Unit I

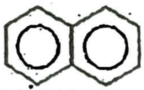
2.18 PETROLEUM

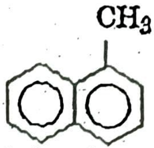
Petroleum or crude oil (*petra* = rock ; *oleum* = oil), *is a dark greenish-brown, viscous oil found deep in earth's crust.* It is composed mainly of various *hydrocarbons* (like straight-chain paraffins, cycloparaffins or naphthalenes, olefins and aromatics), together with small amounts of organic compounds containing oxygen, nitrogen and sulphur. *The oil is, usually, found floating upon a layer of brine and has a layer of gas on top of it.* The average composition of crude petroleum is : C = 79.5 to 87.1% ; H = 11.5 to 14.8% ; S = 0.1 to 3.5% ; N + O = 0.1 to 0.5%.

Classification of petroleum : The chemical nature of the crude petroleum varies with the part of the world in which it is found. There appears, however, to be *three* principle varieties :

(1) *Paraffinic-base type crude* is mainly composed of the saturated hydrocarbons from CH_4 to $C_{35}H_{72}$ and a little of the naphthalenes and aromatics. The hydrocarbons from $C_{18}H_{38}$ to $C_{35}H_{72}$ are semi-solids, called *'waxes'*.

(2) *Asphaltic-base type crude* contains mainly cycloparaffins or naphthalenes with smaller amount of paraffins and aromatic hydrocarbons.


(Naphthalene)


(Methyl naphthalene)

(3) *Mixed-base type crude* contains both paraffinic and asphaltic hydrocarbons and are, generally, rich in *semi-solid waxes.*

Origin of petroleum : According to *modern theory, petroleum has resulted from the partial decomposition of marine animals and vegetable organisms of pre-historic forests.* Changes in earth (like volcano's, etc.) had burried these materials underground, where they have been subjected to intense pressure and heat, during the ages of time. The conversion of these materials into various hydrocarbons has been going on either under the influence of radioactive substances (like uranium) or by the bacterial decomposition under anaerobic and strongly reducing conditions and temperature under high-pressure.

Mining of petroleum done by *drilling holes* in the earth's crust and sinking pipes upto the oil-bearing porous rocks. Oil, usually, gushes out itself due to hydrostatic pressure of natural gas. Alternatively, it may be mechanically pumped up by using either *lift pump* or *air-lift pump*. The latter consists of *two co-axial pipes*, lowered into the base of oil bed. *Compressed air* is forced through the outer pipe, whereby oil comes out through the inner pipe (*see* Fig. 6). The oil is conveyed to refinery by a system of pipelines.

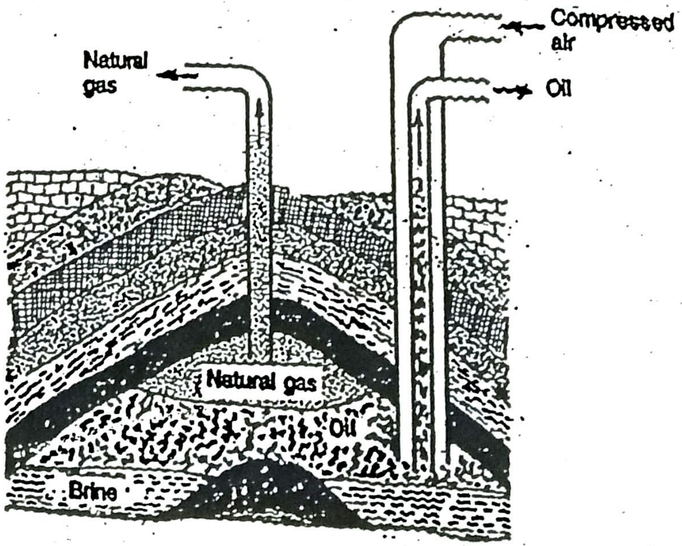


Fig. 6. Mining of crude oil and use of air-lift pump.

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Refining of crude oil : The crude oil is separated into various useful fractions by *fractional distillation* and finally converted into desired specific products. The process is called *"refining of crude oil"* and the plants set up for the purpose, are called the *oil refineries*. The processs of refining involves the following steps :

Step 1. Separation of water (Cottrell's process) : 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.

Step 2. Removal of harmful sulphur compounds involves in *treating oil with copper oxide*. A reaction occurs with sulphur compounds, which results in the formation of copper sulphide (a solid), which is then removed by filtration.

Step 3. Fractional distillation : The crude oil is then heated to about 400°C in an iron retort, whereby all volatile constituents, except the residue (alphalt or coke) are evaporated. The hot vapours are then passed up a *"fractionating column"*, which is a tall cylindrical tower containing a number of horizontal stainless steel *trays* at short distances (*see* Fig. 7). Each tray is provided with small *chimney*, covered with a loose *cap*. As the vapours go up, they become gradually cooler and fractional condensation takes place at different heights of column. *Higher boiling fraction condenses first; while the lower boiling fractions turn-by-turn.* Various principal fractionation products thus obtained are given in Table 5.

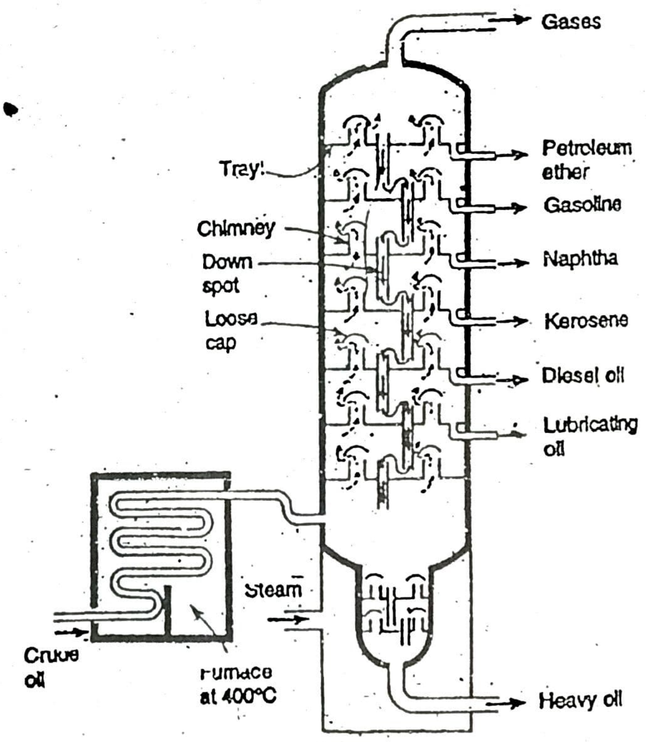


Fig. 7. Fractional distillation of crude petroleum.

The emulsion-free crude is heated in pipes in a furnace heated by burning gas or oil. The vapours are passed through a tall cylindrical fractionating column which is provided with a number of carefully designed fractionating plates, see figure 3.6. As the vapours move upwards, the higher boiling fractions condense and fall back and only lower boiling vapours move to higher plates where further condensation takes place and some more liquid falls back. As the freshly condensed liquid comes to the lower plates, it gets heated and vapourized and again condenses on higher plates. This process of condensation and vapourization takes place many times causing separation of hydrocarbons according to their boiling

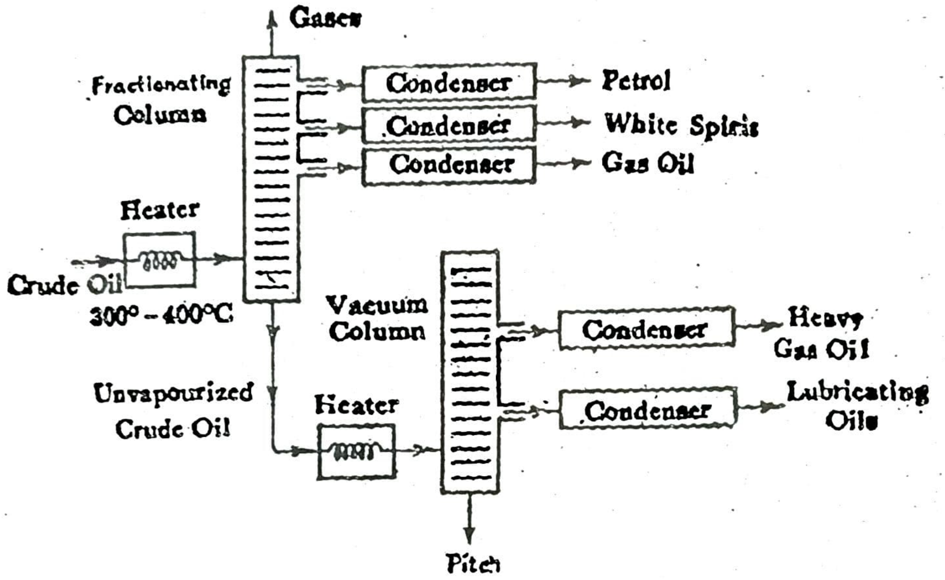


Fig. 3.6 Petroleum distillation

points. Thus the higher boiling fractions condense towards the lower part of the column The lower the boiling point the higher is the position of the plate on which a fraction condenses. Pipes are led off from different points taking out mixture of vapours and liquids of the desired boiling points which are condensed separately and different fractions are obtained. This gives *straight-run* petrol, kerosene (or white oil) and gas oil fractions. Operations from drilling to the final use are shown in figure 3.7.

