



Applied Chemistry (BS103/BS104)





Knocking



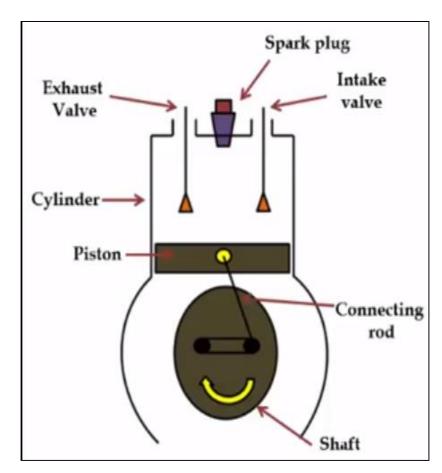
Fractions like petrol and diesel oil are used as engine fuels. Piston engines can be divided into two: spark ignition (SI) and compression ignition (CI) engines. The former consumes petrol and the latter operates on diesel oil.

SI Engines:

- In a four stroke SI engine, petrol vapour is mixed with air in the carburetor.
- It is sucked into the cylinder during the suction stroke.
- The mixture is compressed by the piston in the compression part of the cycle.



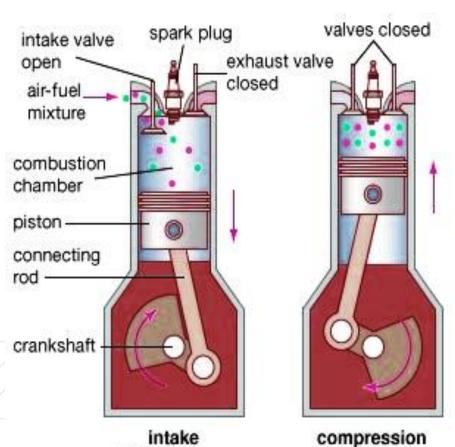
- Then the compressed mixture is ignited by an electric spark.
- The product of combustion increases pressure and pushes the piston out, providing an output of power.
- In the last part of the cycle, the piston ascends and expels the exhaust gases from the cylinder.



- 1. Intake of fuel
- 2. Compression
- 3. Power (Combustion)
- 4. Exhaust

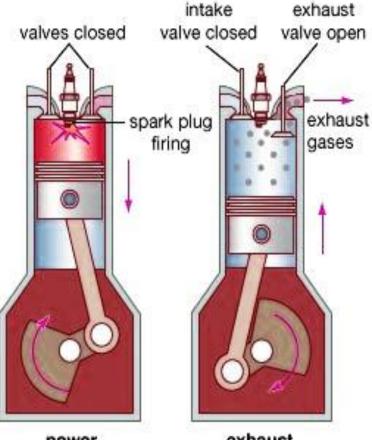
Working principle of four stroke SI engine





intake Air-fuel mixture is drawn in.

compression Air-fuel mixture is compressed.



power Explosion forces piston down.

exhaust Piston pushes out burned gases.



Knocking in Petrol Engines

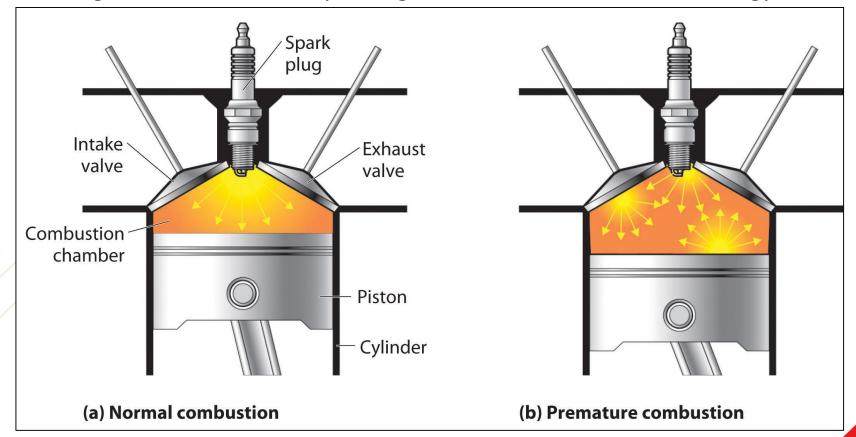


- Normally the fuel air mixture should burn smoothly and rapidly by sparking.
- In some cases, as a result of compression, the fuelair mixture may get heated to a temperature greater than its ignition temperature and spontaneous combustion occurs even before sparking. This is called pre-ignition.
- Further, the spark also is emitted which makes the combustion of the rest of the mixture faster and explosive.

