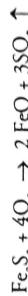




After sometime, when all Fe_2O_3 is changed to Fe_2S_3 , the purifier is exposed to atmospheric air, where Fe_2O_3 is regenerated.



- (vi) **Recovery of gas** The gas after passing through various condensers and scrubbers to remove the byproducts mentioned above is finally collected in a gas holder. It is the coal gas whose calorific value is about 5000 Kcal/m^3 .

1.6 Liquid Fuels

Liquid fuels are used extensively in industrial and domestic fields. Use of liquid fuels in internal combustion engines makes them very important fuels. The single largest source of liquid fuels is petroleum or crude oil (the term petroleum means rock oil. Latin-Petra means rock; oleum means oil) is a dark, greenish-brown viscous oil found deep inside the earth's crust. It is a mixture of hydrocarbons such as straight chain paraffins, cycloparaffins or naphthalene, olefins and aromatics along with small amount of organic compounds containing oxygen, nitrogen and sulphur.

Average composition of crude petroleum is

Element	Carbon	Hydrogen	Sulphur	Nitrogen	Oxygen
Percentage	75.5-87.1%	11.5-14.8%	0.1-3.5%	0.4-0.9%	0.1-0.9%

Classification of petroleum

Petroleum is classified into three categories according to its composition

1. **Paraffinic base petroleum** It is mainly composed of straight chain saturated hydrocarbons from CH_4 to $\text{C}_{35}\text{H}_{72}$ along with small amounts of naphthenes and aromatic hydrocarbons.
2. **Naphthenic or asphaltic base petroleum** It contains mainly cycloparaffins or naphthenes as main constituent along with smaller amount of paraffins and aromatic hydrocarbons.
3. **Mixed base petroleum** It contains both paraffins and asphaltic hydrocarbons.

Table 1.4 Classification of Crude Petroleum

Type of petroleum	Constitution	Residue obtained after distillation	Remarks
Paraffinic base petroleum	Straight chain saturated hydrocarbons from CH_4 to $\text{C}_{35}\text{H}_{72}$ along with small amounts of naphthenic and aromatic hydrocarbons.	Solid paraffin wax	Furnish low octane number straight run gasoline

1. **Separation of water (Demulsification)** The crude oil from the well is an extremely stable emulsion of oil and salt water. The demulsification is achieved by Correll's process. The crude oil is allowed to flow between two highly charged electrodes where colloidal water droplets coalesce to form large drops which separate out from the oil.

2. **Removal of harmful impurities** NaCl and MgCl₂ corrode the refining equipment. These are removed by modern techniques like electrical desalting and dehydration.

Harmful sulphur compounds are removed by treating the crude oil with copper oxide. Sulphur reacts with copper oxide forming copper sulphide, which is removed by filtration.

3. **Fractional Distillation** The crude oil is heated to 400°C in an iron retort whereby all the volatile constituents, except asphalt or coke are evaporated. The vapours are then passed into a fractionating column, which is a tall cylindrical tower. The tower is hot towards the lower end and comparatively cooler at the upper end. It consists of a number of horizontal stainless steel trays at short distances. These trays are provided with individual chimneys which are covered with a loose cap. As the vapours go up, fractional condensation occurs at different heights of the column. Higher boiling fractions condense first, while lower boiling fractions condense later as shown in Fig 1.10.