If the entire crude is distilled at atmospheric pressure, as described above, considerable thermal decomposition of the higher boiling hydrocarbons would take place. About half of the unvapourized crude oil is removed from the bottom and distilled under reduced pressure in a similar fractionating column and heavy gas, oil and lubricating oil fractions are separated. The residue gives pitch.

Of all the fractions collected petrol has the largest demand, but the yield, by the above-described method, is only 20% of the crude. The result is that there is surplus of heavier fractions. Moreover, the straight-run petrol is not of sufficiently high quality for direct use in internal combustion engines. It has to be properly blended. To overcome these difficulties, the heavier fractions are subjected to cracking whereby the larger molecules are broken down to smaller molecules giving lighter fractions which are more useful. Two methods of cracking in use are the thermal and the catalytic cracking.

Table 5. *Fractions by distillation of crude.*

	Name of fraction	*Boiling range*	*Approx. composition in terms of hydrocarbon containing C atoms*	*Uses*
1.	Uncondensed gas.	Below 30°C	C_1 to C_4 (such as ethane, propane, isobutane)	As domestic or industrial fuel under the name L.P.G (liquefied petroleum gas).
2.	Petroleum ether	30 – 70°C	$C_5 - C_7$	As a solvent.
3.	Gasoline or petrol or motor spirit.	40 – 120°C	$C_5 - C_8$ (calorific value = 11,250 kcal/kg)	As motor fuel, solvent and in dry cleaning.
4.	Naphtha or solvent spirit.	120 – 180°C	$C_9 - C_{10}$	As solvent and in dry cleaning.
5.	Kerosene oil	180 – 250°C	$C_{10} - C_{16}$ (calorific value = 11,000 kcal/kg)	As an illuminant, jet engine fuel and for preparing laboratory gas.
6.	**Diesel oil or fuel oil or gas oil.**	250 – 320°C	$C_{16} - C_{18}$ (calorific value = 11,000 kcal/kg)	Diesel engine fuel.
7.	**Heavy oil**	320 – 400°C	$C_{17} - C_{30}$	**For getting gasoline by cracking process**
	This on *refractionation* **gives**			
(a)	Lubricating oil.	-	-	As lubricant.
(b)	Petroleum jelly (vaseline)	-	-	As lubricant and in cosmetics and medicines.
(c)	Grease.	-	-	As lubricant.
(d)	Paraffin wax.			In candles, boot polishes, wax paper, tarpolin cloth, etc.
8.	Residue may be either :	Above 400°C	C_{30} and above.	
(a)	Asphalt	-	-	Water-proofing of roofs and road making.
	or			
(b)	Petroleum coke.	-	-	As a fuel and in moulding arc light rods.

A brief description of *three most important liquid fuels* derived from petroleum is given on next page.

③

Natural Gas

It is an important primary gaseous fuel which is obtained from underground strata either as such or associated with crude oil. It is also found in places quite remote from oil-bearing strata, from where the gas might have migrated through porous rocks. Petroleum consists of low-molecular-weight or lighter hydrocarbons which may be gaseous under the conditions of their occurrence or may become gaseous petroleum is called natural gas. Natural gas consists essentially of a mixture of methane (70 to 90%), ethane, propane and butane (20%) and other gases like CO_2, H_2S, N_2 and traces of rare gases. A natural gas containing mainly methane but not higher hydrocarbons is said to be *lean* or *dry gas* whereas that containing appreciable amounts of propane, butane and other liquid hydrocarbons like pentanes, hexanes, etc. is called *rich* or *wet gas.*

The recovery of higher-molecular-weight hydrocarbons from natural gas is important since they can be used like gasolene after proper treatment. The recovery processes are compression, absorption by oil and adsorption by active charcoal. The wet gas may yield upto 335 litres of gasoline per million litres of the gas and this gasoline is called *natural* or *casing-head gasoline.* The natural gasoline thus obtained cannot be blended with petrol as it contains dissolved propane and butane, which tend to escape by bubbling out. The natural gasoline is thus appropriately called 'wild'. At low pressures, the dissolved gases released in the fuel supply lines cause an interruption in the fuel supply and so such gasolines are susceptible to produce 'vapour lock'. This gasoline is hence stabilized by distillation under pressure to give stabilized natural gasoline and a gas, from which propane and butane may be obtained.

Liquefied petroleum gas (LPG) is a mixture of propane and butane liquified and stored under pressure in steel containers. To detect any possible leakage of the gas it is usual to add tetrahydrothiophen, which even in traces can be detected by its characteristic strong smell. It is widely used as a domestic fuel and is especially suitable as a portable fuel. LPG has also been suggested as an alternative fuel for internal combustion engines since it permits the attainment of high compression ratios without producing knocking (Sec. 7.10.4).

Uses of Natural Gas

Natural gas can be used for generation of electricity by using it in fuel cells (Sec. 4.6.4). In UK and USA it is used in the manufacture of 'town gas' for use as fuel. From natural gas, H_2S and CO_2, if present can be removed by scrubbing with monoethanolamine ($NH_2CH_2CH_2OH$). The reaction with H_2S can be one of the following:

$$2\,HOCH_2CH_2NH_2 + H_2S \longrightarrow (HOCH_2CH_2NH_3)_2S$$

or

$$(HOCH_2CH_2NH_2)_2 \cdot H_2S \text{ and } HOCH_2CH_2NH_3SH$$

On heating these, H_2S gas is liberated. A part of the liberated H_2S is oxidized to SO_2 and it is allowed to react with the remaining H_2S to give S.

$$2\,H_2S + 3\,O_2 \longrightarrow 2\,SO_2 + 2\,H_2O$$

$$2\,H_2S + SO_2 \longrightarrow 3\,S + 2\,H_2O$$

Natural gas besides being used as a fuel can also serve as raw material for the manufacture of carbon black (filler for rubber) and hydrogen (ammonia synthesis). Synthetic proteins have been obtained by microbiological fermentation of methane and gas oil by dispersing yeasts of the *candida* species in a gas-oil-water emulsion containing ammonium salts as nutrients. The mixture is agitated with sterile air. The proteins are reported to be comparable to those of animal origin. At present these are being used as animal feed.

LPG AS A FUEL

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. LPG is dehydrated, desulphurised and traces of odorous *organic sulphides (mercaptans)* are added to give *warning* of gas leak. LPG is supplied under pressure in containers under the trade name like Indane, Bharat gas, etc. Its calorific value is about 27,800 kcal/m^3.

To *operate* the LPG, cylinder valve is first opened and then a lighted match applied to the burner/stove ; while the appliance (stove/burner) valve is opened simultaneously. The gas ignites in an instant and the flame can be adjusted "low" or "medium" or "high" as desired, by turning the tap. To extinguish the flame, the appliance tap (such as of stove) is turned off. *When not in use, the cylinder valve is kept closed, since this ensures safety.*

LPG *consists of hydrocarbons of such volatility that they can exist as gas under atmospheric pressure, but can be readily liquefied under pressure.* The main constituents of LPG are *n*-butane, *iso*butane, butylene and propane, with little or no propylene and ethane.

Uses : The largest use of LPG at present is as *domestic fuel and industrial fuel.* However, there is a increasing trend to use LPG as *motor fuel.*

Advantage of LPG over gaseous fuel : (1) *High efficiency and heating rate.* The calorific valve is roughly 3 times that of natural gas and 7 times that of coal gas. (2) Use of well-designed, durable and neatly-constructed burners ensure complete combustion with *no smoke.* (3) Needs *little care* for maintenance purpose. (4) *Cleanliness* in storage, handling and use. (5) Flexibility and easy control. (6) Easy to manipulate. (7) Portability in steel cylinder/containers make its use possible in remote/isolated places. (8) Comparatively less of health hazard, even in case of leakage, since it contains no carbon monoxide. However, the fire hazards are as great as with any other gaseous fuel.