Knocking in Petrol Engines



- So, we have a sudden, badly controlled burning and explosion resulting in a characteristic metallic or rattling sound from the engine. This is called **knocking** or detonation or pinking.
- Knocking lowers the efficiency of engine which results in loss of energy.





Chemical Structure and Knocking



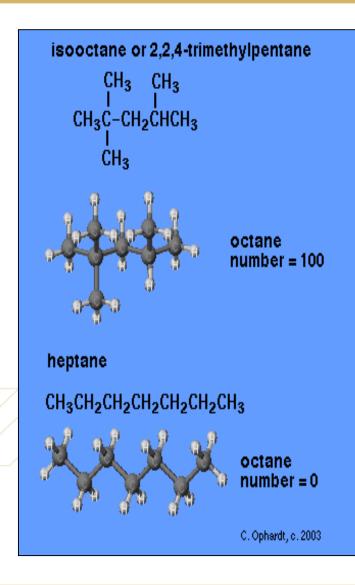
- The knocking tendency decreases with increase in the compactness of the molecule, double bonds and cyclic structure.
- In general, the tendency of a constituent of a fuel to knock is as follows:

n-alkanes \rightarrow iso paraffins \rightarrow olefins \rightarrow naphthenes \rightarrow aromatics

 n-alkanes have lowest antiknock value. So the presence of maximum quantity of aromatics and minimum quantity of nalkanes is desirable in petrol.

Octane Number





- Octane number expresses the knocking characteristics of petrol.
- n heptane (a constituent of petrol) antiknocks very badly, so its anti-knock value has been given zero. On the other hand, isooctane (also a constituent of petrol) gives very little knocking, so its anti-knock value has been given 100.

Octane Number

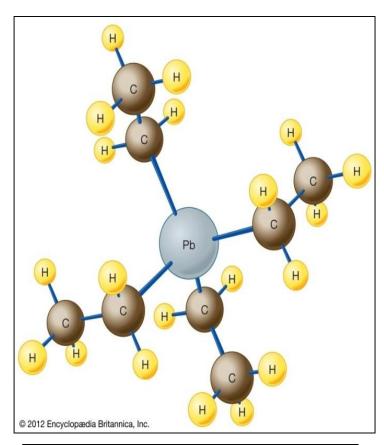


- Percentage of iso-octane present in iso octane & n-heptane mixture, which matches the same knocking characteristics of gasoline mixture test sample.
- If a petrol sample behaves like a mixture of 60% iso-octane and 40% n-heptane, its octane number is taken as 60.

Note: Octane number indicates the tendency of fuels to knock. The higher the octane number the more difficult the auto-ignition. – n-Heptane (C7H16) has a octane number 0, – iso-octane (C8H18) has a octane number 100. – Gasoline has a octane number 93 – 97.

Leaded Petrol –

- Improvement of Anti-knock Value
- Adding some additives in it increases octane number of petrol.
- In motor fuel about 1.0 to 1.5 ml tetra ethyl lead (TEL) is added per litre of petrol.
- Petrol to which TEL is added is called leaded petrol.



Structure of TEL (Tetra ethyl Lead)





Disadvantage of using TEL



- TEL forms lead oxide, which deposits on spark plug and creates problems. So, to remove it, ethylene dibromide is added.
- During burning lead bromide is formed which evaporates away in the heat engines and goes out together with exhaust gases. This creates atmospheric pollution for human beings.
- Hence, at present aromatic phosphates are used instead of TEL.

Mechanism of knocking



- Knocking follows free radical mechanism, leading to a chain growth. If the chains are terminated before their growth, knocking will cease.
- TEL decomposes thermally to form ethyl free radicals, which combines with the free radicals of knocking process and thus the chain growth is stopped.