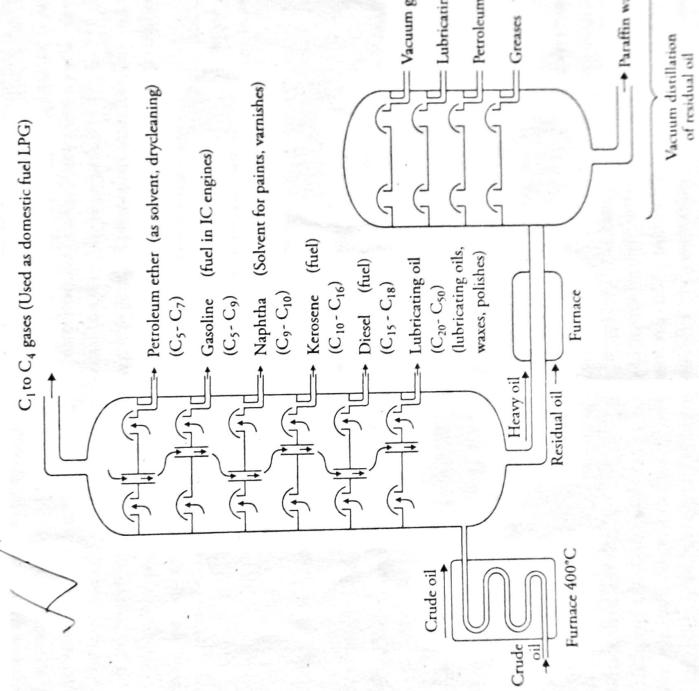


Figure 1.10 Fractional distillation of crude oil

The residue from the bottom of fractionating tower is vacuum-distilled to recover various fractions. The names, approximate composition, range and uses of various fractions are given below in the table 1.5.

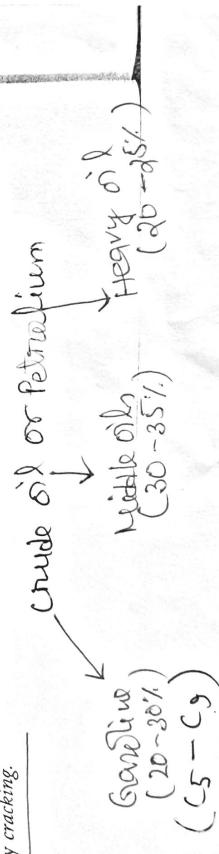
Table 1.5 Major fractions obtained by the distillation of crude oil

S.No	Fraction's name	Boiling Temperature	Approximate composition in terms of hydrocarbons containing C atoms	Uses
1	Uncondensed gases	Below 30°C	C ₁ -C ₄	Used as domestic fuel (LPG)
2	Petroleum ether	30-70°C	C ₅ -C ₇	Solvent for fats, essential oils, used in dry cleaning.
3	Gasoline or petrol or motor spirit	70-120°C	C ₅ -C ₉	As a motor fuel for IC engines, as a solvent and in dry cleaning.
4	Naphtha or solvent spirit	120-180°C	C ₉ -C ₁₀	As a solvent for paints and varnishes and in dry cleaning.
5	Kerosene oil	180-250°C	C ₁₀ -C ₁₆	Fuel for stoves, jet engine fuel and for preparing oil gas used in laboratories.
6	Diesel oil	250-320°C	C ₁₅ -C ₁₈	Diesel engine fuel
7	Heavy oil	320-400°C	C ₁₇ -C ₂₀	Fuel for ships, in metallurgical furnaces and in conversion to gasoline by cracking.
	Heavy oil on vacuum distillation gives			
i.	Lubricating oil		-	As lubricants
ii.	Petroleum jelly (vaseline)	-	-	Used in cosmetics and medicines
iii.	Greases	-	-	As lubricant
iv.	Paraffin wax	-	-	In candles, boot polishes, wax paper, etc
8	Residue: It may be either			
i.	Asphalt (if the crude oil is asphaltic)	>400°C	C ₃₀ and above	Used for water proofing of roofs and for road making.
ii.	Petroleum Coke			As a fuel in moulding electrode rods for cells.

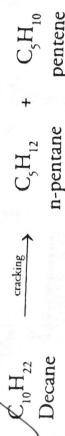
The gasoline obtained by this fractionation is called straight run gasoline

Cracking

The crude oil obtained on fractionation yields approximately 20-30% gasoline, 30-35% middle oils and 20-25% heavy oils. Among all these fractions, gasoline (also called straight run petrol) is in maximum demand because of its use as fuel in the automobile industry. Hence, there is a need to convert the middle oil and heavy oil fractions of gasoline into a more useful fraction gasoline. This is achieved by cracking.



Cracking is defined as the process of converting high molecular weight bigger hydrocarbons into smaller hydrocarbons by the application of heat, with or without a catalyst.



