

Internal Combustion Engines – ME422 Yeditepe Üniversitesi

IC-Engine Fuels

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Internal Combustion Engines

IC Engine Fuels

- Introduction
- Classification of fuels
- Manufacture of engine fuels
- Fuel specifications in general
- Specifications of SI-engine and CI-engine fuels

IC Engine Fuels

In IC engines, the **chemical energy** contained in the fuel is converted into **mechanical power** by burning (oxidizing) the fuel inside the combustion chamber of the engine.

As a result of the chemical reactions which occur inside the cylinder, **heat is released**. The fuel-air mixture (the working fluid before combustion) must stay in the cylinder for a sufficient time so that the chemical reactions can be completed.

Fuels suitable for fast chemical reaction have to be used in IC engines.

- Hydrocarbons in liquid form
- Alcohols (methanol, ethanol)
- LPG (propane and butane)
- Natural gas (methane)
- Hydrogen

Classification of Engine Fuels

Liquid hydrocarbons $C_n H_m$

Fuels are mainly mixtures of hydrocarbons, with bonds between carbon atoms and between hydrogen and carbon atoms.

During combustion these bonds are broken and new bonds are formed with oxygen atoms, accompanied by the release of chemical energy. Principal products are carbon dioxide and water vapour.

Fuels also contain small amounts of O_2 , N_2 , S , H_2O

Alkanes

Alkanes or Paraffins can in general be represented by $C_n H_{2n+2}$

all the carbon bonds are single bonds – they are “saturated”
high number of H atoms, high heat content and low density
(620 – 770 kg/m³)

The carbon atoms can be arranged as, a straight chain or as branched chain compounds.

Straight chain group (normal paraffins)
shorter the chain, stronger the bond
not suitable for SI engines – high tendency for autoignition
according to the value of “n” in the formula, they are in gaseous
(1 to 4), liquid (5 to 15) or solid (>16) state.

Alkanes

Branched chain compounds (isoparaffins)

when four or more C atoms are in a chain molecule it is possible to form
isomers – they have the same chemical formula but different
structures, which often leads to very different chemical properties.

example : iso-octane $C_8 H_{18}$

2. 2 .4 trimethyl pentane

Naphthenes

Also called **cycloparaffins** $C_n H_{2n}$

saturated hydrocarbons which are arranged in a circle
have stable structure and low tendency to autoignite compared to
alkanes (normal paraffins)

can be used both in SI-engines and CI-engines

low heat content and high density (740 – 790 kg / m³)

Alkenes

Also called **olefins**

mono-olefins $C_n H_{2n}$ or **dio-olefins** $C_n H_{2n-2}$

have the same C-to-H ratio and the same general formula as
naphthenes, their behavior and characteristics are entirely different

they are straight or branch chain compounds with one or more
double bond. The position of the double bond is indicated by the
number of first C atom to which it is attached, ie,

CH₂=CH.CH₂.CH₂.CH₃ called pentene-1

CH₃.CH=CH₃ called butene-2

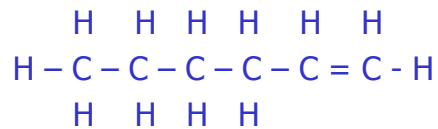
olefinic compounds are easily oxidized, have poor oxidation stability

can be used in SI-engines, obtained by cracking of large molecules

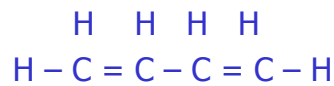
low heat content and density in the range 620 – 820 kg / m³

Alkenes

Hexen (mono-olefin)

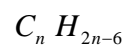


Butadien (dio-olefin)