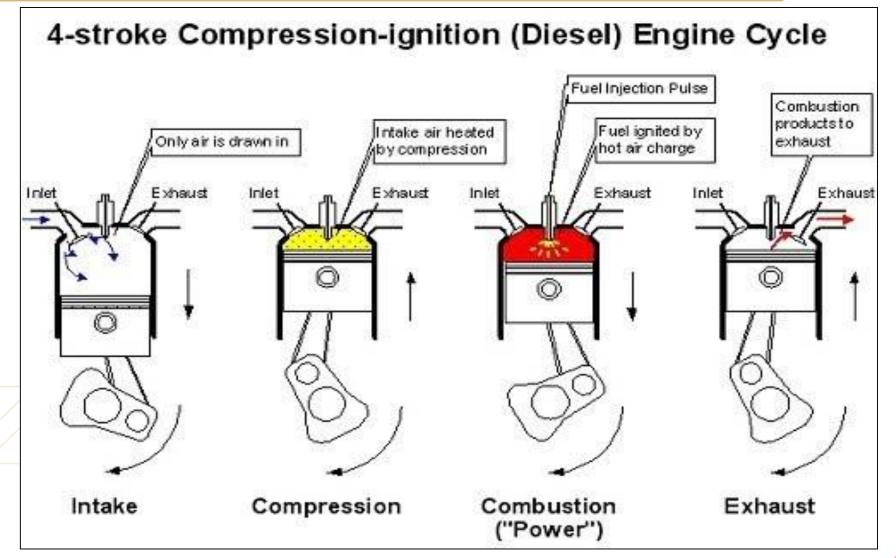
Diesel Engines



- In a CI engine, air is alone compressed. This raises the cylinder temperature as high as 300° C. Then the oil is injected or sprayed, which must ignite spontaneously.
- Now combustion products expand and power stroke begins.

Diesel Engine cycle







Knocking – Diesel Engines



- Some times, even after the compression stroke is over and even after the diesel oil is sprayed, burning may not start. So, more and more fuel is injected automatically and sudden ignition may occur and burn the whole of the oil.
- This delayed ignition results in an uncontrolled, excessive combustion which produces 'diesel knock'.
- So in SI engine, knocking is due to premature or too early ignition and In CI - engines, knocking is due to delayed ignition or ignition lag.

Cetane Number



- Cetane number expresses the knocking characteristics of diesel. Cetane (C_{16} H $_{34}$) has a very short ignition delay and hence its cetane number is taken as 100.
- On the other hand, α -methyl naphthalene has very large ignition delay and hence its cetane number is taken as zero.
- Cetane number is defined as "the percentage of cetane present in a mixture of α –methyl naphthalene and cetane".

Structure of n- Hexadecane (Cetane)

(α-methyl napthalene)





 The knocking tendency in CI - engines increases as follows

n-alkanes → naphthanes → Alkenes → branched alkanes → aromatics

 Octane numbers decreases in this order. Therefore an oil of high octane number has a low cetane number and vice-versa. Consequently, petroleum crude gives petrol of high octane number and diesel of low cetane number.

Cetane Number

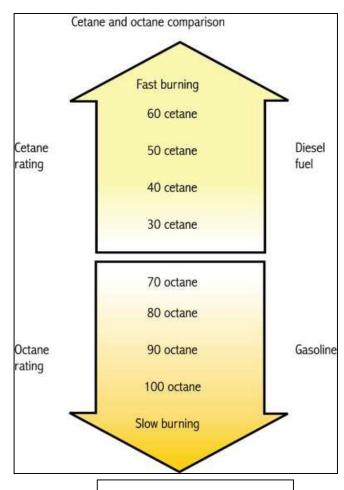


Higher cetane related with:

- improved combustion
- improved cold starting
- reduced noise, white smoke, HC, CO and particulate emissions.

Fuel Ignition Quality

- The ignition characteristics of the fuel affect the ignition delay.
- The ignition quality is defined by its cetane number.



Cetane Rating



THANK YOU

