



SNS COLLEGE OF TECHNOLOGY AN AUTONOMOUS INSTITUTION



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DEPARTMENT OF AGRICULTURAL ENGINEERING

COURSE CODE & NAME: 19AGT301 & HEAT POWER ENGINEERING

III YEAR / V SEMESTER

UNIT : 1 FUELS AND COMBUSTION

TOPIC 5 : Liquid Fuels



LIQUID FUELS



The important liquid fuels are petroleum, petroleum products, tar, alcohols. These are naturally found under the sea surface. Liquid fuels are also obtained synthetically from hydrogenation of coal. Liquid fuels find extensive use in domestic and industrial fields.

Petroleum

- Petroleum or crude oil is a dark greenish brown or black coloured viscous oil found deep in earth's crust. The oil is usually floating over a brine solution and above the oil, natural gas is present. Crude oil containing mixture of paraffinic, olefinic and aromatic hydrocarbons with minor amounts of organic compounds like N, O and S. The average composition of crude oil is C = 80 - 87 %, H = 11-15%, S = 0.1 - 3.5%, (N + O) = 0.1-0.5%.

a) Classification of petroleum

- Petroleum is classified into three types based on variation of chemical nature of crude oil found in the earth.
- i) Paraffinic-base type crude oil: It contains saturated hydrocarbons from CH₄ to C₃₅H₇₂ and little amount of naphthalenes and aromatics.
- ii) Asphaltic-base type crude oil: It contains mainly cycloparaffins or naphthalenes with smaller amount of paraffins and aromatic hydrocarbons.
- iii) Mixed-base type crude oil : It contains both paraffinic and asphaltic hydrocarbons and are generally in the form of semi-solid waxes.



MINING AND REFINING OF PETROLEUM



- The crude oil obtained from the earth crust contains water, sulphur and some unwanted impurities. After removal of water, sulphur and these impurities, the crude oil is separated into various useful fractions by fractional distillation and finally conveyed into desired specific products having different boiling points. The process is called "Refining of Petroleum" and the refining plants are called "Oil refineries". The process of refining involves the following steps.
- **Step -I: Separation of water (Cottrell's process)**
- The crude oil from the oil well is an extremely stable emulsion of oil and salt water. The crude oil is allowed to flow between two highly charged electrodes, where colloidal water droplets coalesce to form large drops, which is then separated out from the oil.
- **Step - II: Removal of harmful impurities**
- a) The presence of NaCl and MgCl in the crude oil can corrode the refining equipment, hence these salts are removed by electrical desalting and dehydration methods.
- b) The sulphur compounds present in the crude oil is removed by treating oil with copper oxide, which results in the formation of copper sulphide (solid), which is then removed by filtration.