Nearly 50% of today's gasoline is obtained by cracking. It is important to note that the characteristics of gasoline obtained by cracking are far more superior to the straight run gasoline. The methods of cracking are summarized below

1. Thermal cracking

When the heavy oils are subjected to high temperature and pressure in the absence of catalyst, it is called thermal cracking. The bigger hydrocarbons breakdown to give smaller molecules of paraffins, olefins and some hydrogen. This process may be carried out either in liquid phase or in vapour phase.

(a) **Liquid phase thermal cracking** By this method any type of oil (residue, fuel oil or gasoline) can be cracked. The charge is kept in liquid form by applying high pressure of the range of 100 kg/cm² at a suitable temperature of 475–530°C. The cracked products are separated in a fractionating column. The octane rating of the product is 65–70

(b) **Vapour phase thermal cracking** This method is suitable for oils which can be readily vapourised. The oil is first vapourised and then cracked at about 600–650°C and under a low pressure of 10–20 kg/cm². It requires less time than the liquid phase method. Petrol obtained from vapour phase cracking has better antiknock properties, but poorer stability than the petrol obtained from liquid-phase cracking.

Table 1.6 Comparison of liquid phase and vapour phase thermal cracking

Characteristic	Liquid phase thermal cracking	Vapour phase thermal cracking
Cracking temperature	475 – 530°C	600–650°C
Pressure	100 kg/cm ²	10–20 kg/cm ²
Octane rating of petrol	65–70	Greater than 70
Type of oil used for cracking	Any heavy oil can be cracked	Oil should be readily vapourised

2. Catalytic cracking

It is carried out in the presence of a catalyst at a much lower temperature and pressure. The catalyst used is usually a mixture of silica and alumina (hydrated aluminium silicate) or zeolites in the form of beads or pellets.

There are two main types of catalytic cracking

- (a) **Fixed bed catalytic cracking** The vapours of the oil are preheated in a pre-heater to a temperature of 420–450°C. It is then passed through a catalytic chamber containing either silica-alumina gel ($\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$) or bauxite mixed with clay and zirconium oxide maintained at 425°C–450°C and 1.5 kg/cm² pressure. Cracking of heavy oil vapours takes place and 30–40% of the charge is converted into gasoline and about 3–4% carbon

of 80.

Decomposition of aromatics removes only side chains but the aromatic ring is not broken.

Synthetic petrol

Petrol can be synthesized by the following methods

1. **Polymerization** In this method small molecules of hydrocarbons are combined to form heavier molecules resembling gasoline.

During cracking large quantities of olefins or unsaturated hydrocarbons (such as ethylene, propene and butene) and alkanes (such as methane, ethane, and butane) are obtained as by products. When this gaseous mixture is subjected to high pressure and temperature, with or without a catalyst, it polymerizes to form higher hydrocarbons resembling gasoline.

The gasoline so obtained is called polymer gasoline. It has high octane number (78 to 83). Polymerization is carried out in two ways

(i) **Thermal polymerization** In this the polymerization of cracked gases is carried out at 500–600°C and 70–350 kg/cm² pressure. The product is gasoline and gas oil which are separated by fractional distillation.

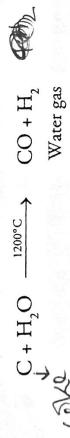
(ii) **Catalytic polymerization** It is carried out in the presence of catalyst like phosphoric acid, sulphuric acid, etc. The process is carried out at a low temperature (150–200°C)

2. **Alkylation** This method is used to convert olefins to gasoline. In this process, alkane and alkene are combined together in the presence of a catalyst under proper temperature and pressure. The most important example is the reaction of isobutane and isobutene in the presence of anhydrous HF at room temperature to give isoctane. This process is used to produce gasoline of improved quality.

Conversion of coal into liquid fuels → Coal → Liquid fuel

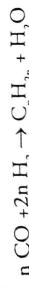
Coal can be converted into gasoline by two methods:

(a) **Fischer Tropsch method** This method was developed by Fischer and Tropsch in 1962 in Germany. In this method the raw material is coke which is converted into water gas ($\text{CO} + \text{H}_2$) by passing steam over red-hot coke.