Aromatics

Aromatic hydrocarbons are so called because of their "aromatic" odor



they are based on a six-membered ring having three conjugated double bonds

aromatic rings can be fused together to give polynuclear aromatics, PAN, also called polycyclic aromatic hydrocarbons, PAH

simplest member is benzene

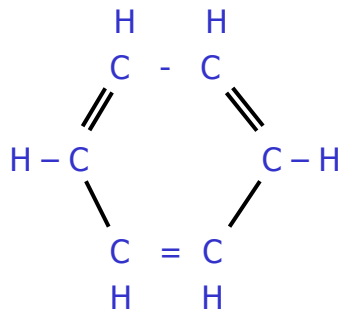


can be used in SI-engines, to increase the resistance to knock
not suitable for CI-engines due to low cetene number

low heat content and high density in the range 800 – 850 kg / m³

Aromatics

Benzen C₆ H₆



Alcohols (monohydric alcohols)

these include **methanol** (methyl alcohol), **ethanol** (ethyl alcohol), propanol (propyl alcohol), butanol (butyl alcohol) **as compounds**

the OH group which replaces one of the H atoms in an alkane, gives these compounds their characteristic properties.

specific heating value is lower than gasoline (42 – 43 MJ/kg)

methanol (19.7 MJ/kg) and ethanol (26.8 MJ/kg)

for air-fuel mixture s.h.v. is comparable with gasoline (MJ/kg-mixture at stoichiometric mixtures)

other alcohol groups such as dihydric and trihydric alcohols are not used as a fuel in IC engines

Alcohols

Methanol CH_3OH

can be obtained from natural gas – has near and long-term potential
has high octane quality (130 RON, 95 MON)
can be used in low-concentration (5-15 %) in gasoline to increase octane number of the mixture

Problems;

poor solubility in gasoline, toxicity, low energy content (about half of gasoline), high latent heat of vaporization and oxygen content contribute to poor driveability, incompatibility with some metals

Ethanol C_2H_5OH

produced from biomass
has high octane number – can be used in low-concentrations in gasoline

Gaseous Fuels

due to storage and transportation problems they are not widely used
reduce volumetric efficiency and power output of engine (5 – 10 %)
have low tendency to knock and low emissions

LPG (liquefied petroleum gas)

consists of propane and butane
provides good mixture with air – cleaner combustion
has excellent cold weather performance
low sulphur content
high octane number (propane 111 RON and 100 MON)
lower density and lower heat content of LPG versus gasoline (23.5 MJ/liter for propane and 32 MJ/liter for gasoline) results a loss in fuel economy – but better combustion efficiency can reduce this loss.

Manufacture of Engine Fuels

crude oil is the liquid part of the naturally occurring organic material composed mostly of HCs that is trapped geologically in underground reservoirs – it is not uniform and varies in density, chemical composition, boiling range etc. for different fields.

Four different crude oils are shown in Table for different boiling ranges :

Table - Main products from crude oil by distillation (%)

Crude type	Arabian light	Nigerian	Brent	Maya
LPG	0.7	0.6	2.1	1.0
Naphtha	17.8	12.9	17.8	11.7
Gas oil/Kerosene	33.1	47.2	35.5	23.1
Residue	48.4	39.3	44.6	64.2

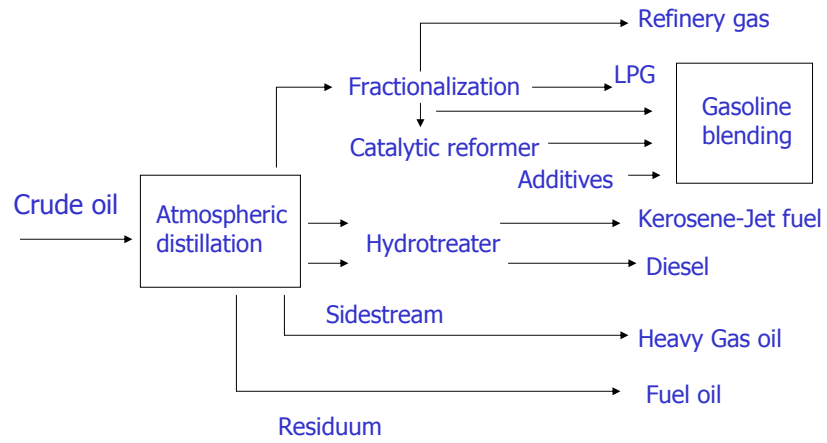
Manufacture of Engine Fuels

naphtha represents the percentage of HC boiling to gasoline range
gas oil-kerosene represents the percentage boiling to diesel fuel range, including jet fuel and kerosene

