down progressively as the block moves. This generates appreciable oil film pressure which carries the load. This type of lubrication where a wedge-shaped oil film is formed between two moving surfaces is called hydrodynamic lubrication. The main advantage of this type of lubrication is that the load carrying capacity of the bearing increases with increase in relative speed of the moving surfaces.

The force required to move the block over the surface depends upon the weight of the block, the speed of movement, and the thickness or viscosity of the oil. This force divided by the pressure caused by the weight of the block is called the coefficient of friction. A higher coefficient of friction signifies a greater force to move the block.

The flat surface lubrication of the kind referred above exists at places such as thrust bearings, valve tips and cam lifters. Many other surfaces which use hydrodynamic lubrication are cylinder wall, valve guide, connecting rod bearings and camshaft bearings.

(b) Elastohydrodynamic lubrication

When the load acting on the bearings is very high, the material itself deforms elastically against the pressure built up of the oil film. This type of lubrication is called elastohydrodynatnic lubrication, occurs between cams and followers, gear teeth, and rolling bearings where the contact pressures are extremely high.

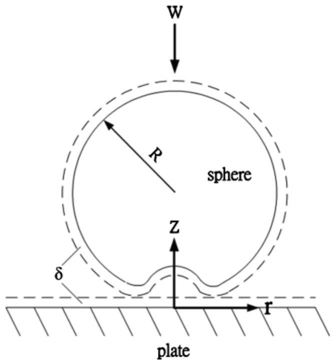


Fig. 4.3. Elasto hydrodynamic lubrication

(c) Boundary lubrication

If the film thickness between the two surfaces in relative motion becomes so thin that formation of hydrodynamic oil film is not possible and the surface high spots or asperities penetrate this thin film to make metal to metal contact then such lubrication is called boundary lubrication. This happens when (i) A shaft starts moving from rest, or (ii) The speed is very low, or (iii) The load is very high, and (iv) Viscosity of the oil is too low.

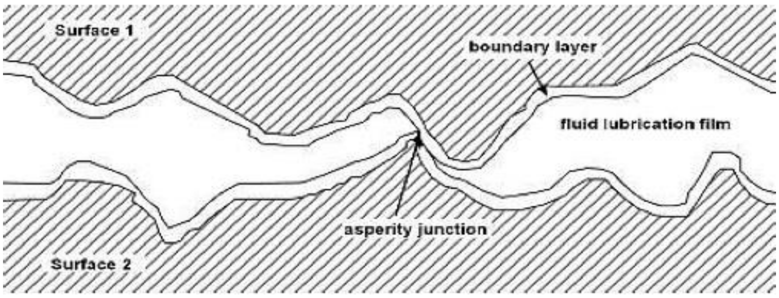


Fig. 4.4. Boundary lubrication

A condition of boundary lubrication always exists when the engine is first started. The shaft is in contact with the bottom of the bearing with only a thin surface film of oil formed on them. The bearing surfaces are not perfectly smooth. They have uneven surfaces which tear this thin film which is constantly formed. While the crankshaft is turning slowly. As the speed increases it switches on to hydrodynamic lubrication. Boundary lubrication may also occur when the engine is under very high loads or when the oil supply to the bearing is insufficient.

(d) Hydrostatic lubrication

In hydrostatic lubrication a thin oil film resists its instantaneous squeezing out under reversal of loads with relatively slow motions. The oil film acts as a cushion. If oil supply is sufficient the oil film thickness is restored before next reversal of load.

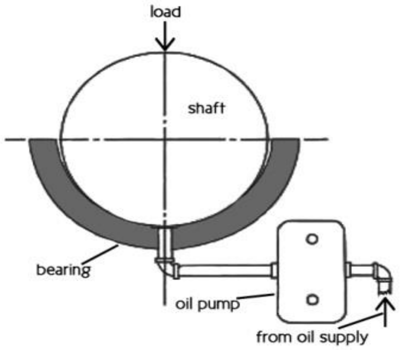


Fig.4.5. Hydrostatic lubrication

LUBRICANTS

In all types of machines, the surfaces of moving or sliding or rolling parts rub against each other. Due to the mutual rubbing of one part against another, a resistance is offered to their movement. This resistance is known as **friction**.

It causes a lot of wear and tear of surfaces of moving parts. Any substance introduced between two moving/sliding surfaces with a view to reduce the friction (or frictional resistance) between them, is known as a **lubricants.**

The main purpose of a lubricant is to keep the moving/sliding surfaces apart, so that friction and consequent destruction of material is minimized. The process of reducing friction between moving/sliding surfaces, by the introduction of lubricants in between them, are called **lubrication.**

Function of Lubricants:

- It reduces wear and tear of the surfaces by avoiding direct metal to metal contact
- Between the rubbing surfaces, i.e. by introducing lubricants between the two surfaces
- It reduces expansion of metal due to frictional heat and destruction of material
- It acts as coolant of metal due to heat transfer media
- it avoids unsmooth relative motion
- It reduces maintenance cost
- It also reduces power loss in internal combustion engines

Classification of Lubricants:

Lubricants are classified on the basis of their physical state, as follows;

- Liquid lubricants or Lubricating Oils,
- Semi-solid lubricants or Greases and
- Solid lubricants.

(a) Liquid lubricants or Lubricating oils: Lubricating oils also known as liquid lubricants and further classified into three categories; (i) Animal and Vegetables oils, (ii) Mineral or Petroleum oils and (iii) blended oils.

Characteristic of good lubricating oils:

- high boiling point,
- low freezing point,
- adequate viscosity for proper functioning in service,
- high resistance to oxidation and heat,
- non-corrosive properties and
- Stability to decomposition at the operating temperatures.

Animal and Vegetables oils:

Animal oils are extracted from the crude fat and vegetables oils such as cotton seed oil and caster oils. These oils possess good oiliness and hence they can stick on metal surfaces effectively even under elevated temperatures and heavy loads. But they suffer from the disadvantages that they are costly, undergo easy oxidation to give gummy products and hydrolyze easily on contact with moist air or water. Hence they are only rarely used these days for lubrication. But they are still used as blending agents in petroleum based lubricants to get improved oiliness.

Mineral or Petroleum oils:

These are basically lower molecular weight hydrocarbons with about 12 to 50 carbon atoms. As they are cheap, available in abundance and stable under service conditions, hence they are widely used. But the oiliness of mineral oils is less, so the addition of higher molecular weight compounds like oleic acid and stearic acid increases the oiliness of mineral oil.

Blended oils:

No single oil possesses all the properties required for a good lubricant and hence addition of proper additives is essential to make them perform well. Such additives added lubricating oils are called blended oils. Examples: The addition of higher molecular weight compounds like oleic acid, stearic acid, palmetic acid, etc. or vegetables oil like coconut oil, castor oil, etc increases the oiliness of mineral oil.

Semi-solid Lubricants or Grease:

A semi-solid lubricant obtained by combining lubricating oil with thickening agents is termed as grease. Lubricating oil is the principal component and it can be either petroleum oil or a synthetic hydrocarbon of low to high viscosity. The thickeners consist primarily of special soaps of Li, Na, Ca, Ba, Al, etc. Non-soap thickeners

Include carbon black, silica gel, polyureas and other synthetic polymers, clays, etc. Grease can support much heavier load at lower speed. Internal resistance of grease is much higher than that of lubricating oils; therefore it is better to use oil instead of grease. Compared to lubricating oils, grease cannot effectively dissipate heat from the bearings, so work at relatively lower temp.