A mixture of water gas and hydrogen is purified by passing through Fe_2O_3 (to remove H_2S) and then through a mixture of $\text{Fe}_2\text{O}_3 + \text{Na}_2\text{CO}_3$ (to remove organic sulphur compounds).

The purified gas is compressed to 5–25 atm. and then passed through a catalytic converter maintained at about 200–300°C. The catalyst consists of a mixture of Cobalt (100 parts), Thoria (5 parts), Magnesia (8 parts) and Keiseltgühr earth (200 parts). A mixture of saturated and unsaturated hydrocarbons is formed.



The reactions leading to the formation of hydrocarbons are all exothermic. The vapors coming out of the reaction chamber are passed through the cooler where liquid resembling

crude oil is obtained. This is then subjected to fractional distillation to yield gasoline, diesel oil and heavy oil. The heavy oil can be reused for cracking to obtain more gasoline.

The gasoline formed by Fischer-Tropsch process is rich in straight chain hydrocarbons, and hence its octane number is only 40. However, the diesel oil obtained is of excellent quality.

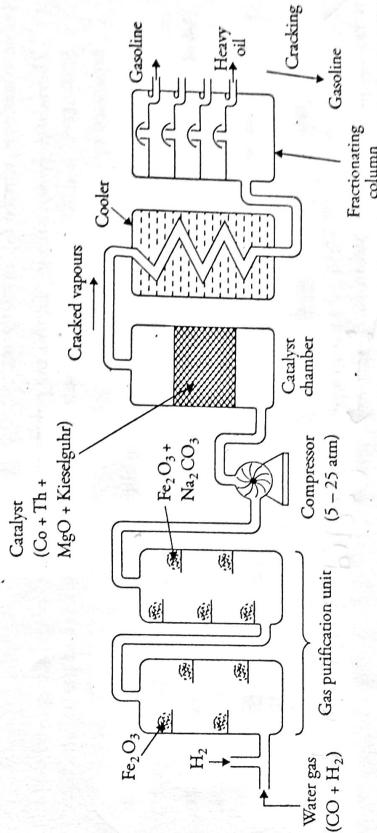


Figure 1.13 Fischer-Tropsch method

(b) Bergius Process

This process developed by Bergius of Germany involves the conversion of low-grade coals, such as bituminous coals or brown coals, into liquid and gaseous fuels by hydrogenating them in the presence of catalyst.

In this process, the low ash coal is powdered and mixed with heavy oil and catalyst (tin and Ni oleate) to make a paste. This paste is heated with hydrogen at 450°C and 200-250 atm pressure for about 2 hrs. The coal undergoes hydrogenation to form saturated hydrocarbons that decompose at prevailing high temperature and pressure to yield low-boiling liquid hydrocarbons. The vapors leaving the catalytic chamber are condensed, where a liquid resembling crude oil is obtained. This is subjected to fractional distillation to give (i) gasoline, (ii) middle oil and (iii) heavy oil.

The middle oil is again hydrogenated to obtain gasoline. Heavy oil is reused for making a paste with fresh coal dust.

The gasoline so obtained contains 74% paraffins, 22% aromatics and 4% olefins. Yield of gasoline is about 60% of the coal dust used.

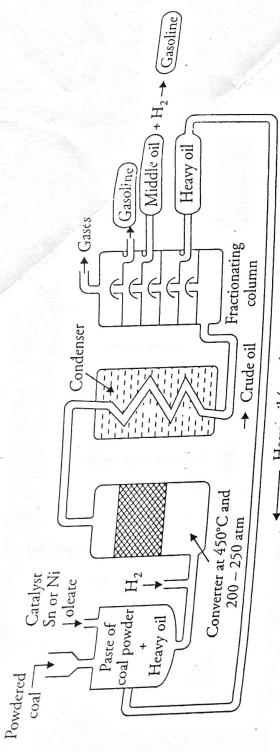


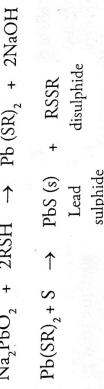
Figure 1.14 Bergius process of hydrogenation of coal to gasoline

Refining of gasoline

- The straight run gasoline obtained from fractionation of crude petroleum or by synthesis contains substances such as (i) unsaturated olefins and (ii) sulphur. These substances are undesirable because olefins undergo oxidation and polymerization leading to gum and sludge formation. These deposit on the walls of the carburetor and stop the engine.
- The sulphur compounds lead to corrosion of internal combustion engine. Moreover, compounds of sulphur such as mercaptans or H_2S have objectionable odors and make the oil sour.