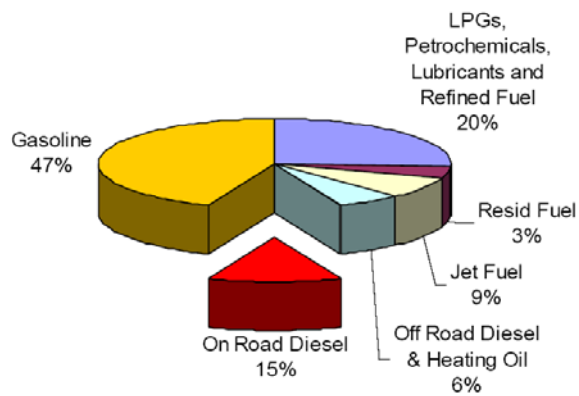
Refineries consist basically of distillation units with processes for upgrading the octane quality of naphtha and for removing sulfur compounds – these are called **hydroskimming refineries**

Refineries today have conversion processes – convert heavier streams to lighter streams by **cracking**

Refinery Process



Typical Refinery Production



Distillation

This is the initial process used in all refineries – aims to separate the crude oil into different boiling range fractions, each of which may be a product in its own right, a blend component or feed for further processing step

Crude oil contains many thousands of different HCs, each has its own boiling point – **lightest** are gases at ambient T but can remain dissolved in heavier liquid HCs unless T is raised, **heaviest** are solids at ambient T but stay in solution unless T is lowered.

Gasoline distillation temperature is	35 – 200 °C
Jet fuel	35 - 150
Diesel fuel	175 – 370
Heavy fuels, oil	370 – 550

Generally distillation of crude oil produces 30% gasoline, 20-40 % diesel fuel, 20 % heavy fuels, 10-20 % heavy oils.

Cracking Process

There are two types of cracking process for engine fuel production :
thermal cracking and **catalytic cracking**

Visbreaking and **coking** are also cracking procedures for fuel oil etc.

Thermal cracking take place through the creation of HC free radicals by C-to-C bond scission

The feed is heated to around 500 - 600 °C and 70 - 100 bars and passed into a soaking chamber where cracking takes place. The cracked products are fractionated. The product is relatively unstable and requires the use of antioxidants and other treatments to prevent gum formation in use. It has relatively poor MON.

Catalytic Cracking

It is the most important and widely used process for converting heavy refinery streams to lighter products – to increase the ratio of light to heavy products from crude oil.

Compared to thermal cracking, it has higher yields, improved quality product for gasoline (not for diesel fuel) and superior economics.

A fluidized bed of catalyst is used – feed is introduced into it. Catalyst flows from one vessel to another through a pipe (between reactor and regenerator). Cracked oil vapour passes to fractionating towers where smaller molecules are separated from heavier products (gas, catalytic naphthas, cycle oils and residue).

Aluminium silicate known as zeolite is used as a catalyst – has high activity and suppress the formation of light olefins.

Hydrocracking and steam cracking mechanisms are also used.

Other mechanisms

Alkylation is a process for producing a high-octane gasoline component (alkylate) by combining light olefins with isobutane in the presence of a strongly acidic catalyst (sulfuric or hydrofluoric acid).

Isomerization is a process for converting straight chain paraffins to branch chain – used to provide isobutane feed for the alkylation process or to convert relatively low-octane quality of straight paraffins to more valuable branch chain molecules.

eg. n-pentane with RON 62 can be converted to isopentane with RON 92

Process involves contacting HCs with a catalyst (platinum on a zeolite base) and separating any unchanged straight paraffins for recycle through the unit. The product is clean burning and has better RON quality.

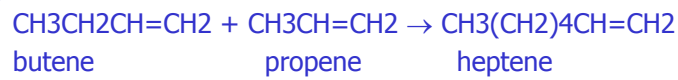
Other mechanisms

Polymerization is a process where light olefins such as propene and butenes are reacted together to give heavier olefins which have good octane quality and low vapour pressure in gasoline.