Solid lubricants:

They are preferred where (1) the operating conditions are such that a lubricating film cannot be secured by the use of lubricating oils or grease (2) contamination

(By the entry of dust particles) of lubricating oils or grease is unacceptable (3) the operating temperature or load is too high, even for grease to remain in position and (4) combustible lubricants must be avoided. . They are used either in the dry powder form or with binders to make them stick firmly to the metal surfaces while in use.

They are available as dispersions in non-volatile carriers like soaps, fats, waxes, etc and as soft metal films.

The most common solid lubricants are graphite, molybdenum disulphide, tungsten disulphide and zinc oxide. They can withstand temperature upto 650° C and can be applied in continuously operating situations. They are also used as additives to mineral oils and greases in

order to increase the load carrying capacity of the lubricant. Other solid lubricants in use are soapstone (talc) and mica.

Graphite:

It is the most widely used of all the solid lubricants and can be used either in the powdered form or in suspension. It is soapy to touch; non-inflammable and stable up to a Temperature of 375° C. Graphite has a flat plate like structure and the layers of graphite sheets are arranged one above the other and held together by weak van Der Waal’s forces. These parallel layers which can easily slide one over other make graphite an effective lubricant. Also the layer of graphite has a tendency to absorb oil and to be wetted of it.

Molybdenum Disulphide:

It has a sandwich- like structure with a layer of molybdenum atoms in between two layers of Sulphur atoms. Poor interlaminar attraction helps these layers to Slide over one another easily. It is stable up to a temperature of 400° C.

Properties of Lubricants:

- Viscosity
- Flash Point and Fire Point
- Cloud Point and Pour Point
- Aniline Point and
- Corrosion Stability

(1) ***Viscosity*:** It is the property of liquid by virtue of which it offers resistance to its own flow (the resistance to flow of liquid is known as viscosity). The unit of viscosity is poise. It is the most important single property of any lubricating oil, because it is the main determinant of the operating characteristics of the lubricant. If the viscosity of the oil is too low, a liquid oil film cannot be maintained between two moving/sliding surfaces . On the other hand, if the viscosity of the oil is too high, excessive friction will result.

Effect of temperature on viscosity: Viscosity of liquids decreases with increasing temperature and, consequently, the lubricating oil becomes thinner as the operating temperature increases. Hence, viscosity of good lubricating oil should not change much with change in Temperature, so that it can be used continuously, under varying conditions of temperature.

The rate at which the viscosity of lubricating oil changes with temperature is measured by an arbitrary scale, known as Viscosity Index (V. I). If the viscosity of lubricating oil falls rapidly as the temperature is raised, it has a low viscosity index. On the other hand, if the viscosity of lubricating oil is only slightly affected on raising the temperature, its viscosity index is high.

(2) ***Flash Point and Fire Point:*** Flash point is the lowest temperature at which the lubricant oil gives off enough vapours that ignite for a moment, when a tiny flame is brought near it; while Fire point is the lowest temperature at which the vapours of the lubricant oil burn continuously for at least five seconds, when a tiny flame is brought near it. In most cases, the fire points are 5° C to 40° C higher than the flash points. The flash and fire do not have any

bearing with lubricating property of the oil, but these are important when oil is exposed to high

Temperature service. A good lubricant should have flash point at least above the temperature at which it is to be used. This safeguards against risk if fire, during the use of lubricant.

(3) ***Cloud Point and Pour Point*****:** When the lubricant oil is cooled slowly, the temperature at which it becomes cloudy or hazy in appearance, is called its cloud point; while the temperature at which the lubricant oil cease to flow or pour, is called its pour point. Cloud and pour points indicate the suitability of lubricant oil in cold conditions. Lubricant oil used in a machine working at low temperatures should possess low pour point; otherwise solidification of lubricant oil will cause jamming of machine. It has been found that presence of waxes in the lubricant oil raise pour point.

(4) ***Aniline Point*****:** Aniline point of the lubricant oil is defined as the minimum equilibrium solution temperature for equal volumes of aniline and lubricant oil samples. It gives an indication of the possible deterioration of the lubricant oil in contact with rubber sealing; packing, etc.

Aromatic hydrocarbons have a tendency to dissolve natural rubber and certain types of synthetic rubbers. Consequently, low aromatic content in the lubricant oil is desirable. A higher aniline point means a higher percentage of paraffinic hydrocarbons and hence, a lower percentage of aromatic hydrocarbons. Aniline point is determined by mixing mechanically equal volumes of the lubricant oil samples and aniline in a test tube. The mixture is heated, till homogenous solution is obtained.

Then, the tube is allowed to cool at a controlled rate. The temperature at which the two phases (the lubricant oil and aniline) separate out is recorded at the aniline point.

(5) ***Corrosion Stability*****:** Corrosion stability of the lubricant oil is estimated by carrying out corrosion test. A polished copper strip is placed in the lubricant oil for a specified time at a particular temperature. After the stipulated time, the strip is taken out and examined for corrosion effects. If the copper strip has tarnished, it shows that the lubricant oil contains any chemically active substances which cause the corrosion of the copper strip. Good lubricant oil should not effect the copper strip. To retard corrosion effects of the lubricant oil, certain inhibitors are added to them. Commonly used inhibitors are organic compounds containing P, As, Cr, Bi or Pb.

Essential requirements or characteristics of a good lubricant are as follows:

[1] It should have a high viscosity index.

[2] It should have flash and fire points higher than the operating temperature of the machine.

[3] It should have high oiliness.

[4] The cloud and pour points of a good lubricant should always be lower than the operating temperature of the machine.

[5] The volatility of the lubricating oil should be low.

[6] It should deposit least amount of carbon during use.

[7] It should have higher aniline point.

[8] It should possess a higher resistance towards oxidation and corrosion.

[9] It should have good detergent quality.

SYNTHETIC LUBRICANTS

Synthetic lubricants ara a combination of synthetic base oil plus thickeners and additives that will give the grease or oil lubricant a number of performance advantages over conventional mineral based lubricants.

Synthetic oil is a lubricant consisting of chemical compounds that are artificially made (synthesized). Synthetic lubricants can be manufactured using chemically modified petroleum components rather than whole crude oil, but can also be synthesized from other raw materials. Synthetic oil is used as a substitute for lubricant refined from petroleum when operating in extremes of temperature, because, in general, it provides superior mechanical and chemical properties to those found in traditional mineral oils. Aircraft jet engines, for example, require the use of synthetic oils, whereas aircraft piston engines do not. Synthetic lubricants are also used in metal stamping to provide environmental and other benefits, when compared to conventional petroleum and animal fat based products. These products are also referred to as "non-oil" or "oil free".