Hence it has to be refined by chemical treatment.

- (a) **Removal of sulphur compounds** The sulphur-containing gasoline is termed as sour gasoline and the process of removal of sulphur is called "sweetening". It is accomplished by treating gasoline with sodium plumbite with controlled addition of sulphur. The sulphur compounds are converted into PbS (removed by filtration) and disulphides (which are extracted with a suitable solvent). The above process is termed as *Doctors process*.



- (b) **Removal of olefins** They are removed by percolating gasoline through fuller's earth which preferentially absorbs colours and olefins.

- (c) **Stabilization of gasoline** Impure gasoline may contain dissolved gases such as methane, ethane, propane and butane. The process of removal of these impurities is called stabilization. For this, impure gasoline is passed through a fractionating tower having plates. The lower plates are heated with steam and are introduced near the upper plates. The stabilized gasoline is removed from the top of the column.

- (d) **Blending** Purified gasoline is blended with high octane number fractions.

applications.

Knocking

It is defined as the metallic sound similar to rattling of hammer produced in internal combustion engine due to immature ignition of fuel air mixture.

An internal combustion engine uses either gasoline or diesel as fuel. In internal combustion engine, a mixture of fuel (gasoline or diesel) is ignited in a cylinder. The ignition is brought about by means of an electric spark (in petrol engines) or by compressing the air (in diesel engines).

The gases evolved during ignition, force the piston down due to high pressure thus producing the power stroke.

In a petrol engine the whole process comprises of four strokes;

- (i) **Suction stroke** The downward moving piston sucks a mixture of air and petrol vapours in the carburetor into the cylinder.
- (ii) **Compression stroke** The piston moves up, compressing the gas mixture. The ratio of initial volume (volume at suction stroke) to final volume (volume at compression stroke) is called compression ratio. It is here that a low octane rating fuel might ignite and cause knocking.
- (iii) **Power stroke** Just before the piston reaches the top centre of the cylinder a spark from the spark plug ignites the gas mixture. The hot gases produced due to combustion increase the pressure and push the piston down.

shape of head, location of plug, ports, etc, and also upon the running conditions.

Chemical structure and knocking

1. The knocking tendency decreases with increase in compactness of the molecule.
2. Knocking decreases with the increase in the number of double bonds and rings (cyclic structure).
3. With normal paraffins, the knocking increases with increase in length of the hydrocarbon chain. Thus, the knocking tendency increases from n-butane to n-heptane.

n-butane < n-pentane < n-hexane < n-heptane

knocking increases →

Knocking decreases as the branching in carbon chain increases.

$\text{A}-\text{heptane} > \text{Z-methylhexane} > \text{Z-dimethylpentane}$

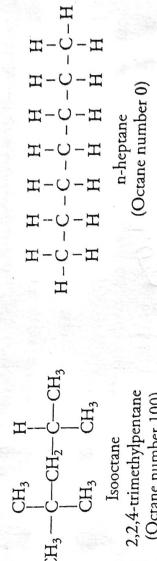
— knocking decreases —

Aromatics such as benzene and toluene have very high octane numbers.

Aromatics such as benzene and toluene have very high antiknock properties. In general the tendency of fuel constituents to knock is in the following order Straight chain paraffins > branched chain paraffins (i.e., isoparaffins) > cycloparaffins (i.e., naphthalenes) > aromatics.

/ Octane rating

In order to classify the fuels according to their knocking property, an arbitrary scale was provided by Edger in 1926, known as octane rating or octane number. It is observed that n-heptane knocks very badly; hence, it was arbitrarily assigned an antiknock value of zero. On the other hand, isoctane (2,2,4-trimethylpentane) has a high resistance to knocking and hence was arbitrarily assigned a value of 100.