Most commonly used catalyst is phosphoric acid on keiselguhr.

The product is almost 100 % olefinic and has relatively poor MON compared with RON.

eg.



Fuel Specifications

Relative density (specific gravity)

Fuel composition

Specific heating value

Flash point

Viscosity

Surface tension

Freezing point

Relative Density

Relative density (specific gravity) is related to the measurement of the ratio of the weight of a given volume of fuel to the weight of the same volume of water, both at 20 °C and 101.325 kPa

American Petroleum Institute, also defines degrees API as,

$$\text{Specific Gravity} = \frac{141.5}{131.5 + API}$$

For gasoline, the relative density is around 0.72 to 0.78 - which is equivalent to an API range of 65 to 50

$$\rho = 700 - 800 \text{ [kg/m}^3\text{]}$$

for unleaded gasoline this value is higher due to the aromatics

For diesel fuel, $\rho = 830 - 950 \text{ [kg/m}^3\text{]}$

Fuel Composition

C and H : carbon content of aromatics is around 89 %, and of paraffins and naphthenes is around 86 %

benzene - max allowable concentration is specified because it is highly toxic material, the level is 5 %

sulphur content – HC fuels contain free sulphur, hydrogen sulphide and other sulphur compounds which are objectionable
it is a corrosive element that can corrode fuel lines, carburettor and injection pump. It will unite with oxygen to form sulphur dioxide, which in presence of water at low T, forms sulphurous acid.

It has low ignition T, promote knock in SI engines.
limited to approx 250 ppm

Fuel Composition

Gum deposits – gasoline with unsaturated HCs forms gum in the engine, paraffin, naphthene and aromatic HCs also form some gum – it causes operating difficulties, sticking valves and piston rings, deposits in the manifold etc.

Water - both dissolved and free water can be present in gasoline, free water is undesirable because it can freeze and cause problems. Dissolved water is usually unavoidable during manufacture.

Lead - for leaded and unleaded gasoline max lead content is specified, lead causes pollution and destroys catalytic converters in the exhaust system.

Manganese - used for antiknock in gasoline (MMT), max amount is specified, 0.00025 to 0.03 gMn/L

Fuel Composition

Oxygenates - oxygenated compounds such as alcohols are used in gasoline to improve octane rating.

In USA gasohol (10% ethanol contains 3.5% oxygen), TBA and methanol up to 3.5% oxygenmethanol up to 5% volume, MTBE up to 15% are used.

In EC monoalcohols and ethers with atm boiling points lower than the final atm boiling point of gasoline in the standards can be used. Higher concentrations require modifications on the vehicles - carburetor or fuel inj system must be modified to compensate for the oxygen content of the fuel.
Blends with 15% methanol can be used.

Specific Heating Value

Specific heating value, H_u is a measure of the energy content of the fuel per unit mass (kJ/kg or kcal/kg)

gaseous fuels sp heating value is given in terms of energy content per unit volume (kJ/liter or kJ/m³, kcal/m³)

in IC engines **lower heating value** is given as the combustion products contain water in vapour form.

For gasoline and diesel fuel $H_u = 42000 - 44000$ [kJ/kg]

$H_u = 10200 - 10500$ [kcal/kg]

heating value of the combustible air-fuel mixture is a decisive factor for engine performance.

Flash Point

Flash point is the lowest temperature of a sample at which the fuel vapour starts to ignite when in contact with a flame (ignition source).

Marcusson method – fuel container is slowly heated, while the fuel vapour is in contact with an open flame – T is measured

For gasoline it is 25 °C, diesel fuel 35 °C and heavy diesel 65 °C

Viscosity

Viscosity is an important parameter for CI engines, also influences fuel metering orifices since Re is an inverse function of fuel viscosity lower the viscosity, smaller the diameter of the droplets in the spray. Below certain limits, low viscosity increases the leaks in the fuel system. It is a strong function of T – must be given at certain T values

at 50 °C, 1.5 – 5.0 Engler

0.5 to 0.6 centistokes

Freezing Point

Freezing point

the precipitation of paraffin crystals in winter can lead to clogged filters. It can be prevented by either removing paraffins from the fuel or adding flow improvers (additives).