Advantages of LPG over gasoline as a motor fuel : (1) It is cheaper than gasoline. (2) It gives better manifold distribution and mixes easily with air. (3) It is highly knock-resistant. (4) Residue and oil contamination is small, as it burns cleanly. (5) Crankcase oil dilution is small, thereby resulting in increased engine life.

Disadvantages of LPG over gasoline as a motor fuel : (1) Due to its faint odour, leakage cannot be easily detected. (2) Handling has to be done under pressure. (3) LPG is advantageous only in engines working under high compression ratios. (4) Its octane number is quite low and the load sensitivity is very high. (5) Its response to blending is very poor. Due to all there factors, the use of LPG is limited only to certain classes of vehicles like trucks and tractors. LPG leaded with TML (tetramethyl lead), however, can be used as the main constituent of diesel fuel for railway diesel locomotives.

④

CRACKING

Cracking is defined as *"the decomposition of bigger hydrocarbon molecules into simpler, low boiling hydrocarbons of lower molecular weight"*, *e.g.*,

$$\underset{\substack{\text{(Decane)}\\ \text{B. p.} = 174\,^\circ\text{C}}}{C_{10}H_{22}} \xrightarrow{\text{Cracking}} \underbrace{\underset{(n\text{-pentane})}{C_5H_{12}} + \underset{\text{(Pentene)}}{C_5H_{10}}}_{\text{B. p.} = 36\,^\circ\text{C}}$$

Of all the fractions obtained by fractionation of petroleum, gasoline has the *largest demand* as a motor fuel, but the yield of this fractions is only 20% of the crude. Also the quality of so-called *'straight-run' gasoline* is not high. It has to be properly blended. Moreover, there is a *surplus of heavier petroleum fractions*. To overcome these difficulties, the middle and heavy fractions are cracked to get petrol. The petrol made by cracking has far better characteristics (as for as the internal combustion engine is concerned) than 'straight-run' petrol. There are *two* methods of cracking in use :

(1) **Thermal cracking** : *The heavy oils are subjected to high temperature and pressure, when the bigger hydrocarbon molecules break down to give smaller molecules of the paraffins, olefines plus some hydrogen.* This process may be carried out either in *'liquid-phase'* or *'vapour-phase'*.

In thermal cracking the heavy oil is subjected to high temperature when the molecules break down to give smaller molecules of the paraffin and olefin series and some hydrogen, but some molecules polymerize to give molecules larger than those originally present. The process can be carried out in vapour phase or in liquid phase. In the vapour phase, higher temperature and lower pressure are employed and the time required is less than in the liquid phase. The heavy oil is heated under pressure (vapour phase, 600° and up to 23 kg/cm²; liquid phase, 450° and up to 100 kg/cm²) when craking takes place. It is then led to a chamber maintained at a lower pressure where the lighter fraction vapourizes and the vapours are taken to a fractionating column and different fractions are separated. The unconverted oil is returned to the heating chamber and processed again. Even under ideal conditions only 50– 60 litres of pertol are obtained from 100 litres of the heavy oil. The petrol contains some unsaturated molecules which are undesirable in aviation petrol. The petrol obtained from vapour phase cracking has better anti-knock properties but poorer stability than petrol from liquid phase cracking.

(a) ***Liquid-phase thermal cracking*** : The heavy oil or gas oil stock is cracked at a suitable temperature of 475–530°C and under pressure of 100 kg/cm². The cracked products are then separated in a fractionating column. The yield is 50-60% and octane rating of the petrol produced is 65–70.

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

Mechanism of Thermal Cracking

On the basis of investigations on model compounds it is believed that thermal cracking involves free-radical chain reactions. Taking *n*-nonane as an example:

Initiation

$$CH_3—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—CH_3 \xrightarrow{heat}$$

$$CH_3—CH_2—CH_2—CH_2—\dot{C}H_2 + H_2\dot{C}—CH_2—CH_2—CH_3$$

Propagation The large radicals formed are thermally unstable and decompose by the fission of the C—C bond β to the radical site to give an olefin and a new radical.

$$CH—CH_2—CH_2—\underset{\beta}{CH_2}—\underset{\alpha}{\dot{C}H_2} \longrightarrow CH_3—CH_2—\dot{C}H_2 + CH_2 = CH_2$$

The *β*-scission continues till a thermally more stable radical is formed.

$$CH_3—CH_2—CH_2—\dot{C}H_2 \longrightarrow CH_3\dot{C}H_2 + CH_2 = CH_2$$

$$CH_3—CH_2—\dot{C}H_2 \longrightarrow \dot{C}H_3 + CH_2 = CH_2$$

$$CH_3—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—CH_3 + \dot{C}H_3 \longrightarrow$$

$$CH_3—CH_2—CH_2—CH_2—CH_2—\underset{\beta}{CH_2}—\underset{\alpha}{\dot{C}H}—CH_2—CH_3\ (A) + CH_4$$

This radical (A) undergoes β-cleavage to give an alkene and another radical

$$\underset{(A)}{CH_3—(CH_2)_3—CH_2 : CH_2 : \dot{C}H—CH_2—CH_3} \longrightarrow$$

$$CH_3—(CH_2)_3—\dot{C}H_2 + H_2C = CH—CH_2—CH_3 \text{ and so on.}$$

$$CH_3\dot{C}H_2 \longrightarrow CH_2 = CH_2 + \dot{H}$$

Radicals having no C—C bond in the β position give rise to H atoms.

Termination

$$\dot{C}H_3 + \dot{C}H_3 \longrightarrow CH_3—CH_3$$

$$2\ CH_3—\dot{C}H_2 \longrightarrow CH_3—CH_2—CH_2—CH_3$$

$$CH_3—\dot{C}H_2 + \dot{H} \longrightarrow CH_3—CH_3$$

Cycloalkanes are more stable to cracking than corresponding paraffins. However, if cracked they give mainly diolefins. Aromatics are quite stable and are not usually changed by cracking. However, the alkyl side chains do undergo cracking like alkanes, leaving the methyl group on the aromatic moiety.

(3) **Bergius process :** The low ash coal is *finely powdered* and made into a *paste* with *heavy oil* and then a *catalyst* (composed of tin or nickel oleate) is

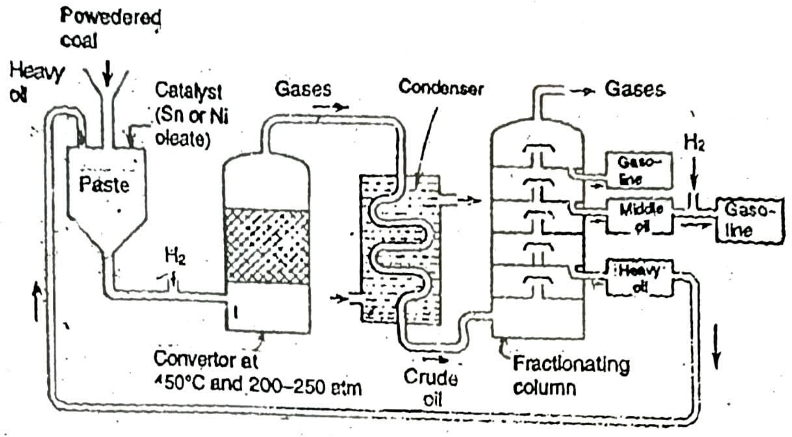


Fig. 11. Bergius process of hydrogenation of coal to gasoline.

incorporated. The whole is heated with hydrogen at 450°C and under a pressure 200–250 atm for about 1.5 hours, during which hydrogen combines with coal to form *saturated hydrocarbons*, *which decompose at prevailing high temperature and pressure to yield low-boiling liquid hydrocarbons.* The issuing gases (from the reaction vessel) are led to *condenser*, where a liquid resembling crude oil is obtained, which is then *fractionated* to get : (*i*) *gasoline*, (*ii*) *middle oil*, and (*iii*) *heavy oil*. The latter is used again for making paste with fresh coal dust. The middle oil is *hydrogenated in vapour-phase* in presence of a solid catalyst to yields more gasoline. *The yields of gasoline in about 60% of the coal dust used.*

2.21 REFINING OF GASOLINE

The **straight-run gasoline** (obtained either from fractionation of crude petroleum or by synthesis) *contains some undesirable unsaturated straight-chain hydrocarbons and sulphur compounds*. The former gets oxidised and polymerized, thereby causing *gum and sludge formation* on storing. Sulphur compounds lead to *corrosion* of internal combustion engine.