Advantages

The technical advantages of synthetic motor oils include:

- Better low- and high-temperature viscosity performance at service temperature extremes
- Better (higher) Viscosity Index (VI)
- Better chemical and shear stability
- Decreased evaporative loss
- Resistance to oxidation, thermal breakdown, and oil sludge problems
- Possibility to extended drain intervals, with the environmental benefit of less used oil waste generated
- Improved fuel economy in certain engine configurations
- Better lubrication during extreme cold weather starts
- Possibly a longer engine life

- Superior protection against "ash" and other deposit formation in engine hot spots (in particular in turbochargers and superchargers) for less oil burn off and reduced chances of damaging oil passageway clogging.
- Increased horsepower and torque due to less initial drag on engine
- Improved Fuel Economy (FE) - from 1.8% to up to 5% has been documented in fleet tests

Disadvantages

The disadvantages of synthetic motor oils include:

- Substantially more expensive (per volume) than mineral oils.
- Potential decomposition problems in certain chemical environments (predominantly in industrial use.)

TESTS ON LUBRICANTS

Basically, there are two different types of lubricant testing

1. chemico-physical

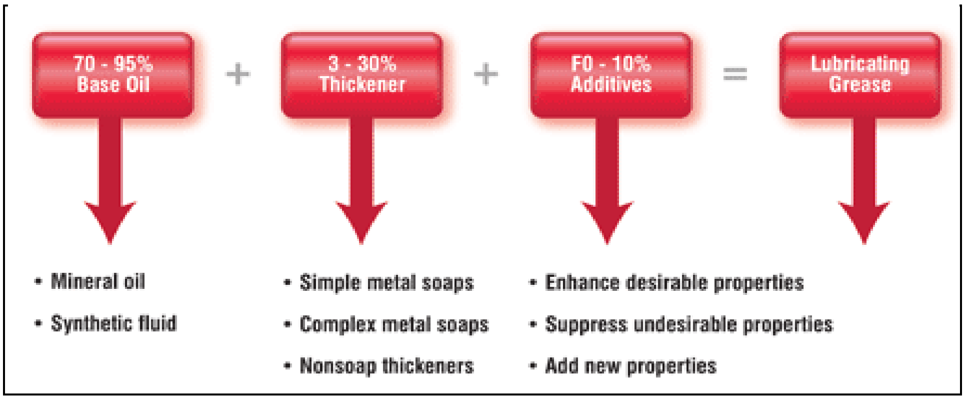
2. mechanico-dynamical.

Chemico-physical tests only concentrate on certain lubricant properties, whereas mechanico-dynamical tests try to simulate the effects of load, speed, media and temperature on the friction and wear behaviour of a tribo-system.

Chemico-physical tests generally precede mechanico-dynamical tests. Depending on the lubricant type and the requirements there are many different test procedures.

GREASE

Lubricating grease is defined as a solid to semi fluid product of dispersion of a thickening agent in liquid lubricant. There are three components that form lubricating grease. These components are oil, thickener and additives. The base oil and additive package are the major components in grease formulations. The thickener is often referred to as a sponge that holds the lubricant (base oil plus additives).



Base Oil

Most greases produced today use mineral oil as their fluid components. These mineral oil-based greases typically provide satisfactory performance in most industrial applications. In temperature extremes (low or high), a grease that utilizes a synthetic base oil will provide better stability.

Thickener

The thickener is a material that, in combination with the selected lubricant, will produce the solid to semifluid structure. The primary type of thickener used in current grease is metallic soap. These soaps include lithium, aluminum, clay, polyurea, sodium and calcium. Lately, complex thickener-type greases are gaining popularity. They are being selected because of their high dropping points and excellent load-carrying abilities.

Additives

Additives can play several roles in lubricating grease. These primarily include enhancing the existing desirable properties, suppressing the existing undesirable properties, and imparting new properties. The most common additives are oxidation and rust inhibitors, extreme pressure, antiwear, and friction-reducing agents.

Function of grease

The function of grease is to remain in contact with and lubricate moving surfaces without leaking out under the force of gravity, centrifugal action or being squeezed out under pressure. Its major practical requirement is that it retains its properties under shear forces at all temperatures it experiences during use.

Functional Properties of Grease

1. Grease functions as a sealant to minimize leakage and to keep out contaminants. Because of its consistency, grease acts as a sealant to prevent lubricant leakage and also to prevent entrance of corrosive contaminants and foreign materials. It also acts to keep deteriorated seals effective.
2. Grease is easier to contain than oil. Oil lubrication can require an expensive system of circulating equipment and complex retention devices. In comparison, grease, by virtue of its rigidity, is easily confined with simplified, less costly retention devices.
3. Grease holds solid lubricants in suspension. Finely ground solid lubricants, such as molybdenum disulfide (moly) and graphite, are mixed with grease in high-temperature service or in extreme high-pressure applications. Grease holds solids in suspension while solids will settle out of oils.
4. Fluid level does not have to be controlled and monitored.

Characteristics of ideal grease

The characteristics commonly found on product data sheets include the following:

Pumpability. Pumpability is the ability of a grease to be pumped or pushed through a system. More practically, Pumpability is the ease with which a pressurized grease can flow through lines, nozzles and fittings of grease-dispensing systems.

Water resistance. This is the ability of grease to withstand the effects of water with no change in its ability to lubricate. Soap/water lather may suspend the oil in the grease, forming an emulsion that can wash away or, to a lesser extent, reduce lubricity by diluting and changing grease consistency and texture.

Consistency. Grease consistency depends on the type and amount of thickener used and the viscosity of its base oil. Grease’s consistency is its resistance to deformation by an applied force. The measure of consistency is called penetration. Penetration depends on whether the consistency has been altered by handling or working. ASTM D 217 and D 1403 methods measure penetration of unworked and worked greases. To measure penetration, a cone of given weight is allowed to sink into a grease for five seconds at a standard temperature of 25°C (77°F).

Dropping point. Dropping point is an indicator of the heat resistance of grease. As grease temperature increases, penetration increases until the grease liquefies and the desired consistency is lost. The dropping point is the temperature at which a grease becomes fluid enough to drip. The dropping point indicates the upper temperature limit at which a grease retains its structure, not the maximum temperature at which a grease may be used.

Oxidation stability. This is the ability of grease to resist a chemical union with oxygen. The reaction of grease with oxygen produces insoluble gum, sludges and lacquer-like deposits that cause sluggish operation, increased wear and reduction of clearances. Prolonged exposure to high temperatures accelerates oxidation in greases.

High-temperature effects. High temperatures harm greases more than they harm oils. Grease, by its nature, cannot dissipate heat by convection like circulating oil. Consequently, without the ability to transfer away heat, excessive temperatures result in accelerated oxidation or even carbonization where grease hardens or forms a crust.

Effective grease lubrication depends on the grease's consistency. High temperatures induce softening and bleeding, causing grease to flow away from needed areas. The mineral oil in grease can flash, burn or evaporate at temperatures greater than 177°C (350°F).

Low-temperature effects. If the temperature of grease is lowered enough, it will become so viscous that it can be classified as hard grease. Pumpability suffers and machinery operation may become impossible due to torque limitations and power requirements. As a guideline, the base oil's pour point is considered the low-temperature limit of grease.

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Unit -5 - ALTERNATE FUELS – SAUA1303

UNIT 5 ALTERNATE FUELS

Alternate fuels for SI engines and CI engines, desirable characteristics, Octane and cetane rating. Introduction to electric, hybrid and fuel cell vehicles

Introduction

Liquid fuels have over the past 100 years evolved as the fuels of choice for transport because of their high energy density and the ease of transport, storage and handling. Conventional fuels are complex mixtures that typically contain more than hundred chemical components whose composition has changed and evolved over time and in connection to engine development. The development has been done in correlation with and in order to meet the engine development demand on power, efficiency and drivability. Over the last decades ever more stringent emissions legislations has been added to the demands on the fuel and engine combination. When discussing alternatives to current fossil based fuels for propulsion and power generation fuel properties are important criteria from a combustion point of view to take into consideration, since the combustion behavior relates to the main purpose of the heat machine, i.e., to convert chemical power to mechanical power. However, the fuel in an internal combustion engine undergoes other processes and passes many systems before it is burned, as exemplified in Figure 1, and these also have to be considered. All the systems will influence the fuel and the fuel's different properties will influence the systems.

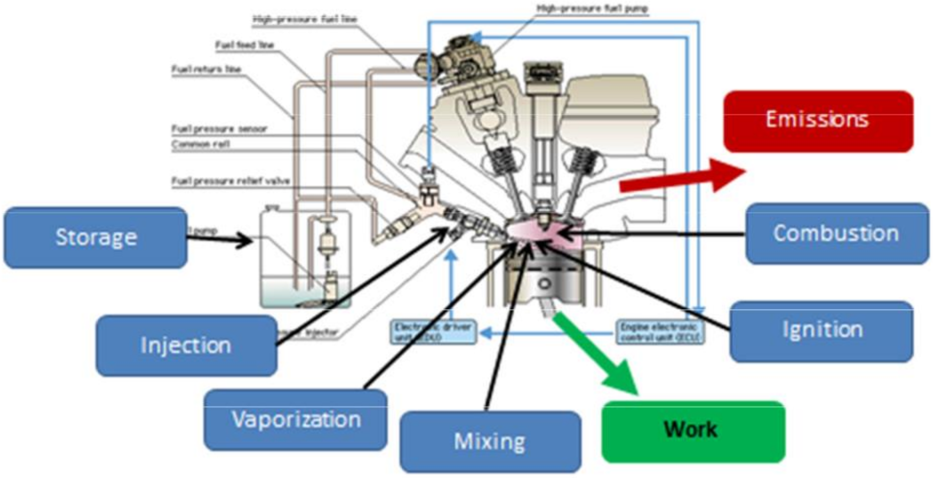


Fig. 5.1. Fuel path through an internal combustion engine

Fuel is filled and stored in a tank of some type. The fuel will interact with materials and impurities in both storage tank and fuel system. The fuel will also be exposed to various ambient conditions such as temperature, moisture and exposure to oxygen in air. Examples of dependence are vapor pressure, connected to high and low temperatures, deposits depending of low temperature solubility and oxidation stability depending on oxygen content and contact. From the storage, fuel is pumped into the fuel system with feed pumps and pressure pumps, depending on the type of fuel and fuel system. This line also includes various number of filtering stages. All these systems will influence and interact with the fuel when facing material interactions which typically could cause deposits and gum formation. Vapor pressure is also important from a pumping and gas phase formation point of view. Filters are inserted in the line to prevent even very small particles to enter the injectors, but the filters are then very sensitive to clogging due to gum formation or phase separation of components.

Finally fuel enters the injectors where the energy provided by the pressure level is converted into velocity to inject the demanded amount of fuel and, in the case of liquid fuels, to provide energy for spray formation and breakup. The injectors contain small passages and nozzles and also include moving parts which are all very sensitive to clogging and material detoriation. The influence and importance of the fuel's physical and chemical properties in addition to its combustion characteristics are as indicated above covering the whole fuel supply chain from source to end use.

Fuel: sources, description, specifications and standards

Fuel standard specifications are applied to commercially available fuels to assure fit-for-purpose with engine performance and engine durability. Certification fuels (fuels used for engine development, calibration and certification) are typically developed to represent commercially available fuels and for "qualifying" engine/vehicle performance and emissions over representative operating scenarios.

Standards typically cover four main areas of interest for the engine manufacturers, the society and the customer:

1. Combustion performance (efficiency, power, drivability) and emissions
2. Engine systems influence
3. Transportability (of fuel)
4. Safety and Environmental impact

Fossil fuel feedstock

Transport fuels are mostly made in refineries starting with petroleum and then blending the products of several refinery processes. Petroleum is first separated into different boiling range fractions by distillation. The lightest phase, Liquid petroleum gas or LPG is made up of dissolved gases which are released when the temperature is increased above ambient and might constitute up to 2% of the crude. Its main component is propane in the range of 75%. The fraction boiling in the range from 20°C to 200°C, is termed 'straight run gasoline' (SRG).

Products in this boiling range are also termed Naptha and can come from different processes in the refinery. Naphtha has to be processed further to improve its auto ignition resistance before it is used as a gasoline component. The fraction in the boiling range of 160°C to 380°C is termed 'middle distillates'. This fraction includes the commercial Diesel fuel. Depending on the source of the crude, between 40% and 60% of the weight of petroleum can be "Residue" with boiling points above 380 C. These heavier fractions have to be converted through further processing into lighter fractions that can be used as fuel components.

A description of refinery and other processes used for making fuel components can be found. Before the various petroleum fractions are used as commercial fuels a number of additives are added to ensure special characteristics of the fuel, apart from the main energy carrying components. These include biofuels as ethanol and other oxygenates such as MTBE (Methyl Tert-Butyl Ether) for gasoline and FAME, HVO (Hydrotrated Vegetable Oil) for diesel. Also bio-based Fischer-Tropsch components and fuels exist but are not commercially available at a significant level. Research is performed on and pilot plants are started and depending on fuel stock and market these components might rise in fraction due to its appealing and tunable characteristics. More details about biofuels can be found.

Alternative present and future fuels/sources

The two main renewable alternative fuels widely used for transportation are: ethanol, and biodiesel (FAME and HVO). Cellulosic and algal renewable fuels will need to emerge with sufficient economic advantage to accelerate alternative fuel usage, and in a manner that better addresses fuel distribution and storage . One way to address the latter is to produce alternative feedstocks that are composed of fully hydrogenated species similar to those found in petroleum derived fuels. Upgrading will require additional hydrogen, and methods for generating hydrogen without increasing carbon emissions are critical needs for the future.

Non-oxygenated fuel feedstocks that are entirely compatible with petroleum have distinct advantages in terms of product refining, distribution, storage, and global fit-for-purpose usage and certification. Examples of this is the HVO from forest and seed base which several fuel producers use as low grade / drop-in in the fossil based diesels. Hydrotreated renewable diesel derived from algae is also under consideration . A variety of oxygenated species have emerged as potential ground transportation fuels/fuel components. In addition to extensive research on alcohols and their blends with petroleum, other types of oxygenated structures such as ethers , carbonate esters valerates, ketones,furans, acetates and oxygenate mixtures of acetonebutanol-ethanol (ABE) have all received interest in the last few years as ground transportation fuel candidates. These are driven by their use as extenders for fossil fuels, in blends with fossil fuels to reduce emissions or increase octane number, and, more recently, for potentially lower processing and refining losses (through bio-refining methods).

Table 5.1 Fuels properties for today's main alternative fuels

	Gasoline/ E10	**Low sulfur Diesel**	**Biodiesel**	**Propane (LPG)**	**Compressed natural gas (CNG)**	**Liquefied natural gas (LNG)**	**Ethanol/ E100**	**Methanol**	**Hydrogen**	**Electricity**
Chemical structure	C_4 to C_{12} and ethanol ≤10%	C_8 to C_{25}	Methyl esters of C_{12} to C_{22} fatty acids	C3H8 majority and C4H10 minority	CH_4 (majority), C_2H_6 and inert gases	CH_4 same as CNG with inert gases <0.5%	CH_3CH_2OH	CH_3OH	H2	N/A
Feedstock	Crude Oil	Crude Oil	Fats and oils from soy beans, waste cooking oil, animal fats, and rapeseed.	A by-product of petroleum refining or natural gas processing	Underground reserves and renewable bioga	Underground reserves and renewable biogas	Corn, grains, agricultural waste, cellulose	Natural gas, coal, woody biomass, waste	Natural gas, methanol, electrolysis of water	Coal, nuclear, natural gas, hydro, wind, solar
Gasoline gallon equivalent (GGE)	97% - 100%	1 gallon of diesel has 113% of the energy of one gallon of gasoline.	B100 and B20 have 103% and 109% of the energy in one gallon of gasoline and 93% and 99% of the energy of one gallon of diesel, respectively.	1 gallon of propane has 73% of the energy of one gallon of gasoline.	5.66 and 6.38 pounds of CNG have 100% of the energy of one gallon of gasoline and diesel respectively.	5.38 and 6.06 pounds of LNG have 100% of the energy of one gallon of gasoline and diesel, respectively.	1 gallon of E10 and E85 have 96.7% and 73-83% of the energy of one gallon of gasoline (variation due to ethanol content in E85).	1 gallon of methanol has 49% of the energy of one gallon of gasoline.	1 kg of H_2 has 100% of the energy of one gallon of gasoline.	33.7 kWh has 100% of the energy of one gallon of gasoline.
Energy content (lower heating value)	112,114–116,090 Btu/gal (31,3-32,4 MJ/l)	128,488 Btu/gal (35,8 MJ7l)	119,550 Btu/gal for B100 (33,4 MJ/l)	84,250 Btu/gal (23,5 MJ/l)	20,160 Btu/lb (46,9 MJ/kg)	21,240 Btu/lb (49,4 MJ/kg)	76,330 Btu/gal for E100 (21,3 MJ/l)	57,250 Btu/ga (16,0 MJ/l)l	51,585 Btu/lb (120 MJ/kg)	3,414 Btu/kWh
Energy content (higher heating value)	120,388–124,340 Btu/gal (33,6-334,7 MJ/l)	138,490 Btu/gal (38,6 MJ/l)	127,960 Btu/gal for B100 (35,7 MJ/l)	91,420 Btu/gal (25,5 MJ/l)	22,453 Btu/lb (52,2 MJ/kg)	23,726 Btu/lb (55,2 MJ/kg)	84,530 Btu/gal for E100 (23,6 MJ/l)	65,200 Btu/gal (18,2 MJ/l)	61,013 Btu/lb (142 MJ/kg)	3,414 Btu/kWh
Physical state	Liquid	Liquid	Liquid	Pressurized Liquid	Compressed Gas	Cryogenic Liquid	Liquid	Liquid	Compressed Gas or Liquid	Electricity
Cetane number	N/A	40-55	48-65	N/A	N/A	N/A	0-54	N/A	N/A	N/A
Pump octane number	84-93	N/A	N/A	105	120+	120+	110	112	130+	N/A
Flash point	-45°F (-43 °C)	165 °F (74 °C)	212 to 338 °F (100-170 °C)	-100 to -150 °F (-73- -101 °C)	-300 °F (-184 °C)	-306 °F (-188 °C)	55 °F (13 °C)	52 °F (11 °C)	N/A	N/A
Autoignition temperature	495 °F (257 °C)	~600 °F (316 °C)	~300 °F (149 °C)	850 to 950 °F (454-510 °C)	1 004 °F (540 °C)	1 004 °F (540 °C)	793 °F (422 °C)	897 °F (481 °C)	1 050 to 1 080 °F (566-582 °C)	N/A

Commercial available fuels standards

In this section the standards for vehicle fuels, both fossil- and bio-based, which are commercially available today are presented. The standards are presented as the specified parameters and the limit values for each parameter. Following to this a short description on the relevance and influence from the parameters and applied test methods are presented.

Diesel fuel specification

The diesel fuel specification is here presented as an example of the properties specified in order to assure the consistency of the fuel to be used in a diesel engine with maintained efficiency, power and mechanical integrity over time. The fuel spec is presented in overview in Table 5.1 Properties described

Table 5.2. Properties described

Property	Unit	Limits	
		Min	Max
Cetane Number	-	51	
Cetane Index	-	46	
Density (@15@°C)	Kg/m^3	820	845
PAH	% (m/m)	-	8
Sulfur	mg/kg	-	10
Manganese content	mg/l	-	6,0/2,0
Flash point	°C	> 55,0	-
Carbon residue (10%distillation)	%(m/m)	-	0,30
Ash content	%(m/m)	-	0,010
Water content	mg/kg	-	200
Total contanimation	mg/kg	-	24
Copper strip corrosion (3h at 50°C)	Rating	Class 1	
FAME	% (v/v)	-	7,0
Oxidation stability	g/m^3 h	- 20	25 -
Lubricity	µm	-	460
Viscosity @40°C	mm^2/s	2,000	5
Distillation	%(v/v) @250°C %(v/v) @350°C 95% recovered °C	- 85 -	<65 - 350

Cetane Index

The cetane index or cetane number is used to describe the self ignition tendency of the fuel. ISO 4264:2007 describes a procedure for the calculation of the cetane index of middle-distillate fuels from petroleum-derived sources. The calculated value is termed the "cetane index by four-variable equation" which throughout the remaining text of ISO 4264:2007, is denoted "cetane index".

Polycyclic Aromatic Hydrocarbons

The polycyclic aromatic hydrocarbons, sometimes referred to as PAH have been found to be precursors and by this contribute to particulate formation. Based on this and the ambition to reduce particulates, as one of the regulated emissions from engines, the PAH content was regulated in the EU fuel specifications in the 1990's.

Sulfur content

Sulfur naturally occurs in crude oil. If the sulfur is not removed during the refining process it will remain in the vehicle fuel. Cross-contamination can also occur in the fuel distribution system. In traditional diesel combustion system the sulfur content is of no or little concern, it even helps lubrication of fuel system. In modern diesel engines which includes various emission reduction systems, such as EGR or SCR catalyst, high sulfur content might cause problem with corrosion. In present European standard the sulfur content is limited to <10ppm which poses no problems.

ISO 20846:2011 specifies an ultraviolet fluorescence test method for the determination of the sulfur content of motor gasolines, including those containing up to 2,7 %(m/m) oxygen, and of diesel fuels, including those containing up to 10 % (V/V) fatty acid methylester (FAME), having sulfur contents in the range 3 mg/kg to 500 mg/kg.

Metallic elements

The presence of metallic and metalloid species in automotive fuels is undesirable, except in the form of additives in order to improve specific characteristics of the fuel. Metallic or metalloid elements may derive from the raw product, such as nickel and vanadium in petroleum-based fuel or phosphorus in biodiesel, or they may be introduced during production and storage, such as copper, iron, nickel and zinc in case of petroleum-based fuel and alcohol or sodium and potassium in the case of biodiesel. The most famous additive to (gasoline) fuel is undoubtedly lead, the use of which has been banned or drastically reduced now in many countries of the world. The problems related to the trace element content may be economic, such as fuel degradation and poisoning of automotive catalysts, and/or environmental, such as the emission of metal compounds to the atmosphere.

Flash point

The flash point of a volatile material is the lowest temperature at which it can vaporize to form an ignitable mixture in air. Measuring a flash point requires an ignition source. At the flash point, the vapor may cease to burn when the source of ignition is removed. The flash point is not to be confused with the auto ignition temperature, which does not require an ignition source, or the fire point, the temperature at which the vapor continues to burn after being ignited. Neither the flash point nor the fire point is dependent on the temperature of the ignition source, which is much higher. The flash point is often used as a descriptive characteristic of liquid fuel, and it is also used to help characterize the fire hazards of liquids. "Flash point" refers to both flammable liquids and combustible liquids. There are various standards for defining each term.

Liquids with a flash point less than 60.5 or 37.8 °C (140.9 or 100.0 °F) — depending upon the standard being applied — are considered flammable, while liquids with a flash point higher than 60.5 or 37.8 °C are considered combustible.

Carbon residue

The carbon residue of a fuel is the tendency of carbon deposits to form under high temperature in an inert atmosphere. It is known that the correlation between carbon residue and diesel engine performance is poor. However, in the absence of any other parameter, this property is included in fuel specifications, indicating the carbonaceous deposit-forming tendencies of the fuel. Many factors can affect the combustion process in diesel engines, including engine loading, engine tuning and the ignition qualities of the fuel which all have an effect on the deposit tendencies of a particular fuel.The carbon residue value of a fuel depends on the refinery processes employed in its manufacture. For straight run fuels, the value is typically 10 - 12% m/m, while for fuels from secondary refining processing the value depends on the severity of the processes applied. In some areas it can be as high as 20% m/m.

Ash content

Diesel fuel can cause abrasive wear of the fuel system and the piston rings if it is contaminated with abrasive inorganic particles. Fuel injectors and fuel injection pumps are particularly susceptible to wear because the high liquid pressures they generate require extremely close tolerances between parts moving relative to one another.

Water content

Water is the most common form of contamination in diesel fuel. There will always be some measure of water in any diesel fuel; however, the total water content is normally less than 200 ppm and— most of the time—measures less than 100 ppm. At around 150 ppm, a slight haze will start to develop in the fuel. However, with adequate filtration and tank maintenance, the occasional presence of slightly hazy fuel should not cause operational problems. When the dissolved water content in fuel repeatedly measures between 200 ppm and 500 ppm, the fuel should be observed and monitored closely. The effects of high or continuous water contamination can lead to:

- Fuel degradation
- Corrosion of certain fuel-wetted components
- Premature plugging of primary and/or secondary fuel filter units
- Fouling of injector nozzles
- Sticking or seizure of critical components within the fuel injector units
- Microbial growth creating sludge and causing additional corrosion and filter plugging

Copper strip corrosion test

Crude petroleum contains sulfur compounds, most of which are removed during refining. However, of the sulfur compounds remaining in the petroleum product, some can have a corroding action on various metals and this corrosivity is not necessarily related directly to the total sulfur content. The effect can vary according to the chemical types of sulfur compounds present. The copper strip corrosion test is designed to assess the relative degree of corrosivity of a petroleum product.

Oxidation stability

The standards describe procedures for the measurement of inherent stability under accelerated oxidizing conditions. The method provides a basis for the estimation of the storage stability, under the conditions of this test, of middle-distillate fuels with an initial boiling point above approximately 175 °C and a 90% (V/V) recovery point below 370 °C. Is not applicable to fuels containing residual components, or any significant component from a non-petroleum source.

CFPP Cold filter plugging point

CFPP is the lowest temperature, expressed in degrees Celsius (°C), at which a given volume fuel still passes through a standardized filtration device in a specified time when cooled under certain conditions. CFPP gives an estimate for the lowest temperature that a fuel will give trouble free flow in certain fuel systems. This is important as in cold temperate countries, a high cold filter plugging point will clog up vehicle engines more easily.

GASOLINE FUEL SPECIFICATION

The gasoline fuel specification EN228 is here presented as an example of the properties specified in order to assure the consistency of the fuel to be used in a diesel engine with maintained efficiency, power, drivability and mechanical integrity over time. The fuel spec is presented in overview in Table 5.3. Some short comments and clarification on the use and implication for the various parameters are enclosed, but for a more thorough description reference is made to ”Worldwide_Fuel_Charter_5ed_2013” .

The European Standard EN 228 Automotive fuels - Unleaded petrol - Requirements and test methods specifies requirements and test methods for marketed and delivered unleaded petrol. It is applicable to unleaded petrol for use in petrol engine vehicles designed to run on unleaded petrol. This European Standard specifies two types of unleaded petrol: one type with a maximum oxygen content of 3.7 % (m/m) and a maximum ethanol content of 10.0 % (V/V) and one type intended for older vehicles that are not warranted to use unleaded petrol with a high biofuel content, with a maximum oxygen content of 2.7 % (m/m) and a maximum ethanol content of 5.0 % (V/V)

Table 5.3. Properties described in EN228, type 1 maximum oxygen content of 3.7 % (m/m) and a maximum ethanol content of 10.0 % (V/V) [1]

Property	Unit	Limits	
		Min	Max
RON		95,0	-
MON		85,0	-
Lead	mg/l	-	5,0
Density (@15@°C)	kg/m3	720,0	775,0
Sulfur	mg/kg	-	10,0
Manganese content	mg/l	-	6,0/2,0
Oxidation stability	Minutes	360	-
Existent gum content	Mg/100ml	-	5
Copper strip corrosion	Rating	Class 1	
Apperance		Clear and bright	
Hydrocarbon type content	Olefins %(v/v)	-	18,0
	Aromatics %(v/v)	-	35,0
Benzene content	%(v/v)	-	1,00
Oxygen content	% (m/m)	-	3,7
Oxygenates content	%(v/v)		
	Methanol	-	3,0
	Ethanol	-	10,0
	Iso-propyl alcohol	-	12,0
	Iso-butyl alcohol	-	15,0
	Tert-butyl alcohol	-	15,0
	Ehters (C>5)	-	22,0
	Other oxygenates	-	15,0
Vapour pressure (VP)	kPa varying at 6 classes here indicated max span	45,0	100,0

Octane number

Octane number is a measure of a gasoline's ability to resist auto-ignition; auto-ignition can cause engine knock, which can severely damage engines. Two laboratory test methods are used to measure octane: one determines the Research Octane Number (RON) and the other determines the Motor Octane Number (MON). RON correlates best with low speed, mild-knocking conditions and MON correlates with high-temperature knocking conditions and with part-throttle operation. RON values are typically higher than MON, and the difference between these values is the sensitivity, which should not exceed 10. In North America, (RON + MON)/2 is typically used to specify the octane rating, while many other markets typically specify RON.

Sulfur

Sulfur naturally occurs in crude oil. If the sulfur is not removed during the refining process it will remain in the vehicle fuel. Cross-contamination also can occur in the fuel distribution system. Sulfur has a significant impact on vehicle emissions by reducing the efficiency of catalysts. Sulfur also adversely affects heated exhaust gas oxygen sensors. Reductions in sulfur will provide immediate reductions of emissions from all catalyst-equipped vehicles on the road.

Lead

Tetra-ethyl lead has been used historically as an inexpensive octane enhancer for gasoline, but it will poison vehicle emission control systems. The lead binds to active sites within the catalyst and oxygen sensor, greatly reducing their effectiveness. The tolerance to lead contamination has steadily declined as catalyst efficiencies and sensors have improved, so even a slight amount of lead in the fuel will irreversibly disable the emission control system. As a result, vehicle hydrocarbon and NOx emissions will increase even when the vehicle returns to using lead-free gasoline. Unleaded gasoline must be available wherever catalyst-equipped vehicles refuel; increasingly, this means every market around the world. A global lead-free market also is essential for public health, given lead's well-known adverse health effects. These concerns have led most countries to require lead-free gasoline; the few that have not yet done so should eliminate the use of this fuel additive as soon as possible.

Manganese (MMT)

Manganese is a key component of methylcyclopentadienyl manganese tricarbonyl (MMT), which also is marketed as an octane-enhancing fuel additive for gasoline. Like lead, manganese in the fuel will irreversibly reduce the efficiency of exhaust emission control systems. Studies have shown that most of the MMT-derived manganese in the fuel remains within the engine, catalyst and exhaust system. The oxidized manganese coats exposed surfaces throughout the system, including spark plugs, oxygen sensors and inside the cells of the catalytic converter. These effects result in higher emissions and lower fuel economy. The effect is irreversible and cumulative.

Oxygenates

Oxygenated organic compounds, such as MtBE and ethanol, often are added to gasoline to increase octane or extend gasoline supplies. Oxygenating the fuel also may affect vehicle emissions (tailpipe, evaporative or both), performance and/or durability. Adding ethanol also affects the distillation of the gasoline blend

Olefines

Olefins are unsaturated hydrocarbons and, in many cases, are also good octane components of gasoline. However, olefins in gasoline can lead to deposit formation and increased emissions of reactive (i.e., ozone-forming) hydrocarbons and toxic compounds. More details on fermentation produced olefins can be found.

Aromatics

Aromatics are fuel molecules that contain at least one benzene ring. In general, aromatics are good octane components of gasoline and high-energy density fuel molecules. Fuel aromatic content can increase engine deposits and increase tailpipe emissions, including CO2.

Volatility

Proper volatility of gasoline is critical to the operation of spark ignition engines with respect to both performance and emissions. Volatility may be characterised by various measurements, the most common of which are vapour pressure, distillation and the vapour/liquid ratio. The presence of ethanol or other oxygenates may affect these properties and, as a result, performance, driveability and emissions as well.

Deposit control additives

Combustion of even good quality gasoline can lead to deposit formation. Such deposits will increase engine-out emissions and affect vehicle performance. High quality fuel contains sufficient deposit control additives to reduce deposit formation to acceptable rates.

LIQUEFIED PETROLEUM GAS, LPG SPECIFICATION (EN 590)

Liquefied Petroleum Gas, LPG, consists of the gaseous components of the crude oil feed mainly propane, butane and heptane. Propylene, butylenes and various other hydrocarbons are usually also present in small concentrations. HD-5 limits the amount of propylene that can be placed in LPG to 5%, and is utilized as an autogas specification. Composition, with larger fraction of longer hydro carbons may vary depending on feed source and region where fuels are distributed. This is reflected in the wide range temperature stipulated for vapor pressure for different grades. A powerful odorant, ethanethiol, is added so that leaks can be detected easily.

Table 5.4. Properties described in EN589 [2]

Property	Unit	Limits	
		Min	Max
MON		89,0	-
Total dienes content	Mole %	-	0,5
Hydrogen suphide		Negative	
Total sulfur content	mg/kg	-	50
Copper strip corrosion	rating(1 h @ 40°C)	Class 1	
Evaporation residue	mg/kg	-	60
Vapour pressure	kPa(g)	-	1550
Vapour pressure	Min 150kPa(g) @ temp Grade A Grade B Grade C Grade D Grade E		 -10 -5 0 +10 +20
Water content		Pass	
Odour		Unpleasant and distinct at 20% LFL	

Biofuels demands, specification and guidelines

As biofuels are of high interest for reasons such as climate change, security of supply and economy the demand for the different fuels is steadily increasing from both governmental and users as passenger and heavy duty vehicles. The switch to bio-based fuels will not be done over a night since it takes time to build up production capacity, which in turn faces challenges such as limited raw material supply, production processes and production sites, read more in. This in reality means that the sources of biomass and the types of fuels will vary depending on legislative, economical, technological and regional variations. Also the fleet of vehicles and engines can't and will not be replaced in one instance but is also a matter of gradual replacement. Fuels which are to be introduced and used at a rate which is to have an impact on the fundamental reasons for introducing biofuels will have to meet the same requirements set for fossil fuels. Also the alternative bio-based fuels will have to have a potential to be blended into existing fuels in order to meet fuel demands, at least in a short term perspective.

For diesel applications Fatty Acid Methyl Esters (biodiesel/FAME) is one type of fuels which is viable and is in spread use today. Other promising renewable fuels for diesel applications comprise Hydrated Vegetable Oil (HVO), Biomass To Liquid (BTL based on Fischer Tropsch synthesis) and Fermentation based fuels like Farnesene.

Spark ignition fuels based on renewable sources, include alcohols (methanol, ethanol, propanol, butanol), derivates of alcohols and different ethers. Many of the spark ignition type fuels are also in various ways used or tested to be used as blend/drop-in fuels in diesel fuel depending on the need for large amounts of fuels in the commercial vehicle applications which tends to use diesel engines.

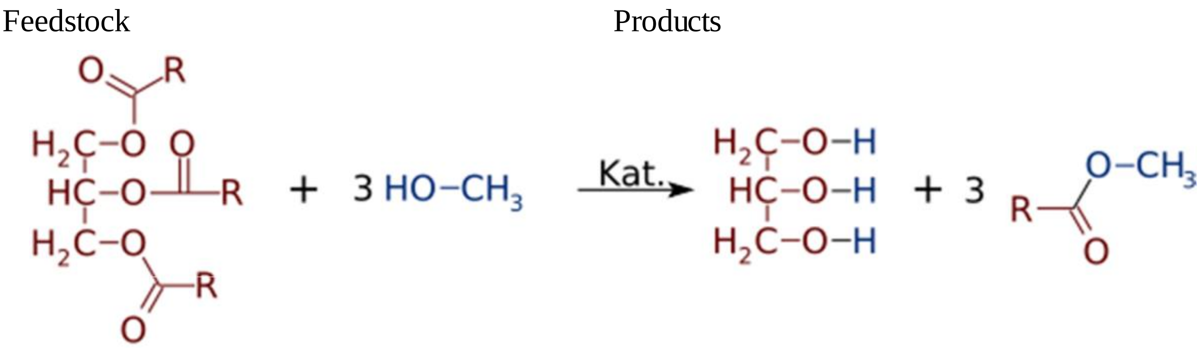
As mentioned previously the fuel standards for fossil based fuels have evolved over a century and thus contains a large number of, sometimes costly, experiences on how to handle and specify the fuels to assure safe storage and operation. For every suggested or introduced new renewable fuel these standards and the findings behind them has to be taken into consideration.