Antifreezing properties are determined by its filterability.

For gasoline freezing point is -65 °C and for diesel fuel -10 °C

Surface Tension

Surface tension is a parameter which effects the formation of fuel droplets in sprays

increasing the surface tension will reduce mass flow and air-fuel ratio in gasoline engines

lower the value, smaller the droplet diameter

diesel fuel	0.023 – 0.032 N/m
gasoline	0.019 – 0.023 N/m

Fuel Specifications for Gasoline

Volatility

Antiknock quality

Gasoline Volatility

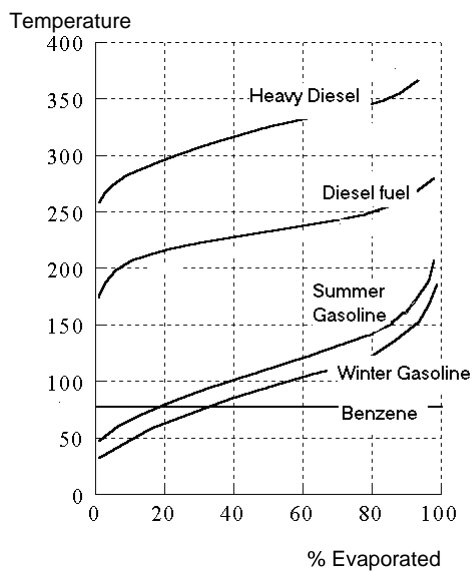
Benzene for example has vapor pressure of 0.022 MPa at 38 °C
in a closed container of 38 °C, benzene evaporates until the partial p has a value of 0.022 MPa, If T is raised to 80.5 °C, then saturation p will be 0.1 MPa and will be constant during the boiling

For gasoline it is not possible to indicate a single value of evaporation T or vapor pressure.

Gasoline contains large number of compounds - up to about 400

It has a smooth distillation curve - with good fractionation efficiency

Gasoline Distillation Curve



Low fractionation efficiency effects engine performance at different operating conditions :

if distillation curve is displaced downward, gasoline becomes more volatile - poor hot start, vapor lock, high evaporative losses

Gasoline Distillation Curve

Gasoline having boiling point up to 70 °C controls ease of starting and hot weather problems such as vapor lock

Mid-range controls the driving in cold weathers, particularly at warm up period of engine. It also influences the ice forming in carburetor.

Back end of the curve contains all the heavier, high boiling point compounds and these have high heat content - they are important in improving fuel economy for fully warmed up engine.

Some of the heavier compounds may pass into the crankcase and dilute the crankcase oil. They are not readily combusted as the lighter compounds - cause combustion chamber deposits.

Gasoline Distillation Curve

%10 evaporation point should be at low T for start up at cold temperatures - at hot weathers this may cause problems - vapor lock.

50% evaporation should be slightly above 100 °C at summer and slightly below 100 °C at winter. For warmed up engine conditions this point is not important.

90% evaporation must not be high - produces fuel film on intake manifold walls and dilutes lubricating oil. Back end of the curve must not exceed 215 °C.

Gasoline volatility should be arranged according to weather conditions - particularly ambient T. Altitude has some minor effect due to pressure changes.

It is also effected by the characteristics of the vehicle itself (drivability, fuel system design etc).

Cold Starting

For SI engines to start, A/F ratio must be within the ignitable range, ie in general must be between 7:1 to 20:1 by weight.

When the engine is cold, it is difficult to ignite lean mixtures, because fuel may not vaporize sufficiently - under these conditions the mixture is richened to bring it to ignitable range.

This is done by inc the injection time or by the use of a **choke** with carburetted engines.

Measurement of Gasoline Volatility

Tests usually define Reid Vapor Pressure - ASTM Distillation test and Vapor/Liquid ratio.