FRACTIONAL DISTILLATION

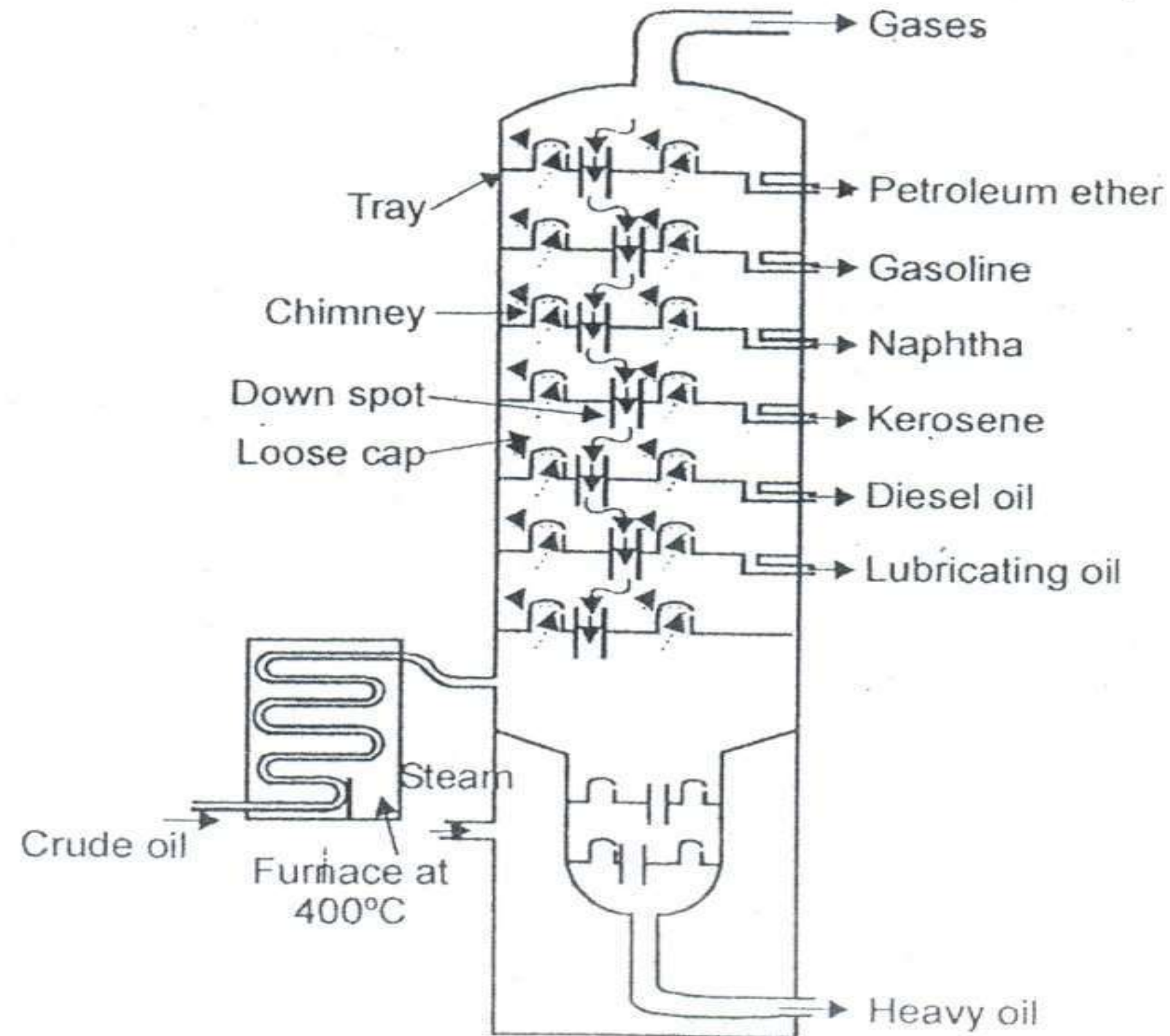


• **Step - III: Fractional distillation**

- The crude oil is then heated to about 400°C in an iron retort, whereby all volatile substances (except asphalt or coke) are evaporated. The hot vapors are then passed up a fractionating column, which is a tall cylindrical tower containing a number of horizontal stainless steel trays at short distances. Each tray is provided with small chimney covered with a loose cap. (Figure)
- When the vapours of the oil go up in the fractionating column, they become gradually cooler and get condensed at different heights of column. The fractions having higher boiling points condense at lower trays whereas the fractions having lower boiling points condense at higher trays. The gasoline obtained by the fractional distillation is called straight --run gasoline. Various fractions obtained at different trays are given in table.



FRACTIONAL DISTILLATION OF CRUDE OIL





Various fractions of crude oil and their composition and uses

Sn.	Name of the fractions	Boiling range (°C)	Composition of Hydrocarbons	Uses
1.	Uncondensed gases	Below 30°C	C ₁ to C ₄	As domestic and industrial fuel under the name LPG
2.	Petroleum ether	30 - 70 °C	C ₅ to C ₇	As a solvent.
3.	Gasoline (or) petrol.	40 - 120 °C	C ₅ to C ₉	As motor fuel, solvent and in dry cleaning.
4.	Naphtha (or) solvent spirit	120. - 180 °C	C ₉ to C ₁₀	As solvent and in dry cleaning.
5.	Kerosene oil.	180 - 250 °C	C ₁₀ to C ₁₆	As fuel for jet engines and an illuminant.
6.	Diesel oil (or) gas oil	250 - 320 °C	C ₁₀ to C ₁₈	As Diesel engine fuel.
7.	Heavy oil.	320 - 400 °C	C ₁₇ to C ₃₀	Production of gasoline by cracking process.



Various fractions recovered from Heavy Oil

Sn. Sn.	Name of the fractions Name of the fractions	Boiling range (°C) Boiling range (°C)	Composition of Hydrocarb ons Composition of Hydrocarb ons	Uses Uses
1.	Lubricating oil	-	C_{17} to C_{20}	Used as lubricants
1.	Lubricating oil	-	C_{17} to C_{20}	Used as lubricants
2.	Petroleum jelly (Vaseline)	-	-	Used in medicines and cosmetics
2.	Petroleum jelly (Vaseline)	-	-	Used in medicines and cosmetics
3.	Paraffin wax	-	C_{20} to C_{28} C_{20} to C_{28}	Used in candles, wax paper, boot polish, etc
3.	Paraffin wax	-		Used in candles, wax paper, boot polish, etc
4.	Grease	-	-	Used as lubricants.
4.	Grease	-	-	Used as lubricants.
5.	Asphalt or bitumen	Above 400°C	C_{30} and above	Used for making roads, water proof roofing, etc
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Cracking

- The decomposition of bigger hydrocarbon molecules into simpler, low boiling hydrocarbons of lower molecular weight is called cracking.
- The gasoline obtained from the fractional distillation of petroleum, has the highest demand as a motor fuel, but the yield of this fractions is only 20-30% (Crude oil) and also quality as straight-run gasoline which is not good an_ hence is used only after proper blending. To overcome these difficulties, the higher boiling fractions (e.g. fuel oil and gas oil) are converted into lower boiling fractions gasoline (petrol) by cracking process.
- The cracked gasoline gives better engine performance i.e., they are suitable for spark - ignition engines of automobiles. In cracking process, higher saturated hydrocarbon molecules are converted into simpler molecules such as paraffinic and olefinic hydrocarbons,
- There are two methods of cracking in use
- 1. Thermal cracking 2. Catalytic cracking



- **Thermal cracking** .
- In this process, the heavy oil is subjected to high temperature and pressure, when the bigger hydrocarbon molecules break down to give smaller molecules of the paraffins, olefins and hydrogen.
- The cracked products are then separated by fractional distillation.
- This process is carried out in liquid phase at a temperature of $475 - 530^{\circ}\text{C}$ and under pressure of 100 kg/cm^2 is called Liquid-phase thermal cracking or at a temperature of $600-650^{\circ}\text{C}$ (heavy oil is vapourised) and under a low pressure of $10-20\text{ kg/cm}^2$, such process is called Vapour-phase thermal cracking.



Catalytic cracking



- In this process, cracking is carried out in presence of a catalyst at lower temperature (300°C to 450°C) and pressures (1 to 5 kg/cm^2). The catalyst like aluminium silicate [$\text{Al}_2(\text{SiO}_3)$] or alumina [Al_2O_3] used in cracking gives higher yield and better quality of gasoline. There are two types of catalytic cracking in use .
 - **i) Fixed-bed catalytic cracking**
 - The heavy oil is passed through the heater, where the oil is vapourised and heated to 400 to 500°C and then forced through a catalytic chambers containing the catalyst of silica alumina gel (SiO_2 , Al_2O_3) or bauxite, is mixed with clay and zirconium oxide maintained at 400 to 500°C and $1.5 \text{ kg}/\text{cm}^2$ pressure. During their passage through the tower, cracking takes place about 30-40% of the charge is converted into gasoline and about 2- 4% carbon is formed which gets deposited on the catalytic bed. (Figure)



- The vapours produced are then passed through a fractionating column, where heavy oil fractions condensed. The vapours are then admitted into a cooler, where some of the gaseous products 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.

- When substantial amount of carbon is deposited on the catalyst bed, during cracking, the catalyst stops functioning. It is reactivated by burning off the deposited carbon in a stream of hot air. During the reactivation of catalyst, the vapours are diverted through another catalyst chamber.

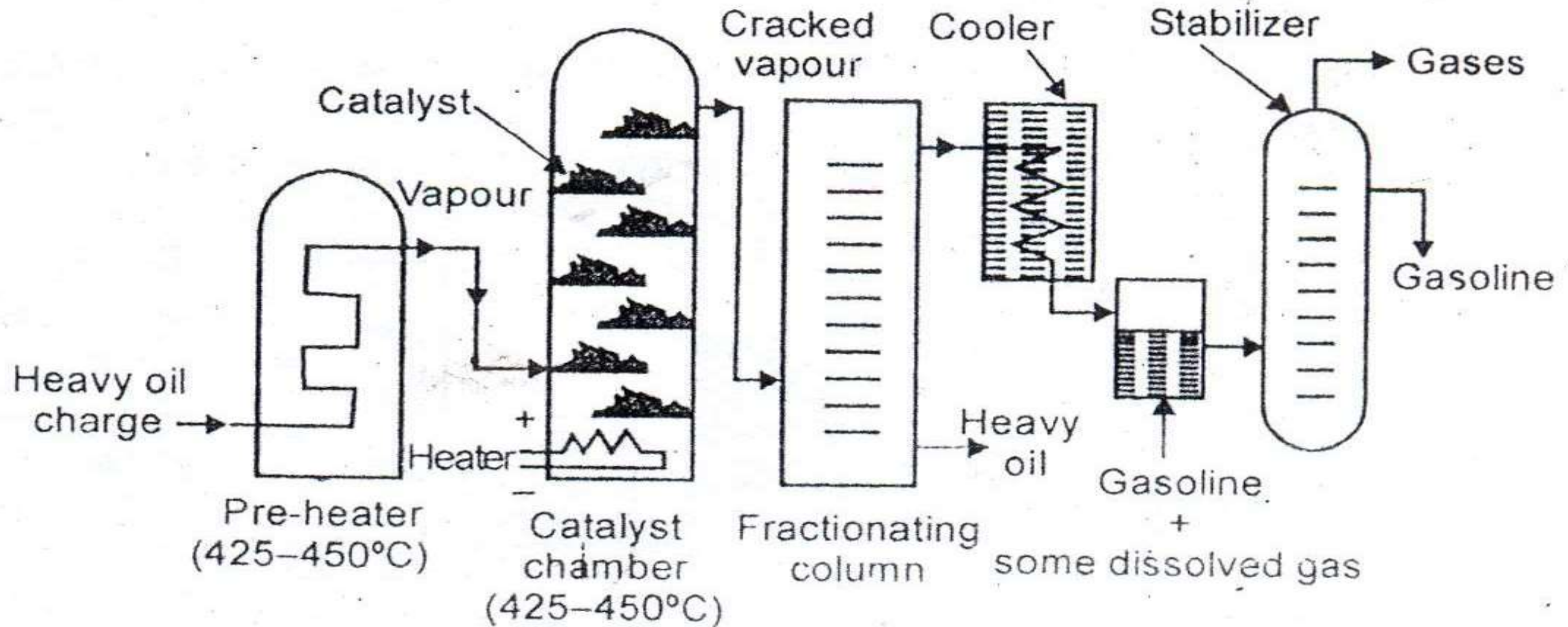


ii) Fluid (Moving)-bed catalytic cracking

- In this process, solid catalyst is 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 fluidized catalyst is forced up into a large reactor bed in which cracking of the heavier molecules into lighter molecules occurs at a temperature of 530°C and pressure of about 3' to 5 kg/cm².
- The top of the reactor, there is a centrifugal separator, which, allows the low boiling lighter molecules move up to the top of the reactor and enter into the fractionating column but retains all the catalyst powder in the reactor itself.
- The carbon deposited on the catalyst powder are burnt off in the regenerator and the temperature rises to about 590°C or more.
- The cracked gases and gasoline are removed from the top of the fractionating column and sent to a cooler, where gasoline is condensed. It is then sent to a stabilizer to recover pure gasoline.
- The product contains a higher proportion of aromatics and iso-paraffins.