In the coming sections a number of introduced fuels are presented.

Fatty Acid Methyl Ester (FAME) / Biodiesel

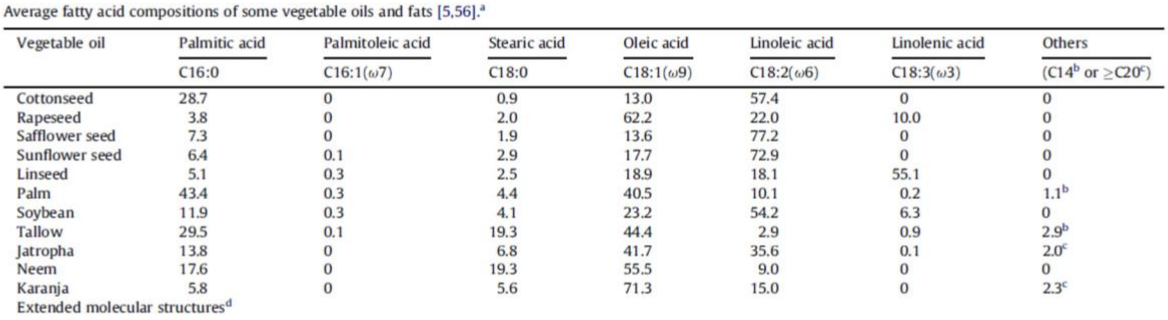
Biodiesel is today widely spread and used as fuel in various ways, starting as a low grade (7%) blend in the standard diesel over high grade blends of 10%, 20% and 30% up to usage as 100% neat fuel.

FAMEs are typically produced by an alkali-catalyzed reaction between fats and methanol in the presence of a base such as sodium hydroxide or sodium methoxide, see Figure 2.



$$\mathrm{Triglyceride} + 3\,HO{-}CH_3 \xrightarrow{Kat.} \mathrm{Glycerol} + 3\,R{-}COOCH_3$$

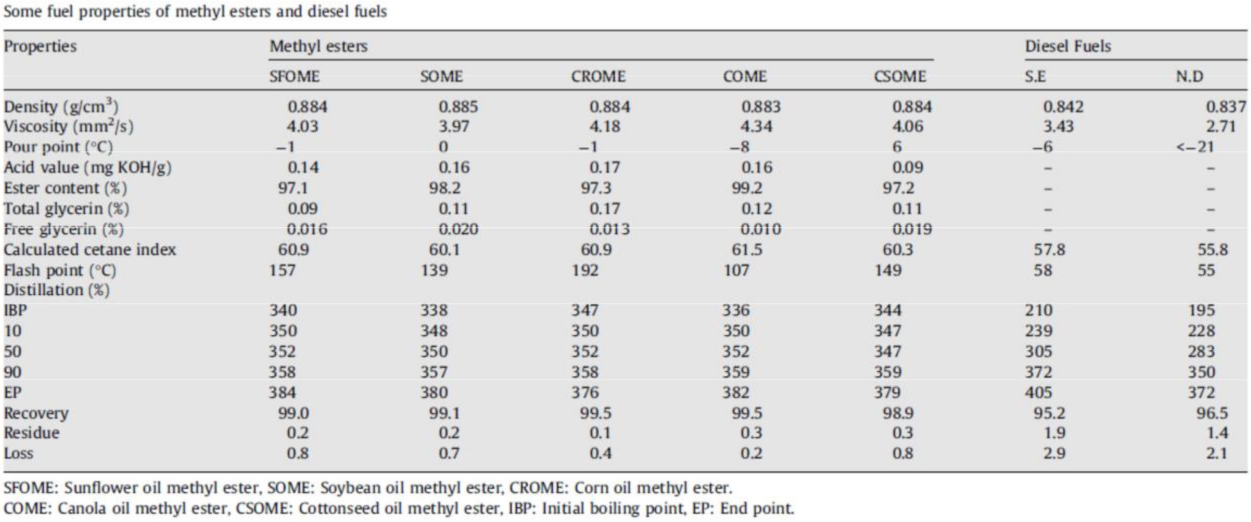
Figure 5.4 Transesterification FAME [6]



Average fatty acid compositions of some vegetable oils and fats [5,56].[a]

Vegetable oil	Palmitic acid	Palmitoleic acid	Stearic acid	Oleic acid	Linoleic acid	Linolenic acid	Others
	C16:0	C16:1(ω7)	C18:0	C18:1(ω9)	C18:2(ω6)	C18:3(ω3)	(C14[b] or $\geq$C20[c])
Cottonseed	28.7	0	0.9	13.0	57.4	0	0
Rapeseed	3.8	0	2.0	62.2	22.0	10.0	0
Safflower seed	7.3	0	1.9	13.6	77.2	0	0
Sunflower seed	6.4	0.1	2.9	17.7	72.9	0	0
Linseed	5.1	0.3	2.5	18.9	18.1	55.1	0
Palm	43.4	0.3	4.4	40.5	10.1	0.2	1.1[b]
Soybean	11.9	0.3	4.1	23.2	54.2	6.3	0
Tallow	29.5	0.1	19.3	44.4	2.9	0.9	2.9[b]
Jatropha	13.8	0	6.8	41.7	35.6	0.1	2.0[c]
Neem	17.6	0	19.3	55.5	9.0	0	0
Karanja	5.8	0	5.6	71.3	15.0	0	2.3[c]
Extended molecular structures[d]							

Figure 5.5. Fatty acid compositions from various oils



Some fuel properties of methyl esters and diesel fuels

Properties	Methyl esters					Diesel Fuels	
	SFOME	SOME	CROME	COME	CSOME	S.E	N.D
Density (g/cm^3)	0.884	0.885	0.884	0.883	0.884	0.842	0.837
Viscosity (mm^2/s)	4.03	3.97	4.18	4.34	4.06	3.43	2.71
Pour point (°C)	−1	0	−1	−8	6	−6	<−21
Acid value (mg KOH/g)	0.14	0.16	0.17	0.16	0.09	–	–
Ester content (%)	97.1	98.2	97.3	99.2	97.2	–	–
Total glycerin (%)	0.09	0.11	0.17	0.12	0.11	–	–
Free glycerin (%)	0.016	0.020	0.013	0.010	0.019	–	–
Calculated cetane index	60.9	60.1	60.9	61.5	60.3	57.8	55.8
Flash point (°C)	157	139	192	107	149	58	55
Distillation (%)							
IBP	340	338	347	336	344	210	195
10	350	348	350	350	347	239	228
50	352	350	352	352	347	305	283
90	358	357	358	359	359	372	350
EP	384	380	376	382	379	405	372
Recovery	99.0	99.1	99.5	99.5	98.9	95.2	96.5
Residue	0.2	0.2	0.1	0.3	0.3	1.9	1.4
Loss	0.8	0.7	0.4	0.2	0.8	2.9	2.1

SFOME: Sunflower oil methyl ester, SOME: Soybean oil methyl ester, CROME: Corn oil methyl ester.
COME: Canola oil methyl ester, CSOME: Cottonseed oil methyl ester, IBP: Initial boiling point, EP: End point.

Figure 5.6. Properties of biodiesels from various feedstocks

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