Reid vapor pressure - obtained at air-to-liquid ratio of 4:1 and temperature 37.8 °C.

Fuel is filled into a metal chamber which is connected to an air chamber and that is connected to a pressure gauge. The apparatus is immersed in water bath at 37.8 °C and is shaken until constant p is obtained - Reid VP

For gasoline allowable RVP is 0.7 bar in summer and 0.9 bar in winter (at 37.8 °C)

ASTM Distillation procedure - distillation rate is controlled by the heat input - distillation curve is plotted (temperature vs % evaporated).

Antiknock Quality of Gasoline

Knock occurs when the unburnt gases ahead of flame front (the end gases) spontaneously ignite causing a sudden rise in pressure accompanied by a characteristic pinging sound - this results in a loss of power and can lead to damage the engine.

Combustion chamber shape, spark plug location, ignition timing, end gas temperatures, in cylinder gas motion, air-fuel ratio of the mixture, fuel specifications etc effects the occurrence of knock.

Compression ratio of the engine also strongly effects knock. The higher the CR, the better the **thermal efficiency** - but the greater the tendency for knock to occur.

Critical compression ratio - when knock starts

So higher **fuel octane quality** is required.

Antiknock Quality of Gasoline

Autoignition of the end gases causes a rapid inc of p , producing p waves which resonate in the combustion chamber at a frequency of between 5000 - 8000 Hz, depending on the geometry of the chamber

Knock results in an inc of T in the cylinder and causes a severe damage to engine components like cylinder head gasket, piston, spark plugs etc.

Measurement of Gasoline Antiknock Quality

Prior to 1929, fuels were rated using an engine in which CR could be varied between 2.7:1 to 8:1 - each fuel was run in this engine at various A/F ratios and ignition timing to obtain conditions for max power output.

Fuels were assigned values in terms of Highest Useful Compression Ratio, HUCR

in 1929 Octane scale was proposed by Graham Edgar. In this scale two paraffinic HCs have been selected as standards (PRF, primary reference fuels)- **iso-octane** (2-2-4 trimethyl pentane) with very high resistance to knock (arbitrary assigned a value of 100) and **n-heptane** with extremely low knock resistance (assigned a value of 0).

Octane number of the fuel is the volume percentage of iso-octane in a blend with n-heptane (PRF), that shows the same antiknock performance as test fuel tested in standard engine and standard conditions.

Octane Number

Test engine for determining Octane values, was developed by Cooperative Fuel Research Committee (CFR). It is a single cylinder, variable CR engine.

Two different test conditions specifies the **Research Octane Number** (RON) and the **Motor Octane Number** (MON)

RON correlates with low speed, mild driving conditions, MON relates to high speed, high severity conditions. Most gasolines have higher RON than MON. This difference is called **fuel sensitivity** (=RON-MON) - for fuels of same RON, high sensitivity gasoline has lower MON.

Antiknock Index = $(RON + MON) / 2$

For PRF, Octane Number changes linearly (for paraffinic fuels)

Test Conditions for RON and MON

Test	Research	Motor
ASTM method	D2699	D2700
Engine rpm	600	900
Intake air temp, °C	depends on p (~ 51.7 °C)	38
Mixture temp, °C	not specified	149
Humidity, kg/kg dry air	0.0036 - 0.0072	
Coolant temp, °C	100	100
Ignition advance, °CA	13 BTDC	varies with CR (14 - 26 BTDC)
A/F ratio	adjusted for max knock	

Test Conditions for RON and MON

Test engines -

CFR : D = 3.25", H = 4.50", CR = 4 - 12

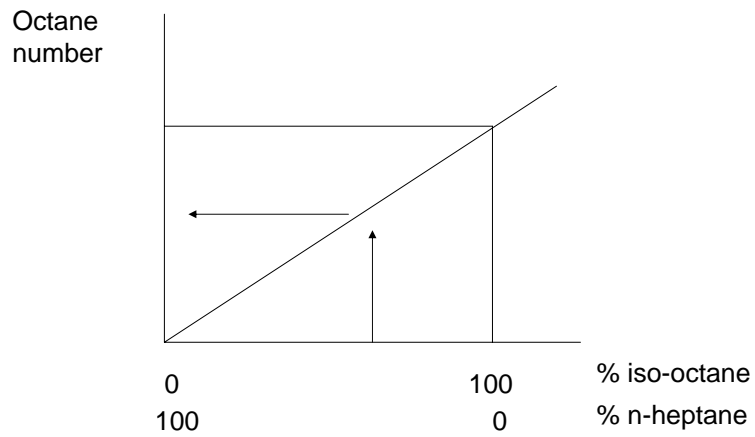
BASF : D = 65 mm, H = 100 mm, CR = 4 - 12

Critical compression ratio -

autoignition occurring at CRs for different fuel Octane numbers

CR	6	7	8	9	10	11	12
ON	78	85	91	96	100	103	106

Octane Number Measurement



for fuels with ON greater than 100, the sample is mixed with certain amount of n-heptane - a linear correction is done according to the percentage of n-heptane added.

Octane Number Measurement

For non paraffinic fuels, ON relation is not linear

TEL is added to the PRF to increase the ON above 100

or n-heptane is added to the sample to reduce ON below 100, then nonlinear extrapolation is applied

Increasing Octane Number

Modern gasoline contains some chemical additives designed to improve fuel quality. These are used to raise ON, control surface ignition, reduce spark plug fouling, resist gum formation, prevent rust, reduce carburetor icing, remove carb or inj system deposits, minimize deposits in intake system, prevent valve sticking.

ON can be increased by antiknock agents - at less expense than modifying HC composition by refinery process.

Most effective agents are lead alkyls -

TEL - tetraethyl lead, $(C_2H_5)_4 Pb$

TML - tetramethyl lead,

MMT

addition of about 0.8 g lead per liter, provides a gain of about 10 ON in gasoline

Diesel Fuel Specifications

Viscosity

Surface tension

Cetane number

Diesel Fuel Viscosity

Viscosity of a fluid indicates its resistance to flow - higher the viscosity, the greater the resistance to flow.

It may be expressed as absolute viscosity (Poise, P) or kinematic viscosity (stoke, St).

It varies inversely with temperature, usually given at 20 - 40 °C

Fuel atomization depends on viscosity
2 - 8 mm²/s (cSt) at 20 °C

Cetane Number

Cetane number is used to specify the ignition quality of diesel fuel.
Running on low cetane number will produce cold start problems. Peak cylinder p, combustion noise and HC emissions will increase - more fuel will be injected before ignition, less time for combustion.

Higher CN results in a sooner ignition - extremely high CN may ignite before adequate F-A mixing can take place - higher emissions. Power output can be reduced if burning starts too early.

Cetane Number Measurement

Cetane number is measured by comparing the "ignition delay time" of the sample fuel with a mixture of cetane (C₁₆H₃₄) and alphanaphtane (C₁₀H₇ CH₃). The cetane percentage in the mixture gives the CN of the sample fuel.

CN of the reference fuel cetane is arbitrarily set at 100, and of alphanaphtane at 0.

CFR engine is used to measure the compression ratio at which ignition starts. CR is gradually increased while the engine is driven by an electric motor - a curve of CN vs critical CR is obtained.

Inlet air temp is 30 °C and cooling water temp is at 100 °C

Cetane Number Measurement

An easier and practical method to obtain Cetane Number is by calculating the Diesel Index.

Increasing the DI, increases the tendency to ignite.

$$DI = \frac{\text{annilin point } [^{\circ}\text{F}] \times \text{API} [\text{at } 60^{\circ}\text{F}]}{100}$$

AP is obtained by heating equal amounts of annilin and diesel fuel. While cooling down, the temp at which the annilin separates from the mixture is the AP

Cetane Number values

Cetane number is in the range of,

50 - 60 for high speed Diesel engines

25 - 45 for low speed Diesel engines

Normal Diesel fuel CN is 40 - 55

DI of 50 gives a CN of around 50