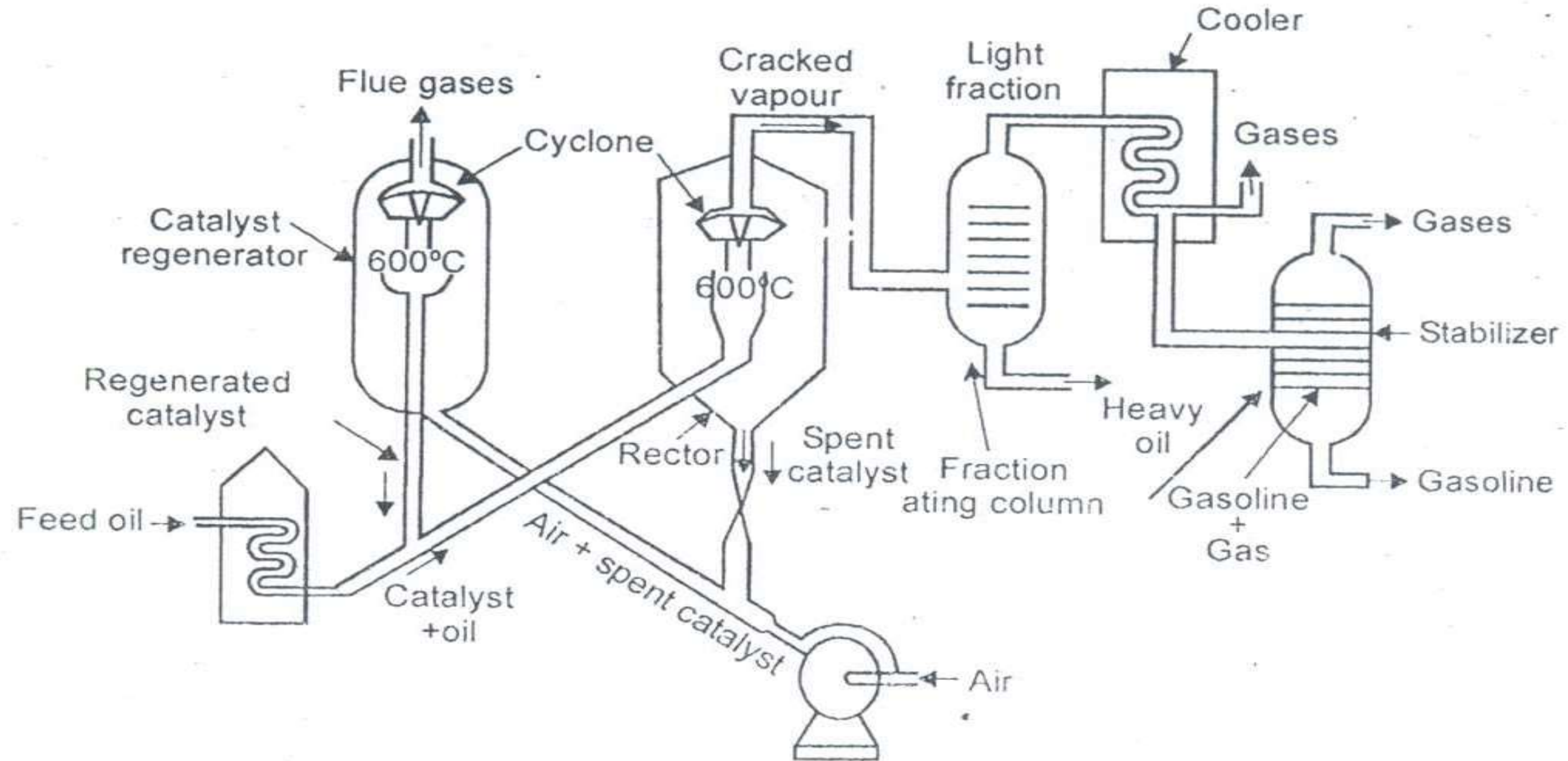


Fixed-bed catalytic cracking





Fluid (Moving)-bed catalytic cracking





• **Synthesis of Gasoline**

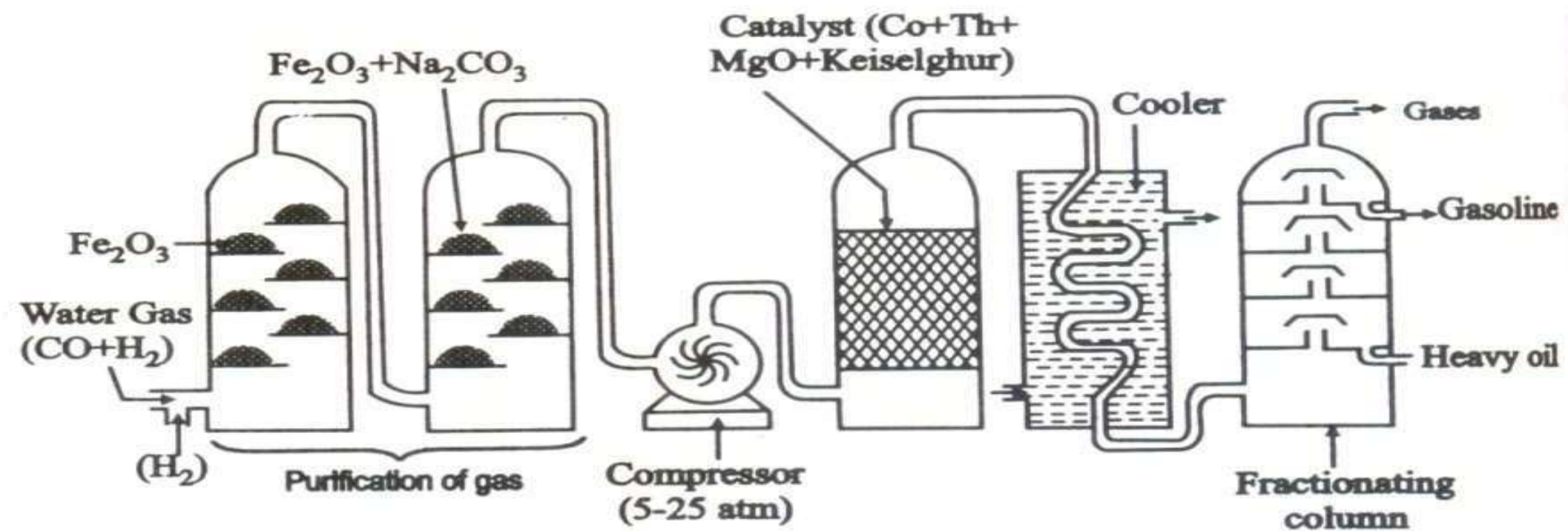
- The gasoline obtained from the fractional distillation of crude petroleum oil is not enough to meet the requirement of the present community due to vast increase of automobiles. Hence an alternate source need of finding out to manufacture synthetic petrol.
- Synthetic petrol can be manufactured by the process of hydrogenation of coal. The preparation of liquid fuels from solid coal is called hydrogenation of coal.
- Gasoline is synthesised by the following methods.
- 1. Fischer- Tropsch process.
- 2. Bergius process.

1. Fischer- Tropsch process

- In this process, coal is first converted into coke. Then water gas is produced by the action of steam over red hot coke. It is mixed with hydrogen and the mixture is compressed to 5-25 atmospheres. The compressed gases are then led through a converter which is maintained at a temperature of 200-300°C. The converter is provided with a suitable catalyst consisting of a mixture of 100 parts cobalt, 5 parts thoria, 8 parts magnesia and 200 parts kieselguhr. A mixture of saturated and unsaturated hydrocarbons occurs as a result of polymerisation.



- The reactions are strongly exothermic. Hence, the hot out coming 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 gasoline and high boiling heavy oil. The heavy oil is used for cracking to get more gasoline



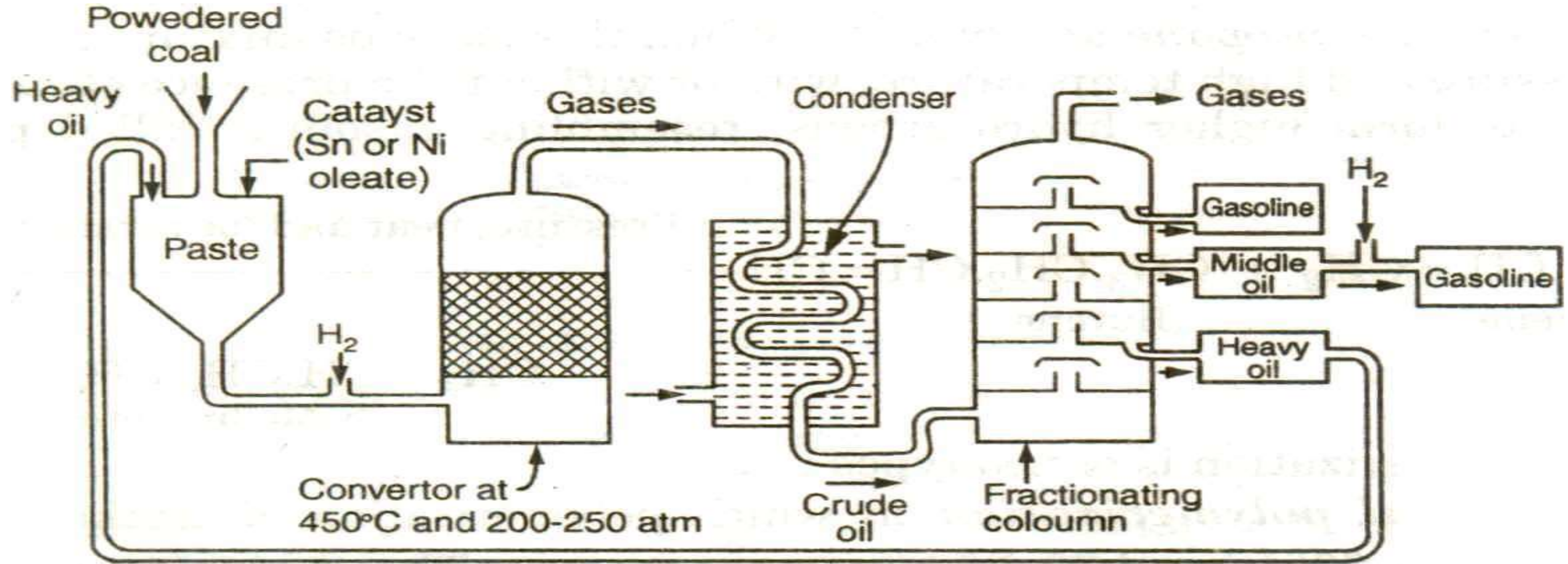


Bergius process.

- This method was developed by Bergius in Germany during the First World War. 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 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.



Bergius process





THANK YOU..!!