Characteristics of an ideal gasoline : (1) It must be cheap and readily available. (2) It must burn clean and produce no corrosion, etc., on combustion. (3) It should mix readily with air and afford uniform manifold distribution, *i.e.*, it should easily vaporise. (4) It must be knock-resistant. (5) It should not preignite easily. (6) It should not tend to decrease the volumetric efficiency of the engine. (7) It must have a high calorific value.

Refining : (1) The *sulphur compounds* are, generally, removed by treating gasoline with an alkaline solution of sodium plumbite with controlled addition of S. This refining process (called '*sweetening*') converts sulphur compounds into disulphides (*Doctor's process*).

$$2\,RSH + Na_2PbO_2 \longrightarrow \underset{\text{Lead plumbite}}{Pb(SR)_2} + 2\,NaOH$$

$$Pb(SR)_2 + S \longrightarrow PbS\,(s) + \underset{\text{Disulphide}}{RSSR}$$

The PbS (*s*) is removed by filtration. Since the disulphides in gasoline are also objectionable, so the the disulphides so-formed are extracted with a suitable solvent.

(2) Olefines and colouring matter of gasoline are, usually, removed by percolating gasoline through '*fuller's earth*', which adsorbs preferentially only the colours and olefins.

(3) After the refining of gasoline, some *inhibitors* are added. These retard the oxidation reactions, thereby improving storing qualities of gasoline.

Even after refining, the gasoline does not have good combustion qualities and it is, generally, *blended* suitably with other fractions produced by catalytic cracking processes to meet the required specifications.

2.20 SYNTHETIC PETROL

Petrol is synthesised by any of the following three methods :

(1) Polymerization : The gases obtained as a by-product from cracking of heavy oils, etc., contain *olefins* (like *ethylene, propene* and *butenes*) and *alkanes* (such as *methane, ethane, propane* and *butane*). When this gaseous mixture is subjected to high pressure and high temperature, with or without the presence of catalyst, it *polymerises* to form higher hydrocarbons, resembling gasoline, called **polymer gasoline.**

$$\underset{\text{(Propene)}}{CH_3.CH=CH_2} + \underset{\text{(Butene–1)}}{CH_3.CH_2.CH=CH_2} \xrightarrow{\text{Pressure, heat and/or catalyst}} \underset{\text{5–Methyl hexene–1}}{CH_2=CH.CH_2.CH_2.CH(CH_3)_2}$$

The polymerization is of *two* types :

(*i*) ***Thermal polymerization*** in which polymerization of cracked gases is carried out at 500–600°C and 70–350 kg/cm^2 pressure. The product is gasoline and gas oil mixture, which are separated by fractionation.

(*ii*) ***Catalytic polymerization*** is carried out in presence of catalyst like phosphoric acid. In this case, lower temperature of 150–200°C is employed. Products are gasoline and unpolymerized gas. The latter is separated and recycled for polymerization.

(2) Fischer-Tropsch method : *Water gas* ($CO + H_2$), produced by passing steam over heated coke, is mixed with hydrogen. The gas is purified by passing through Fe_2O_3 (to remove H_2S) and then into a mixture of $Fe_2O_3 . Na_2CO_3$ (to remove organic sulphur compounds). The purified gas is compressed to 5 to 25 atm and then led through a *convertor* (containing a catalyst, consisting of a mixture of *100 parts cobalt, 5 parts thoria, 8 parts magnesia, and 200 parts keiselgular earth*), maintained at about 200–300°C. A mixture of saturated and unsaturated hydrocarbons results :

$$n\,CO + 2n\,H_2 \longrightarrow C_nH_{2n} + n\,H_2O$$
$$n\,CO + (2n+1)\,H_2 \longrightarrow C_nH_{2n+2} + n\,H_2O$$

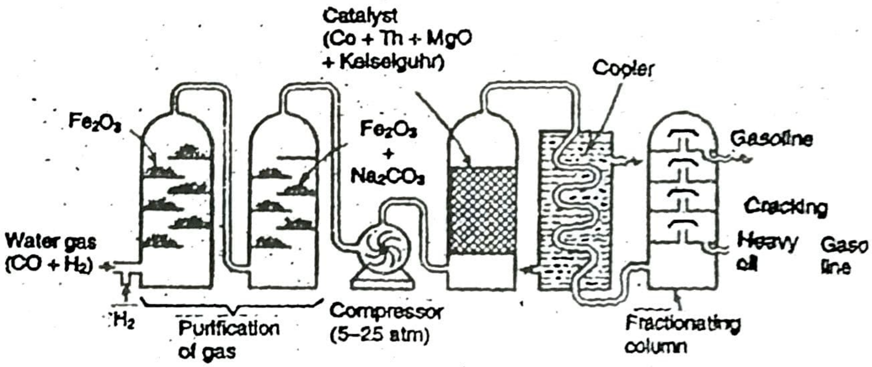


Fig. 10. Fisher-Tropsch method.

The reaction is *exothermic*, so outcoming hot gaseous mixture is led to a *cooler*, where a liquid resembling *crude oil* is obtained. The crude oil thus obtained is then *fractionated* to yield : (*i*) gasoline, and (*ii*) high-boiling heavy oil. The heavy oil is reused for cracking to get more gasoline.

The hydrogen thus-evolved during catalytic reforming is used to : (*a*) hydrogenate alkenes, (*b*) promote cracking of large alkane molecules (*hydrocracking*), and (*c*) remove sulphur in the feed-stock as H_2S gas.

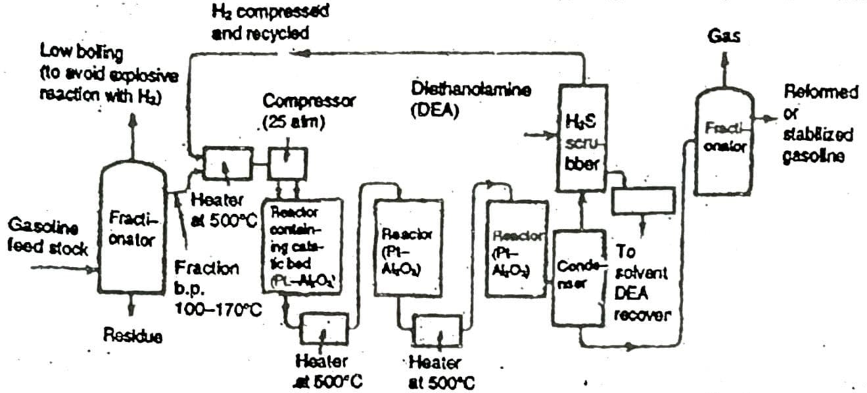


Fig. 13. Fixed-bed catalytic reforming process. (Plat- forming ~~Pro~~ Process

The hydrogen evolved is used to hydrogenate alkenes, promote cracking of larger alkane molecules (hydrocracking) and also to remove S in the feedstock as H_3S.

In the plat-forming process, the feedstock is heated and fractionated to remove low-boiling constituents, water and oxygen (to avoid any explosive reaction with hydrogen). The fraction (b.p. = 100–190°C) is mixed with compressed hydrogen and heated to 500°C. The mixture compressed to about 35 atm passes through a series of three reactors each containing the catalyst bed. The reforming reactions are endothermic, and hence the vapours are preheated before passing from one reactor to the other. The products are then allowed to separate into a liquid phase and a gas phase consisting of H_2 and H_2S (derived from S compounds in the feed). The H_2S from the gas phase is absorbed in diethanolamine (DEA) and a part of the hydrogen is recycled. Any excess hydrogen is used for other purposes. The DEA can be regenerated by boiling and is used again for scrubbing. The residue from the separator is fractionated to remove the gases and also the higher-boiling fractions. The liquid fractions are called *plat-formates*. The catalyst is not regenerated once it becomes inactive, but is replaced. The mechanisms of reforming reactions are speculative. While dehydrogenation catalysts are effective in dehydrogenation of cycloalkanes, dehydrocyclization requires dual function (acidic and dehydrogenation) catalysts. The alkene derived from dehydrogenation of an alkane is adsorbed on the catalyst to undergo successive dehydrogenations. The mechanism has not been well understood. Isomerization reactions are believed to proceed via dehydrogenation of alkane to alkene followed by protonation to give a carbonium ion.

ⓑ

REFORMING

Reforming *is a process of bringing about* ***structural modifications*** *in the components of straight-run gasoline (prepared by the fractional distillation of the crude oil), with the primary object of improving its anti-knock characteristics.* It is carried out either *thermally* or in the presence of a *catalyst*.

(1) **Thermal reforming** is carried out in a *reactor* (or heater) at 500–600°C and a pressure of 85 atm. The feed-stock is straight-run gasoline. To avoid the formation of gas (at the expense of gasoline), the conditions are controlled carefully by *quenching* (rapid cooling) the products by spray of cold oil. The reformed products are then fractionated to remove residual gas (*stabilizing*).

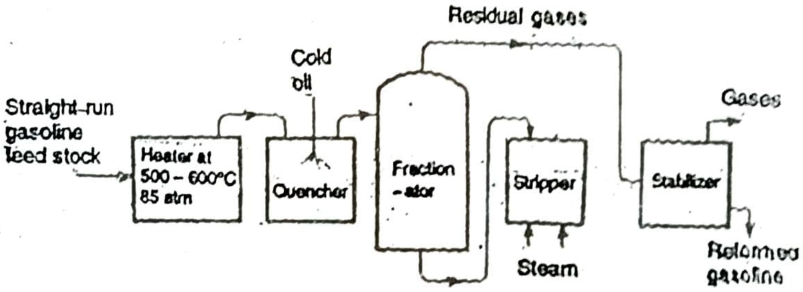
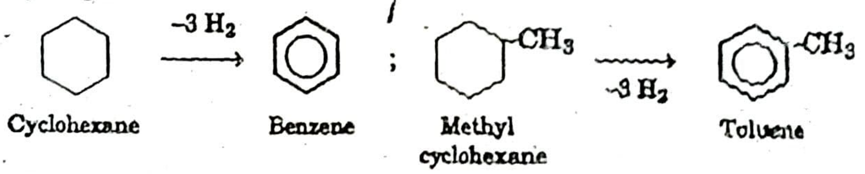


Fig. 12. Thermal reforming of straight-run gasoline.

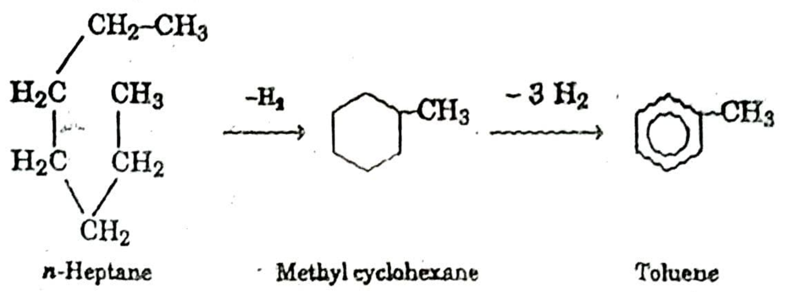
During thermal reforming, some cracking also occurs to yield alkanes and alkenes ; and these might undergo dehydrogenation, followed by cyclization (*dehydrocylization*) to yield naphthalenes (*aromatization*). Conversion of *n*-alkanes to branched-chain alkanes also takes place during thermal reforming.

(2) **Catalytic reforming :** To get better grade and yield of gasolines, catalytic reforming [Pt (0.75%) supported on alumina] is carried out by using either a fixed-bed or fluidized-bed at 460–530°C and 35-50 atmospheric pressure. The main *reactions* during catalytic reforming process are :

(*i*) *Dehydrogenation* :



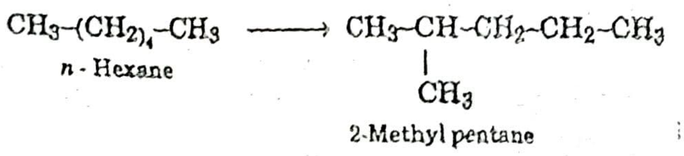
(*ii*) *Dehydrocyclization* :



(*iii*) *Hydrocracking* :

$$\underset{n\text{-Decane}}{CH_3-(CH_2)_8-CH_3} + H_2 \xrightarrow{[Pt]} 2\,\underset{n\text{-Pentane}}{CH_3-(CH_2)_3-CH_3}$$

(*iv*) *Isomerization* :



$$\underset{n\text{-Hexane}}{CH_3-(CH_2)_4-CH_3} \longrightarrow \underset{\text{2-Methyl pentane}}{CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CH_2-CH_3}$$

(b) ***Moving-bed catalytic cracking*** : The solid catalyst is *very finely powdered*, so that it behaves almost as a *fluid*, which can be circulated in gas stream. The vapours of *cracking stock* (gas oil, heavy oil, etc.) mixed with *fluidised catalyst* is forced up into a large *reactor 'bed'* in which cracking of the heavier into lighter molecules occurs (*see* Fig. 9). Near the top of the reactor, there is a centrifugal separator (called *cyclone*), which allows only the cracked oil vapours to pass on to the *'fractionating column*, but retains all the catalyst powder in the reactor itself. The catalyst powder gradually becomes *heavier*, due to coating with carbon, and settles to the bottom, from where it is forced by an air blast to *regenerator* (maintained at 600°C).

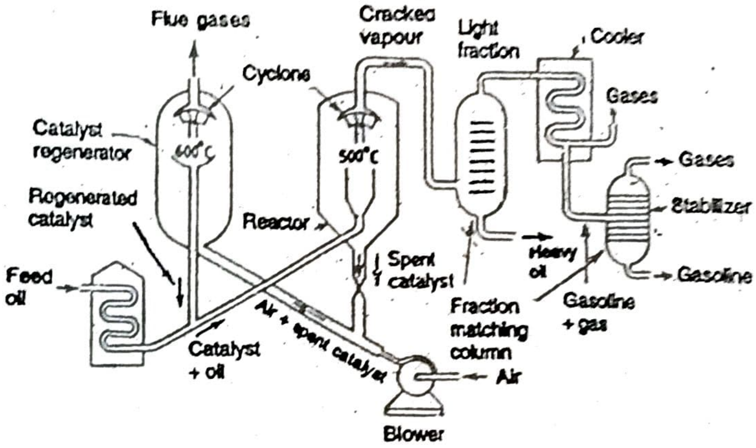


Fig. 9. Moving-bed type catalytic cracking.

In regenerator, carbon is burnt and the regenerated catalyst then flows through a *stand-pipe* for mixing with fresh batch of incoming cracking oil. At the top of the regenerator, there is a *separator*, which permits only gases (CO_2, etc.) to pass out, but holds back catalyst particles.

(2) **Catalytic cracking :** The quality and yield of gasoline produced by cracking can be greatly improved by using a suitable *catalyst* like aluminium silicate, $Al_2(SiO_3)_3$ or alumina, Al_2O_3.

Advantages : (1) The yield of petrol is *higher*. (2) The quality of petrol produced is *better*. (3) *No external fuel* is necessary for cracking. The heat required for cracking is derived from the coal, embedded in the catalyst. (4) A much *lower pressure* (about 1–5 kg/cm^2) is needed in catalytic cracking. (5) The cracking process can easily be controlled, so the desired products can be obtained. (6) The evolution of by-product gases can be minimised, thereby the yield of desired petrol is *higher*. (7) The product of cracking contains a higher amount of aromatic and hence, it possesses *better anti-knock* characteristics. (8) Isomerization to branched-chain compounds (*iso*-paraffins) occur, thereby *better petrol* is produced. (9) The product contains a very little amount of undesirable S, because a major portion of it escapes out as H_2S gas, during cracking. (10) The percentage of gum or gum-forming compounds is *very low*. (11) Catalysts are selective in their action and, therefore, they permit cracking of *only* the high-boiling hydrocarbons. (12) In presence of catalyst, cracking is more of naphthenic materials than of paraffinic. So the products of catalytic cracking are *more paraffinic*. (13) Decomposition of aromatics removes only the side chains, but *no ring itself is broken.*

There are *two* methods of catalytic cracking in use :

(a) ***Fixed-bed catalytic cracking :*** The oil vapours are heated in a pre-heater to cracking temperatures (420–450°C) and then forced through a catalytic chamber (containing artificial clay mixed with zirconium oxide) maintained at 425–450°C and 1.5 kg/cm^2 pressure. During their passage through the tower, about 40% of the charge is converted into gasoline and about 2-4% carbon is formed. *The latter gets adsorbed on the catalyst bed.* The vapours produced are then passed through a *fractionating column*, where heavy oil fractions condense. The vapours are then led through a *cooler*, where some of the gases are condensed along with gasoline and uncondensed gases move on. The gasoline containing some dissolved gases is then sent to a '*stabilizer*, where the dissolved gases are removed and pure gasoline is obtained (*see* Fig. 8).

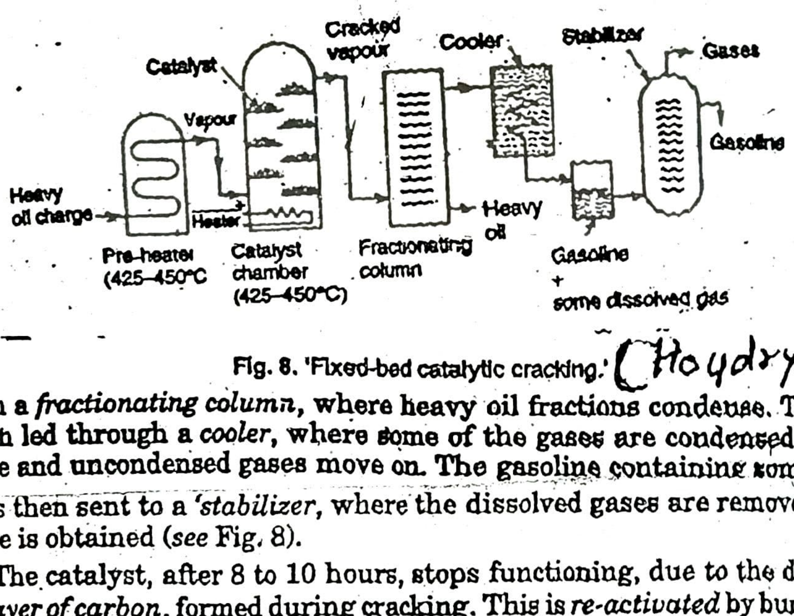


Fig. 8. 'Fixed-bed catalytic cracking.' (Hoydry Process)

The catalyst, after 8 to 10 hours, stops functioning, due to the deposition of *black layer of carbon*, formed during cracking. This is *re-activated* by burning off the deposited carbon. *During the re-activation interval, the vapours are diverted through another catalyst chamber.*

2.27 NON-PETROLEUM FUELS

1. **Benzol** *is a product of coal carbonization, having a distillation range of 70–150°C and it contains about 70% benzene (C_6H_6), 18% toluene ($C_6H_5CH_3$), 6% xylenes [$C_6H_4(CH_3)_2$], and rest other hydrocarbons.* Its calorific value is about 10,200 kcal/kg and octane rating ranges between 87–90. It is a good fuel for internal combustion engines. *However, its freezing point is 55°C, so it cannot be used in cold climates.* It is mostly used as a *blending agent* with gasoline.

2. **Power alcohol :** *When ethyl alcohol is used as a fuel for internal combustion engine, it is called* '**power alcohol**'. Ethyl alcohol is not used as a prime fuel, but it is only used as *an additive to motor fuel.* ***Blends** containing upto 25% of alcohol with petrol are used.*

Advantages of alcohol-blended petrol : (1) Alcohol has an octane value of about 90 ; while petrol has octane value of 60-70. Consequently, addition of alcohol to petrol *increases* its octane number. Hence, alcohol blended-petrol possesses *better anti-knock* properties. (2) Alcohol-petrol blends have *lesser starting difficulties.* (3) The great advantages of adding alcohol to petrol is that alcohol is capable of *absorbing any traces of moisture* present, which may otherwise find its way into the petrol system.

Disadvantages of alcohol-blended petrol : (1) Alcohol *lowers the calorific value* of petrol, because its calorific value is only two-third that of petrol. (2) Because of its considerable surface tension, alcohol is *difficult to atomize,* particularly at low temperatures. Hence, specific arrangements for starting alcohol-petrol blends in carburetor is to be provided, (3) Alcohol is *easily oxidised* to acids. Hence, alcohol may cause corrosion.

Manufacture of power alcohol : In India, alcohol is manufactured from *molasses,* a viscous semi-solid material, left after the crystallization of sugar from concentrated sugar-cane juice. It contains about *50 to 60% sucrose plus invert sugar (glucose + fructose).* The molasses are *diluted* with water to bring its sugar concentration to about 10-12%. Then, some *nutrients* (like ammonium sulphate and ammonium phosphate) and some sulphuric acid are added to bring its *pH value between 4 and 5.* Then, proper quantity of *yeast* (an enzyme mixture) is added and the temperature is maintained at about 30°C. The *invertase* (of the yeast) converts sucrose into glucose and fructose,

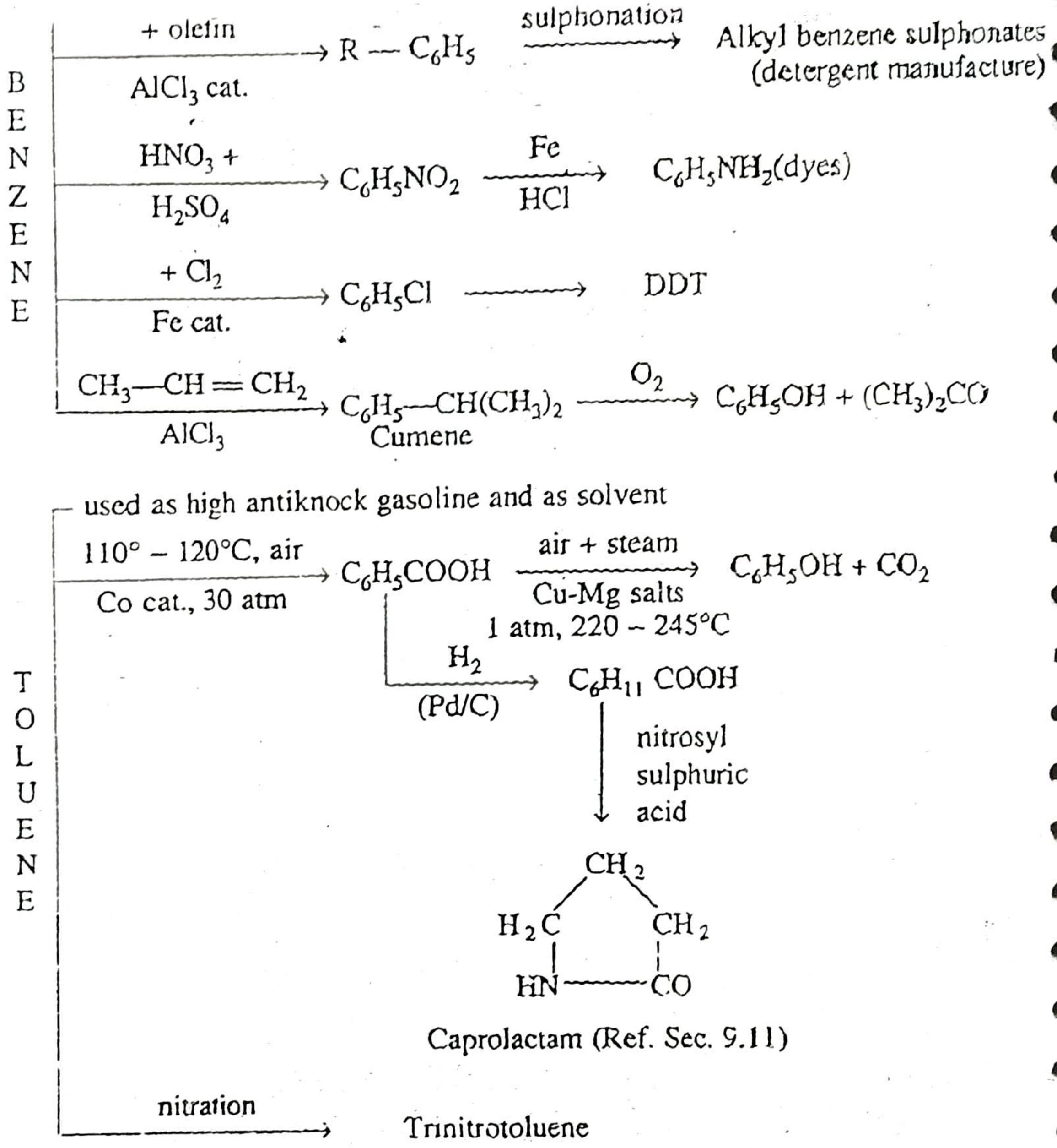
$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[\text{(in yeast)}]{\text{Invertase}} \underset{\text{(Glucose)}}{C_6H_{12}O_6} + \underset{\text{(Fructose)}}{C_6H_{12}O_6}$$

and the *zymase* (of yeast) converts glucose and fructose into *ethyl alcohol* and carbon dioxide, the latter produces a lot of froth during this so-called *fermentation process.*

$$C_6H_{12}O_6 \xrightarrow[\text{(in yeast)}]{\text{Zymase}} 2\,C_2H_5OH + 2\,CO_2(g)$$

The total time required for the completion of the fermentation process is about *36 to 38 hours.* The fermented liquid (called '*wash*') contains about 18-20% alcohol. The wash is then fractionally distilled to get *rectified spirit,* which contains 90-95% alcohol. For getting ***absolute alcohol*** (*i.e.*, 100% alcohol), the rectified spirit is digested with lime for 2 days and then distilled. The first and last fractions are rejected.

(2)



Xylenes are oxidized to the respective phthalic acids and the esters of these are used as plasticizers, in producing polyester fibres, alkyd resins, etc. Ethylbenzene is dehydrogenated to give styrene, a valuable monomer.

7.3 INDUSTRIAL PRACTICE

A large number of the industrially-adopted processes are quite different from those used in laboratory preparations. The yield of the desired end-product is no doubt important but at the same time one has to look into the economies of the preparative method. For a process to be industrially successful, the following criteria are important: (i) the raw materials should be available in plenty and at a reasonable price, (ii) as far as possible there should be either suitable demands for the by-products, if any, formed or the by-product should be capable of being converted back into the reactant economically and (iii) energy requirements must not be too heavy.

ETHENE

$\xrightarrow{+\,HCl}$ C_2H_5Cl (for tetraethyl lead, TEL)

$\xrightarrow[\text{cat. (Wacker Process)}]{+\,O_2 + PdCl_2 - CuCl_2}$ $CH_3CHO \xrightarrow{[O]} CH_3COOH$

$\xrightarrow{+\,CH_3COOH + PdCl_2 + OAc^-}$ Vinyl acetate (for polyvinylacetate, PVAc)

$\xrightarrow[+\,\text{anhyd. } AlCl_3]{+\,C_6H_6}$ $C_6H_5—CH_2—CH_3 \xrightarrow[Fe_2O_3 + Cr_2O_3 + K_2O]{\text{superheated steam}}$ → Styrene (monomer)

$\xrightarrow[\text{100 atm, (oxo-process)}]{+\,CO + H_2\ (Co—Th\ cat.)}$ $CH_3—CH_2—CHO + (C_2H_5)_2CO$

PROPENE

$\xrightarrow{\text{Ziegler cat. } 75°C,\ 10\text{ atm}}$ Polypropylene

$\xrightarrow{(i)\ HOCl,\ (ii)\ Ca\ (OH)_2}$ Propylere oxide ⟶ Glycol esters (polyesters manufacture)

$\xrightarrow[90°C,\ <65\text{ atm}]{C_6H_5C\ (OOH)(H)CH_3}$ Propylene oxide $\xrightarrow[\text{cat.}]{\text{Lithium phosphate}}$ $CH_2 = CH—CH_2OH$

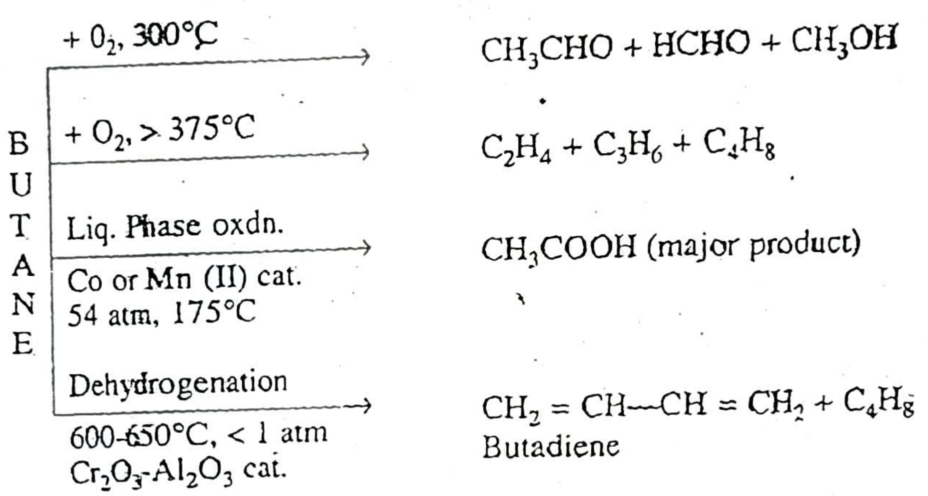
$\xrightarrow{(i)\ H_2SO_4\ (ii)\ \text{hydrolysis}}$ $(CH_3)_2CHOH \xrightarrow[80–120°C]{[O]} (CH_3)_2\,CO + H_2O$

$\xrightarrow[\text{ammoxidation (Sec. 7.8)}]{+\,NH_3 + O_2\ \text{(Bismuth phosphomolybdate)}}$ $CH_2 = CH — CN \xrightarrow[H_2SO_4]{\text{dil}} CH_2 = CH.CONH_2$ (flocculating agent)

$\xrightarrow{+\,CO + H_2\ \text{(oxo-process)}}$ Butanals $\xrightarrow{H_2}$ Butanols

$\xrightarrow[250°C,\ 25\text{ atm}]{+\,C_6H_6 + \text{supported } H_3PO_4}$ $C_6H_5CH\ (CH_3)_2$ cumene $\xrightarrow{+\,O_2}$ $C_6H_5C\ (CH_3)_2OOH$ cumene hydroperoxide $\xrightarrow{\text{dil.}H_2SO_4}$ Phenol + Acetone

$\xrightarrow[200\text{ atm}]{+\,Al\ (C_2H_5)_3,\ 200°C}$ 2-methyl-1-pentene $\xrightarrow{\text{zeolite}}$



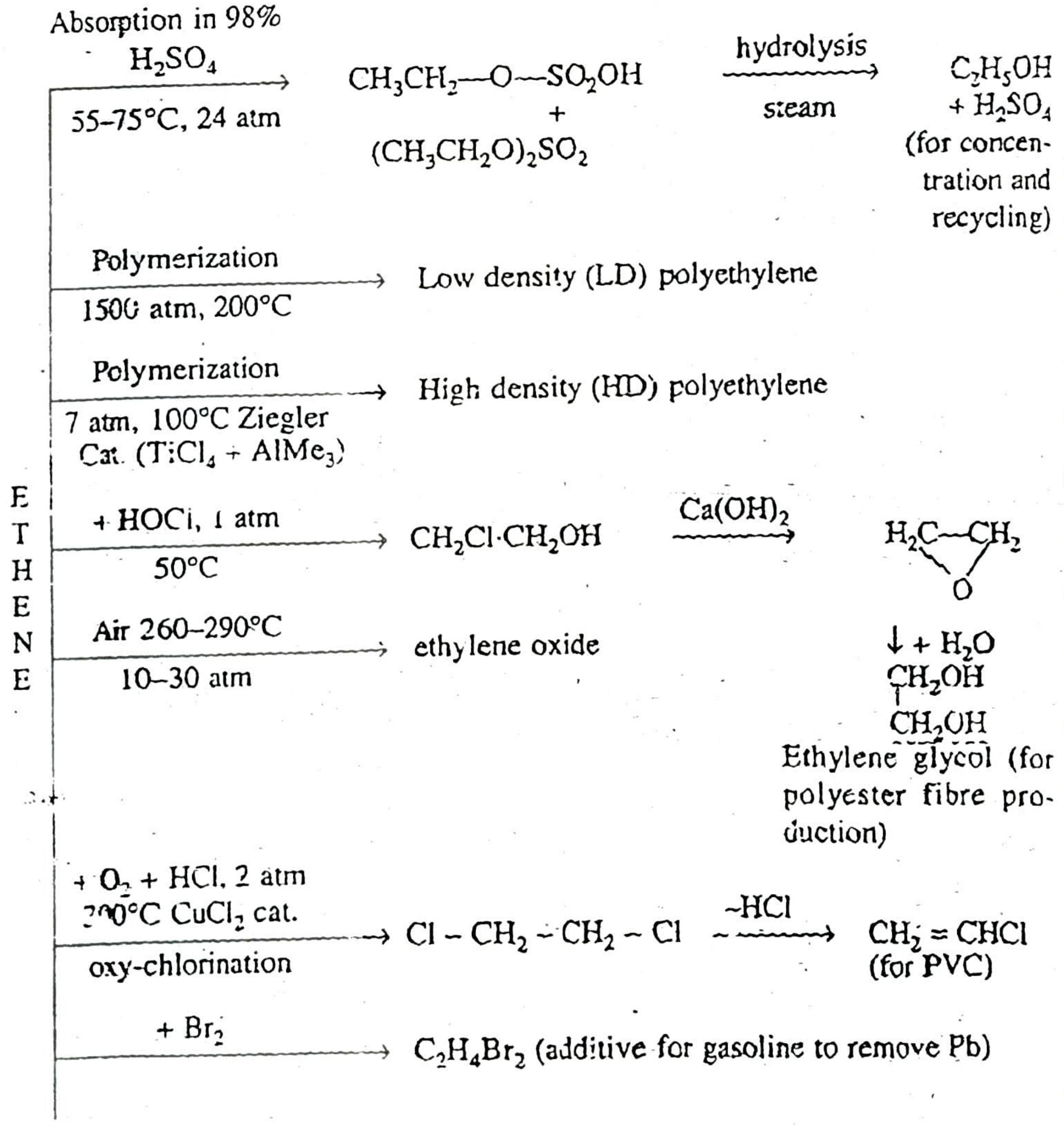
$$\text{BUTANE} \xrightarrow{+ O_2,\ 300°C} CH_3CHO + HCHO + CH_3OH$$

$$\text{BUTANE} \xrightarrow{+ O_2,\ > 375°C} C_2H_4 + C_3H_6 + C_4H_8$$

$$\text{BUTANE} \xrightarrow[\text{Co or Mn (II) cat.; 54 atm, 175°C}]{\text{Liq. Phase oxdn.}} CH_3COOH \text{ (major product)}$$

$$\text{BUTANE} \xrightarrow[600\text{-}650°C,\ < 1\ \text{atm};\ Cr_2O_3\text{-}Al_2O_3\ \text{cat.}]{\text{Dehydrogenation}} \underset{\text{Butadiene}}{CH_2 = CH{-}CH = CH_2} + C_4H_8$$

7.7.2 Petrochemicals from Alkenes



$$\text{ETHENE} \xrightarrow[55\text{–}75°C,\ 24\ \text{atm}]{\text{Absorption in 98% } H_2SO_4} CH_3CH_2{-}O{-}SO_2OH + (CH_3CH_2O)_2SO_2 \xrightarrow[\text{steam}]{\text{hydrolysis}} C_2H_5OH + H_2SO_4 \text{ (for concentration and recycling)}$$

$$\text{ETHENE} \xrightarrow[1500\ \text{atm},\ 200°C]{\text{Polymerization}} \text{Low density (LD) polyethylene}$$

$$\text{ETHENE} \xrightarrow[7\ \text{atm},\ 100°C\ \text{Ziegler Cat. } (TiCl_4 + AlMe_3)]{\text{Polymerization}} \text{High density (HD) polyethylene}$$

$$\text{ETHENE} \xrightarrow[50°C]{+ HOCl,\ 1\ \text{atm}} CH_2Cl{\cdot}CH_2OH \xrightarrow{Ca(OH)_2} \text{ethylene oxide}$$

$$\text{ETHENE} \xrightarrow[10\text{–}30\ \text{atm}]{\text{Air } 260\text{–}290°C} \text{ethylene oxide} \xrightarrow{+ H_2O} \underset{\text{Ethylene glycol (for polyester fibre production)}}{CH_2OH{-}CH_2OH}$$

$$\text{ETHENE} \xrightarrow[\text{oxy-chlorination}]{+ O_2 + HCl,\ 2\ \text{atm},\ 2?0°C\ CuCl_2\ \text{cat.}} Cl - CH_2 - CH_2 - Cl \xrightarrow{-HCl} CH_2 = CHCl \text{ (for PVC)}$$

$$\text{ETHENE} \xrightarrow{+ Br_2} C_2H_4Br_2 \text{ (additive for gasoline to remove Pb)}$$

METHANE

$\xrightarrow[\text{Pt-Rh cat. (1000°C, (1 atm)}]{NH_3 + O_2}$ $HCN + H_2O$ (HCN for preparing acrylonitrile and adiponitrile)

$\xrightarrow[\text{400°C (UV)}]{+ Cl_2 \text{ (10:1)}}$ Mostly CH_3Cl (Silicone resins)

$\xrightarrow{+ Cl_2 \text{ (2:1)}}$ Mixture of chloromethanes (solvents)

$\xrightarrow[\text{680°C, 2 atm}]{+ S \text{ (vapour)}}$ $CS_2 + H_2S$

$CS_2 + H_2S \xrightarrow{+ CH_4} CS_2 + H_2$ (returned to $CS_2 + H_2S$)

$CS_2 + H_2S \xrightarrow{+ Cl_2} CCl_4$ (fluorocarbons)

$\xrightarrow[\text{supply of air}]{\text{Burnt in restricted}}$ Carbon black (rubber industry, vulcanization)

ETHANE

$\xrightarrow[\text{900°C}]{\text{Steam, cracking}}$ C_2H_4

$\xrightarrow[\text{Ethane in excess}]{+ Cl_2}$ $C_2H_5Cl + HCl$

$C_2H_5Cl + HCl \xrightarrow{+ C_2H_4} C_2H_5Cl$ (returned to $C_2H_5Cl + HCl$)

$\xrightarrow[\text{10 atm, 400°C}]{+ HNO_3}$ $C_2H_5NO_2$ (Propellants, solvents)

PROPANE

$\xrightarrow{\text{Cracking}}$ C_2H_4

$\xrightarrow[\text{(chlorinolysis)}]{+ Cl_2\text{, 600°C}}$ $CCl_2 = CCl_2 + CCl_4 + HCl$

$\xrightarrow[\text{1atm}]{+ O_2\text{, 350°C}}$ $HCHO + CH_3CHO + CH_3OH$

$\xrightarrow[\text{1 atm}]{+ O_2 \text{ 400°C}}$ $C_3H_6 + H_2O$

$\xrightarrow{> 450°C}$ $C_3H_6 + C_2H_4 + CH_4 + H_2$

etroleum fractions and products having a higher boiling point (diesel fuels for example) are subjected to hydro-desulphurizing in order to remove S-containing impurities. The oil is hydrogenated under pressure at about 400°C in the presence of Co-Mo oxide catalyst supported on alumina. This process not only removes sulphur compounds as H_2S but also effects reduction of unsaturated compounds. The products are condensed from the gas phase, and H_2S is dissolved out by DEA. H_2S in the liquid phase is removed during heating and fractional distillation. Diesel fuels containing more sulphur than gasoline are hydro-desulphurized to remove sulphur compounds.

Lubricating oils are usually obtained by the vacuum distillation of the heavy residues from paraffin-base crude oils. These are de-waxed, and extracted with phenol or furfural to remove the aromatics and then with liquid propane to remove asphaltic materials.

Kerosene contains, besides paraffins, some aromatic hydrocarbons also. These are extracted with liquid SO_2 (Edeleanu process). The raffinate (the phase immisicble with the solvent) is washed free of SO_2 with aqueous NaOH, and from the extract the valuable aromatics can be recovered.

7.7 PETROCHEMICALS

A large variety of alkanes and alkenes are obtained as byproducts of the physical and/or chemical processing of petroleum and its primary fractions. These can be used as raw materials for the production of chemicals like acetic acid, ethanol, ammonia, vinyl monomers, etc. to name a few. Alternative methods for preparing these chemicals from non-petroleum sources were already known. Chemicals manufactured from raw materials derived from petroleum and its fractions are called *petrochemicals* or petroleum chemicals.

The credit for laying the foundations of the petrochemicals industry must go to USA which found outlets for the alkenes and alkanes from the cracking-refining plants by utilizing these to manufacture chemicals which were traditionally prepared from sources other than petroleum. The raw materials for the manufacture of petroleum chemicals are summarized in Table 7.9 (p. 279).

The separation of the components from a fraction either from refineries or from cracking plants is a difficult and costly process, involving fractional distillation under pressure and condensing the fractions by using refrigerants such as liquid NH_3, liquid C_2H_4 or liquid methane.

7.7.1 Petrochemicals Derived from Alkanes