Octane number of a fuel is defined as the percentage of iso-octane in a mixture of iso-octane and n-heptane, which has the same knocking characteristics as that of the fuel under examination, under same set of conditions. Thus, a fuel with octane number 80 is one which has the same combustion characteristics as a 80:20 mixture of iso-octane and n-heptane.

Antiknocking agents Octane number of gasoline can be increased by addition of additives like benzene and alcohol. Toluene, xylene, and n-heptane.

The antiknock properties of gasoline are usually increased by adding tetrathy^l lead (TEL) $Pb(C_2H_5)_4$ and the process is called "doping". TEL is a colourless liquid with a sweet odour but it is highly poisonous. About 0.5 ml of TEL per litre is added for motor fuels and about 1 ml of TEL per litre is added for aviation fuel. Gasoline containing TEL is coloured with 2% red dye to indicate its poisonous nature.

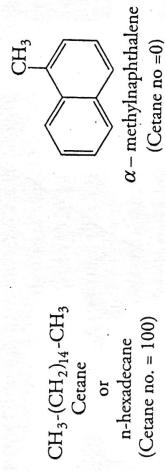
It is believed that knocking is a free radical mechanism. During combustion $\text{Pb}(\text{C}_2\text{H}_5)_4$ forms Pb and PbO. These act as free radical chain inhibitors and hence the propagation of the chain reaction leading to knocking does not take place.

However lead and lead oxide vapours so formed contaminate the atmosphere. Lead oxide is rapidly reduced to metallic lead which is deposited on the spark plug, cylinder walls and piston head. Hence, it is harmful to the engine. In order to solve this problem, the following methods have been adopted:

Benzole or Benzid is a coal-tar product consisting mainly of benzene and toluene.

Chemically, diesel engine fuels consist of straight chain hydrocarbons with minimum amount of branched chain and aromatic hydrocarbons. Thus, in contrast to gasoline, the diesel engine fuel should have low spontaneous ignition temperature so as to minimize the induction lag.

Cetane Rating/Cetane number Cetane number is a measure of ignition quality of a diesel fuel. It is often mistaken as a measure of the fuel quality. It is actually a measure of the fuel's ignition delay. It is the measure of the ease with which the fuel will ignite under compression. The hydrocarbon Cetane (n-hexadecane) has a very short ignition delay as compared to any diesel fuel and is assigned an arbitrary value of 100. α -methyl naphthalene has a long ignition delay compared to any other diesel fuel and hence is assigned a value of 0 (zero).



The cetane number of a diesel fuel is defined as the percentage of cetane (n-hexadecane) in a mixture of cetane and α -methyl naphthalene, which will have the same ignition characteristics as the fuel under test, under the same conditions. For example, a diesel fuel will be assigned a cetane number of 60 if it has the same ignition characteristics as that of a mixture of 60% cetane (n-hexadecane) and 40% α -methyl naphthalene. The cetane value of a fuel depends upon the nature and composition of hydrocarbon. The straight chain hydrocarbons ignite quite readily, although aromatics do not ignite easily. Ignition quality order among the constituents of diesel engine fuels in order of decreasing cetane number is as follows:

n-alkanes > naphthalene > alkenes > branched alkanes > aromatics

Thus, hydrocarbons which are poor gasoline fuels are quite good diesel fuels.
The cetane number of a diesel fuel can be raised by addition of small quantity of certain "pre-ignition dopes" such as ethyl nitrite, isoamyl nitrite, acetone peroxide etc.)

High-speed and Low speed diesel In a high-speed diesel engine the time lag in getting the diesel droplets heated to ignition point is very small, about $1/50^{\text{th}}$ of a second. Such diesel engines require diesel with cetane number in excess of 45 (up to 60). On the other hand, low speed diesel requires a cetane number of about 25. Cetane number of medium speed diesel is about 35.

Reforming

Reforming is the process of improving the antiknocking characteristics of gasoline by bringing about certain structural modifications in it. The modifications are due to the rearrangement of molecules without disturbing their average molecular weight. The main reactions involved in reforming process are: