CHAPTER : 1

INORGANIC CHEMICALS

1.1 INTRODUCTION

There are many chemical industries which are producing chemical products which are not organic i.e., the product in which no amount or very less amount of carbon content is present are called inorganic products, such as

- Sulfuric Acid (H_2SO_4)
- Sodium Hydroxide (NaOH)
- Chorine (Cl_2)
- Hydrochloric Acid (HCl)
- Nitric Acid (HNO_3)

Sulphuric Acid Industry (DCDA process)

Melting point temperature : 10.4 °C

Boiling point temperature : 340 °C

Contact Process

Raw material : Sulphur , oxygen and catalysts V_2O_5 in pellet form dispersed on a porous carrier.

Process Description

1) Burning of sulphuric in presence of dry atmospheric air (which is dried with help of H_2SO_4). Dry air is required to avoid corrosion problems and fumes in the product)

$$S + O_2 \rightarrow SO_2 \text{ (Highly Exothermic)}$$

2) Product is cooled to 250 °C from 400 °C with the help of a recovery boiler.

3) Then this SO_2 is fed to multistage catalytic converter having beds of V_2O_5 catalyst.

$$S + 1/2\ O_2 \rightarrow SO_2 \text{ (Less Exothermic)}$$

Slowest Step

In the first bed, conversion of about 80% is achieved and temperature is maintained at 550 – 600 °C. Then it is passed to second bed to achieve 98% conversion.

4) The SO_3 product so formed is mixed with oleum absorption tower followed by sulphuric acid absorption tower to from 99% conc. oleum and H_2SO_4.

$$H_2SO_4 + SO_3 \rightarrow H_2S_2O_7$$

$$SO_3 + H_2O \rightarrow H_2SO_4$$

Advantage of V_2O_5

I. Immune to poison

II. Required in less amount (almost 10 kg in 1 ton production of H_2SO_4)

III. Low initial capital investment.

IV. Only 5% is to be replaced per year.

Disadvantage

I. Less reactive to increase reactivity , we use dilute SO_2 i.e., O_2 / SO_2 → high.

II. Feed to catalytic converter is 7 – 10 % SO_2 before V_2O_5 ,platinum was used as a catalyst because of high reactivity but it gets easily poisoned and high capital investment , that's why V_2O_5 is used.

Chamber Process	Contact Process
Previously used	Now used
80% conc. H_2SO_4 produced	98% conc. H_2SO_4 achieved
Homogenous process catalyst used which is Fumes of nitrous acid.	Heterogeneous process catalyst V_2O_5 (Solid)

Chlor Alkali

Production of NaOH and Chlorine

$$Cl^- \rightarrow \frac{1}{2}Cl_2 + e^-$$

$$Na^+ + Hg \rightarrow NaHg$$

$$NaHg + H_2O \rightarrow NaOH + Hg + \frac{1}{2}H_2$$

$$NaCl + H_2O \rightarrow NaOH + Hg + \frac{1}{2}H_2 + \frac{1}{2}Cl_2$$

Step. (I) Brine is purified by adding Na_2CO_3 and NaOH . H_2SO_4 is used for drying purpose.

Step. (II) The brine is then fed to diaphragm cell which then produces 10 – 12 % concentrated NaOH, which is concentrated to 50 % by multi effect evaporator.

Step. (III) More purified brine is then fed to mercury cell and then to denuding tower to produce 70% conc. NaOH.

Step. (IV) Chlorine is washed, dried with H_2SO_4 and then refrigerated and stored.

Difference between Diaphragm Cell, Mercury Cell and Membrane Cell Process.

Diaphragm Cell Process	Mercury Cell Process	Membrane Cell Process
Less purified brine can be used	More purified brine is required	More purified brine is required
10 – 12 % conc. NaOH is produced And that's why the product needs further Concentration.	70% Conc. NaOH and therefore no further concentration is required	33% Conc. NaOH is produced and therefore no further concentration is re required.
Asbestos is used	Mercury is used	Membrane is used.
Chlorine produced contains oxygen	Chlorine produced is pure and free from oxygen	Chlorine produced contains O_2
Energy consumption is very less	Energy consummation is high	Energy consumed is intermediate of that of mercury cell process.
Problem of disposing asbestos	Problem of disposing mercury	Environment friendly. Present high cost and short life time of membrane is the main challenge to this process.

end use are paper and pulp, soap and detergent, fertilizer pharmaceuticals etc.

CHAPTER-II

FERTILIZERS

2.1 INTRODUCTION

Any natural or manufactured material, which contains at least 5% of one or more of the three primary nutrients (N, P_2O_5, K_2O) can be called fertilizer. Industrially manufactured fertilizers are called mineral fertilizers.

Fertilizers that contains only one primary nutrient are referred to as straight fertilizers. Those containing two or three primary nutrients are called multi-nutrient fertilizers, sometimes also binary (two – nutrient)or ternary (three- nutrient) fertilizers.

Where, the primary nutrients are commonly expressed as percent $N - P_2O_5 - K_2O$ (sometimes with the addition of Mg – S – trace elements). They are always given in this sequence. Thus , in an 17-17-17 formula, the first number is the percentage of N, the second number the percentage of P_2O_5 and the third number the percentage of K_2O.

Some of the most important (as well as the regionally important) straight fertilizers are as follows:

- Urea
- Ammonium sulphate
- Calcium Ammonium Nitrate
- Single Super Phosphate
- Triple Super Phosphate
- NPK (Nitrogen – Phosphorous – Pottassium)

2.2 UREA

Urea , with 46 % N , is the world's major source of nitrogen due to its high concentration and its usually attractive price per unit of N. However , its application requires exceptionally good agricultural practices to avoid in particular, evaporation losses of ammonia to the air. Urea should be applied only when it is possible either to incorporate it into the soil immediately after spreading or when rain is expected within the few hours following the application.

2.2.1 UREA SYNTHESIS

Urea is made from ammonia and carbon dioxide. The ammonia and carbon dioxide are fed into the reactor at high pressure and temperature, and the urea is formed in a two step reaction.

$$2NH_3 + CO_2 \rightleftharpoons NH_2COONH_4 \text{ (Ammonium Carbamate)}$$

$$NH_2COONH_4 \rightleftharpoons H_2O + NH_2CONH_2 \text{ (Urea)}$$

The urea contains un-reacted NH_3 and CO_2 and ammonium carbamate. As the pressure is reduced and heat applied the NH_2COONH_4 decomposes to NH_3 and CO_2. The ammonia and carbon dioxide are recycled.

The urea solution is then concentrated to give 99.6 % w/w molten urea, and granulated for use as fertilizer and chemical feedstock.

2.2.2 THE UREA MANUFACTURING PROCESS

Urea is produced from ammonia and carbon dioxide in two equilibrium reactions :

$$2NH_3 + CO_2 \rightleftharpoons NH_2COONH_4 \text{ (Ammonium Carbamate)}$$

$$NH_2COONH_4 \rightleftharpoons H_2O + NH_2CONH_2 \text{ (Urea)}$$

The urea manufacturing process, as shown in the figure (a) given below, is designed to maximize these reactions while inhibiting biuret formation:

$$NH_2CONH_2(\,Urea\,) \rightleftharpoons \underset{\text{(biuret)}}{NH_2CONHCONH_2} + NH_3$$

This reaction is undesirable , not only because it lowers the yield of urea, but because biuret burns the leaves of plants. This means that urea which contains high levels of biuret is unsuitable for use as a fertilizer. The structure of these compounds are shown in figure (b) given below.

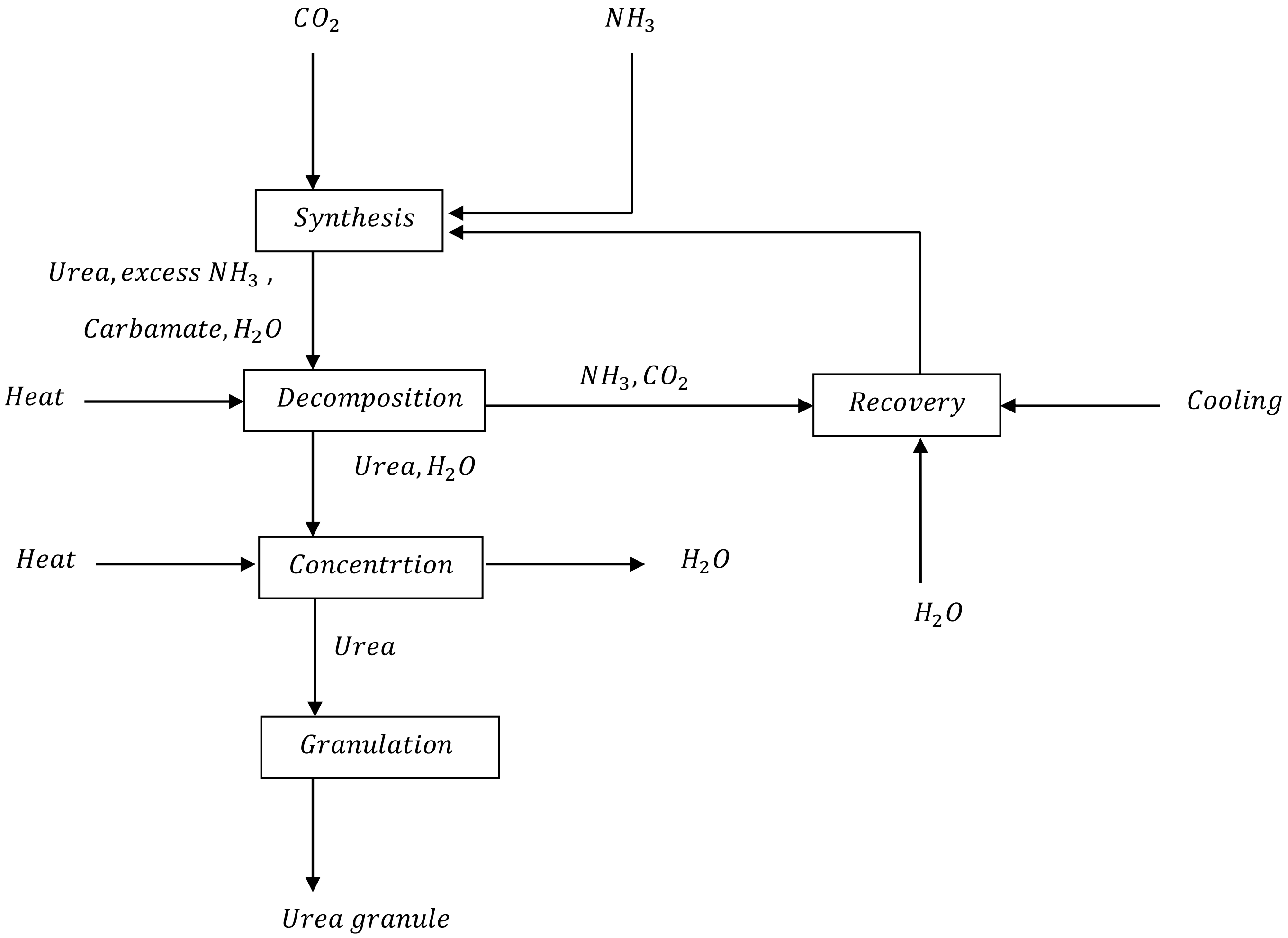


Figure (a): Schematic representation of Urea synthesis

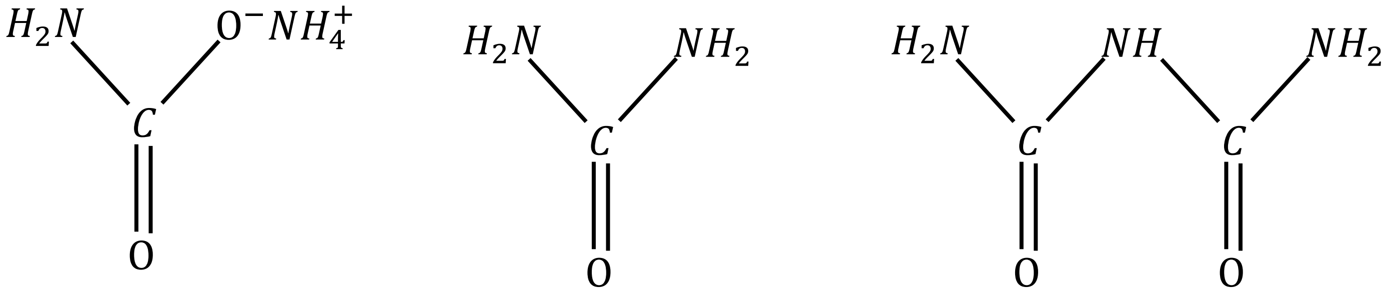


Figure (b): Some chemicals of interest in urea production

STEP-1 SYNTHESIS

A mixture of compressed CO_2 and ammonia at 240 bar (gauge) is reacted to form ammonium carbamate. This is an exothermic reaction, and heat is recovered by a boiler which produces steam. The first reactor achieves 78 % conversion of the carbon dioxide to urea and the liquid is then purified. The second reactor receives the gas from the first reactor and recycles solution.

STEP-2 PURIFICATION

The major impurities in the mixture at this stage are water from the urea production reaction and unconsumed reactants (ammonia , carbon dioxide and ammonium carbonate). The unconsumed reactants are removed in three stages.
Firstly, the pressure is reduced from 240 bar (gauge) to 17 bar (gauge) and the solution is heated , which causes the ammonia carbamate to decompose to ammonia and carbon dioxide.

$$NH_2COONH_4 \rightleftharpoons 2\,NH_3 + CO_2$$

At the same time, some of the ammonia and carbon dioxide flash off. The pressure is then reduced to 2.0 bar (gauge) and finally to – 0.35 bar (gauge), with more ammonia and carbon dioxide being lost at each stage. By the time the mixture is at – 0.35 (gauge) a solution of urea dissolved in water and free of other impurities remains.

At each stage the unconsumed reactants are absorbed into water solution which is recycled to the secondary reactor. The excess ammonia is purified and uses as feedstock to the primary reactor.

STEP – 3 CONCENTRATION

75% of the urea solution is heated under vacuum, which evaporates off some of the water, increasing the urea concentration from 68% w/w to 80 % w/w. At this stage some urea crystals also form. The solution is then heated from 80 to 110 °C to re-dissolved these crystals prior to evaporation. In the evaporation stage molten urea (99% w/w) is produced at 140 °C.

The remaining 25 % of the 68% w/w urea solution is processed under vacuum at 135 °C , in a two series evaporator-separator arrangement.

STEP-4 GRANULATION

Urea is sold for fertilizer as 2 – 4 mm diameter granules. These granules are formed by spraying molten urea onto seed granules which are supported on a bed of air. This occurs in a granulator which receives the seed granules at one end and discharges enlarged granules at the outer as molten urea is sprayed through nozzles. Dry cool granules are classified using screens. Oversized granules are crushed and combined with undersized ones for use as seed. All dust air from the granulator is removed by a fan into a dust scrubber, which removes the urea with a water solution then discharges the air to the atmosphere. The final product is cooled in air, weighed and conveyed to bulk storage ready for sale.

Table : Urea granule specification

Component	Concentration
Nitrogen	46% minimum by weight
Biuret	1.0% maximum by weight
Moisture content	0.3% maximum by weight
Sizing	90% , 2 – 4 mm by weight

2.2.3 UTILITIES

HEAT RECOVERY

The heat of the reaction in which ammonia carbamate produces steam at 7 bar (gauge). This is used in the decomposition and evaporation sections for heating.

AMMONIA AND CARBON DIOXIDE RECOVERY

During urea decomposition a mixture of gaseous carbon dioxide and ammonia is collected and absorbed into a dilute aqueous urea solution. This mixture is recycled by being fed back into the secondary urea reactor. The excess ammonia is condensed and used as feed stock to the primary reactor.

WATER RECYCLING

Evaporated water from the concentration step is used during the third stage of decomposition as the initial recycle solution .

2.3 AMMONIA

Ammonia or azane is a compound of nitrogen and hydrogen with the molecular formula NH_3 . It is a colorless gas with a characteristic pungent smell. Ammonia contributes significantly to the nutritional needs of terrestrial organisms by serving as a precursor to food and fertilizers. Ammonia , either directly or indirectly, is also a building block for the synthesis of many pharmaceuticals and used in many commercial cleaning products.

2.3.1 AMMONIA SYNTEHIS

Ammonia is synthesized from hydrogen (from natural gas) and nitrogen (from the air). Natural gas contains some sulfurous compounds which damage the catalyst used in this process. These are removed by reacting them with zinc oxide.

Examples : $ZnO + H_2S \rightarrow ZnS + H_2O$

The methane from the natural gas is then converted to hydrogen:

$CH_4 + H_2O \leftrightarrows 3\,H_2 + CO$

$CH_4 + 2\,H_2O \leftrightarrows 4\,H_2 + CO_2$

$CO + H_2O \leftrightarrows H_2 + CO_2$

Air is mixed in with the gas stream to give hydrogen : nitrogen ration of 3:1.

Water , carbon monoxide and carbon dioxide (all of which poison the iron catalyst used in the ammonia synthesis) are removed. The carbon monoxide is converted to carbon dioxide for use in urea production, and the carbon dioxide removed.

$$CO + H_2O \leftrightarrows CO_2 + H_2$$

The remaining traces of CO and CO_2 are converted to methane and then the gases cooled until the water becomes liquid and can be easily removed.

The nitrogen and hydrogen are then reacted at high temperature and pressure using an iron catalyst to form ammonia.

$$N_2 + 3H_2 \leftrightarrows 2NH_3$$

2.3.2 THE AMMONIA MENUFACTUREING PROCESS

Ammonia is produced in a process known as the Haber process, in which nitrogen and hydrogen react in the presence of an iron catalyst to from ammonia. The hydrogen is formed by reacting natural gas and steam at high temperatures and the nitrogen is supplied from the air. Other gases (such as water and carbon dioxide) are removed from the gas stream and the nitrogen and hydrogen passed over an iron catalyst at high temperature and pressure to form the ammonia. The process is shown schematically in the figure (c) given below.

STEP 1 – HYDROGEN PRODUCTION

Hydrogen is produced by the reaction of methane with water. However, before this can be carried out , all sulfurous compounds must be removed from the natural gas to prevent catalyst poisoning. These are removed by heating the gas to 400 °C and reacting it with zinc oxide.

$$ZnO + H_2S \rightarrow ZnS + H_2O$$

Following this, the gas is sent to the primary reformer for steam reforming, where super-heated steam is fed into the reformer with the methane. The gas mixture heated with natural gas and purge gas to 770 °C in the presence of a nickel catalyst. At this temperature the following equilibrium reactions are driven to the right, converting the methane to hydrogen, carbon dioxide and small quantities of carbon monoxide.

$$CH_4 + H_2O \leftrightarrows 3H_2 + CO$$

$$CH_4 + 2H_2O \leftrightarrows 4H_2 + CO_2$$

$$CO + H_{2O} \leftrightarrows H_2 + CO_2$$

This gaseous mixture is known as synthesis gas.

STEP 2 – NITRIGEN ADDITION

The synthesis gas is cooled slightly to 735 °C . It then flows to the secondary reformer where it is mixed with a calculated amount of air. The highly exothermic reaction between oxygen and methane and produces more hydrogen. Important reactions are:

$$CO + H_2O \leftrightarrows CO_2 + H_2$$

$$O_2 + 2CH_4 \leftrightarrows 2CO + 4H_2$$

$$O_2 + CH_4 \leftrightarrows CO_2 + 2H_2$$

$$2O_2 + CH_4 \leftrightarrows H_2O + CO_2$$

In addition, the necessary nitrogen is added in the secondary reformer.

As the catalyst that is used to form the ammonia is pure iron, water, carbon dioxide and carbon monoxide must be removed from the gas stream to prevent oxidation of the iron. This is carried out in the next three steps.

STEP 3 – REMOVAL OF CARBON MONOXIDE

Here the carbon monoxide is converted to carbon dioxide (which is used later in the synthesis of urea) in a reaction known as the water gas shift reaction.

$$CO + H_2O \leftrightarrows CO_2 + H_2$$

This is achieved in two steps, firstly , the gas stream is passed over a Cr/Fe_3O_4 catalyst at 360 °C and then over a Cu/ZnO/Cr catalyst at 210 °C. The same reaction occurs in both steps , but using the two steps maximizes conversion.

STEP 4 – WATER REMOVAL

The gas mixture is further cooled to 40 °C, at which temperature the water condenses out and is removed.

STEP 5 – REMOVAL OF CARBON OXIDES

The gases are then pumped up through a counter – current of UCARSOL™ solution (and MDEA solution). Carbon dioxide is highly soluble in UCARSOL, and more than 99.9% of the CO_2 in the mixture dissolved in it. The remaining CO_2 (as well as any CO that was not converted to CO_2 in step 3) is converted to methane (methanation) using a Ni/Al_2O_3 catalyst at 325 °C.

$$CO + 3H_2 \leftrightarrows CH_4 + H_2O$$

$$CO_2 + 4H_2 \leftrightarrows CH_4 + 2H_2O$$

The water which is produced in these reaction is removed by condensation at 40 °C as above. The CO_2 is stripped from the UCARSOL and used in urea manufacturing. The UCARSOL is cooled and reused for CO_2 removal.

STEP 6 – SYNTHESIS OF AMMONIA

The gas mixture is now cooled, compressed and fed into the ammonia synthesis loop (see figure (c) above). A mixture of ammonia and un-reacted gases which have already been around the loop are mixed with the incoming gas stream and cooled at 5 °C. The ammonia present is removed and the un-reacted gases heated to 400 °C at a pressure of 330 bar (gauge) and passed over an iron catalyst. Under these conditions 26 % of the hydrogen and nitrogen are converted to ammonia. The outlet gas from the ammonia converter is cooled from 220 °C to 30 °C. This cooling process condenses more the half ammonia, which is then separated out. The remaining gas is mixed with more cooled, compressed incoming gas. The reaction occurring in the ammonia converter is:

$$N_2 + 3H_2 \leftrightarrows 2NH_3$$

The ammonia is rapidly decompresses to 24 bar (gauge). At this pressure, impurities such as methane and hydrogen becomes gases. The gas mixture above the liquid ammonia (which also contains significant levels of ammonia) is removed and sent to the ammonia recovery unit. This is an absorber – stripper system using water as solvent. The remaining gas (purge gas) is used as fuel for the heating of the primary reformer. The ammonia remaining is mixed with the pure ammonia form the initial condensation above and is ready for use in urea production, for storage or for direct sale.

Ammonia product specifications are given in below table :

TABLE –AMMONIA SPECIFICATIONS

COMPONENTS	COMPONSITIONS
Ammonia	98% minimum
Moisture	1500g T^{-1} maximum
Oil	85 g T^{-1} maximum
Iron	1.0 g T^{-1} maximum

2.3.3 UTILITIES

HEAT RECOVERY

The heat of the gas from the primary reformer (Step 1) is used to produce steam for the primary reformer using a boiler. The gas is then discharged. Heat form the process gas form the from the secondary reformer (Step 2) is used to produce steam for a turbo-generator.

WATER RECYCLLING

Excess water from the water gas shift converter, the methanator and ammonia synthesis loop is used for boiler feed water and as the absorbing water for ammonia recovery.

CARBON DIOXIDE STRIPPER

The used UCARSOL is sent to carbon dioxide stripper. Here the UCARSOL is heated to remove a mixture of CO_2 and water, cooled and reused. The water is removed from the CO_2 by condensation and the pure CO_2 sent directly to the urea plant for compression and use in urea synthesis.

AMMONIA RECOVERY

Gases purged from the ammonia synthesis loop and gases collected during ammonia decompression are mixed and sent to the ammonia recovery system. Here the gas mixture is introduced at the bottom of a column and passes up through a counter – current of cold water. 96% of the ammonia is the gas is absorbed into the water, leaving a gas mixture that is used as a fuel gas to heat the primary reformer. The ammonia is distilled out of the ammonia – water mixture, condensed and pumped to join the rest of the ammonia from the ammonia synthesizer.

2.4 AMMONIUM SULPHATE

Ammonia sulphate (AS) with 21% of N (in the form of ammonia) is not as concentrated as urea. However, it contains, in addition to N, 23 percent sulphure, a plant nutrient that is of growing importance. It is used by preference of irrigated crops and where sulphur has to be applied. The same holds true for ammonium sulphate nitrate (ASN) with 26% of N (about 2/3 in the form of ammonia and 1/3 in the form of nitrate) and 13 to 15 percentage of sulphure.

2.5 CALCIUM AMMONIUM NITRATE

Calcium ammonium nitrate (CAN) with up to 27 % N (equal parts of ammonia and nitrate nitrogen) is a fertilizer of preference on crops in semi-arid regions of the subtropics.

2.6 SINGLE SUPER PHOPHATE

Single super phosphate is a chemical Fertilizer which contains Phosphorous as a major plant nutrient. Single super phosphate with 16 to 20%of P_2O_5 contains in addition 12 % of sulphure and more than 20 % calcium oxide (CaO) . It is relatively very cheap and contains many micro nutrients like calcium, Magnesium, Iron, Aluminum , Sulphure and Gypsum. The Gypsum works as a SOIL CONDITIONER. The SSP is manufactured by the reaction of finely grounded ROCK PHOSPHATE with diluted Sulphuric Acid. The SSP is available in power and granulated form. The power form is called as PSSP and the granulated form is called as GSSP.

2.6.1 MANUFACTURING PROCESS

The ROCK PHOSPHATE brought from the mines is stored in rock storage shade. This is very important because it is very difficult to ground wet ROCK PHOSPHATE. If the rock phosphate is received wet, first of all it has to be dried with the help of Rock dryer. The rock dryer contains a datum connected with a hot air generator and cyclone with ID fan and scrubber. The dried rock is fed to BALL MILL to grind it to – 100 mesh (90%). The ground Rock is stored in the Ground Rock Hopper. Th sulphuric acid received from the manufacturer is stored in the sulfuric acid storage tanks. The special linked tank may be used for the spent acid storage.

The reaction between the raw materials tales place in the mixer. The mixer is a vessel with acid and heat resistant lining. The ground Rock Phosphate is controlled, weighted and fed to the mixer with the help of rotary airlocks, screw conveyors and elevator. The sulphuric acid is pumped, controlled, measured and fed into the mixer with the help of pumps, pipelines, Rota-meter and valves. The mixed material is kneaded for some time and dumped into a Den. The den is a enclosed . acid and heat resistant lined and slow moving conveyor. The materials keep on reacting for about an hour. The mixer and den are connected to an ID fan through the scrubbers to scrub the emitted gases. The mixed material which was a free flowing slurry in the mixer becomes a semi solid in the den and becomes a cake at the discharge end of the den. At the discharge end of the den the cake is disintegrated by den cutter. The reaction is very fast and exothermic. The reaction rate depends on many parameters but most importantly it depends on the origin of rock phosphate.

The material is discharged from the den and it is heaped in the green SSP shade with the help of an Electric Overhead Travel Crane. The reaction continues in the heap and it may complete in 5 days to 21 days. This period depends entirely on the origin of Rock Phosphate as the relativity of the rock is related to its origin. The heaps are regularly monitored and as soon as the material is cured it is shifted for manufacturing either GSSP. The reaction between the rock phosphate and acid is called as acidulation and proceeds with the emission of Fluorine based gases. These gases are scrubbed by the state of the art Ventury scrubbers which have 90 to 95 % efficiency , convert the gases into Hydro-Fluoro Silicic Acid and silica. The Hydro Fluoro Silicic Acid is recycled back into the mixer. The silica formed is used as a filler in PSSP and GSSP manufacture. So a zero effluent system is used.

2.6.2 MANUFACTURING PROCESS OF GRANULATED SINGLE SUPER PHOSPHATE

The measured quantity of the cured SSP us mixed properly with filler in a mixture. The homogenous mass is then processed in the granulated drum. The granulator drum rotates at very low RPM. The material goes up with the well of granulator for some height and then starts rolling back. A fine spray of water at this stage starts the process of granulation and as the material rolls on the size if the granules increases. This material is transferred to the dryer drum with the help of a conveyor belt.

The furnace attached to the dryer generates hot air which is made to pass through this wet material. The evaporation and condensation of water gets deposited on the small granulated and further enhance the size of the granules. With the hot air stream the material gets dried. The material is then passed through the cooler drum for cooling. The cooled material is transferred to the screens to remove the oversize and undersized granules form the product. The oversized granules after crushing and under sized granule are mixed with the raw feed for reprocessing. The plant is equipped to deal with air pollution inside the plant and stack flue gases.

2.7 TRIPLE SUPER PHOSPHATE

Triple superphosphate is a fertilizer produced by the action concentrated phosphoric acid on ground phosphate rock. The active ingredient of the product, mono-calcium phosphate , is identical to that of superphosphate, but without the presence of calcium sulfate that is formed if sulphuric acid is used instead of phosphoric acid. The phosphorus content of triple superphosphate (17 to 23 % of P , 44 to 52 % of P_2O_5) is therefore greater than that of superphosphate ((7 to 9.5% of P , 16 to 22 % of P_2O_5). It is produced in granulated and non-granulated form and is used both in fertilizer blends (with potassium and nitrogen) and by itself.

2.7.1 MANUFACTURING PROCESS

The figure below shown the block flow diagram for manufacturing if triple superphosphate. This types of fertilizer is much more concentrated than the ordinary superphosphate, Containing 45 to 46 % of available P_2O_5 . Triple superphosphate is manufactured by the action of phosphoric acid on phosphate rock. The main reaction is :

$$CaF_2 . 3\,Ca_3(PO_4)_2 + 14\,H_3PO_4 \rightarrow 10\,Ca(H_2PO_4)_2 + 2HF\uparrow$$

(Phosphate Rock) (Triple Superphosphate)

A process similar to single super phosphate production is used, in which pulverized phosphate rock is mixed with phosphoric acid in a two – stage reactor. The resultant slurry is sprayed into the granulator. The slurry is sprayed into the drum granulated co-current with flue gases of fired fuel (natural gas or fuel oil and air). The product is screened and off sized is recycled back to the granulator. The on-size product is cooled and stored ready for being bagged. The exhausted gases from the reactor, granulator and cooler are scrubbed to remove fluoric compounds.

2.7.2 UTILITIES

A drying tower is used to dry the air in which the molten sulfur is burned. This is a packed tower in which air is blown counter – current against a stream of concentrated sulfuric acid. Which absorbs any moisture.

The heat generated by the exothermic reaction between molten sulfur and oxygen is recovered in a waste heat boiler to produce steam which is then used for process heating and also to drive steam turbine which produces electricity.

The electricity is used on site and any excess is exported to the local power supplier. In addition a gas scrubber is used to prevent any hydro–fluosilicic acid from being released into the atmosphere.

2.8 AMMONIA (NH_3)

Melting point temperature = - 32.7 °C

Boiling point temperature = - 77.7 °C

Solubility = Soluble in water

It is used in making urea.

Raw material = N_2 and H_2

N_2 → Air

H_2 → It is obtained form water gas.

Catalyst → FeO

Haber's process, Temperature (T) → 500 to 600 °C at the pressure 100 to 1000 atm.

$2N_2 + 2H_2O \rightarrow 2\,NH_3$

Endothermic

The main problem is maintaining the temperature as catalyst diffuses over 620 °C.

UREA

NH_2CONH_2

BP → Decompose

Soluble in water
Raw material carbon dioxide (from syn gas or water gas)

Ammonia – from ammonia plant

Urea is used as nitrogen fertilizer either in solid form or liquid form

In solid form → 40 to 42 % N_2

Liquid form → 45 % N_2

1. Ammonia and CO_2 stream are compressed separately and fed to reactor at 185 °C and 200 atm where the following reaction takes place.
   $2NH_3 + CO_2 \rightarrow NH_4COONH_2$ (Ammonium Carbamate)

2. Urea, ammonium carbonate and unreacted reactant, water stream are heated and depressurized and sent to flash evaporator, operated at 27 atm, where NH_3 and CO_2 streams react completely.

3. Urea, carbamate and water stream are then fed to atmosphere flash drum followed by vacuum evaporator which converts 99% of carbamate into urea.

4. The 99 % molten urea us then sprayed from prilling tower and temperature is maintained just above Melting point of urea to minimize the production of biuret which is undesirable.

The final product is in the form prills which is packed and sold.
Main point to remember.

PHOSPHOROUS FERTILIZER

Super-Phosphate , Triple Super Phosphate
(SSP) (TSP)

They are form of calcium phosphate

SSP	TSP
I. Calcium phosphate rock	I. Calcium Phosphate
II. Raw material phosphate rock((P_2O_5) + H_2SO_4 (60%)	II. Raw material Phosphate Rock (P_2O_5)+H_3PO_4(75%)
III. 16 to 20 % (P_2O_5) content in phosphate rock.	III. 40 to 45 % (P_2O_5) content in phosphate rock.
IV. Phosphate rocks are crushed mixed with H_2SO_4 which is 60% Concentrated, passed through blender, passed through rotary granulator and rotary dryer to get SSP.	IV. Same process
V. To make ammonium sulfite NH_3 is added before rotary granulator.	V. To make ammonic phosphate NH_3 is added before rotary granulation.
VI. Final product formed required 24 hours storage. Also known as Den and Silo arrangement.	VI. No storage is required.

To make SSP now a days , nitric acid is used. The process that uses nitric acid gives SSP having high phosphorous content as compared to previous process.

CHAPTER – 3

NATURAL PRODUCTS

3.1 INTRODUCTION

Nature synthesizes many organic compounds strings basically from the $CO_2- O_2$ photosynthesis process. The principal industries based on natural products are

- Oil and Fats
- Pulp and Paper
- Sugar

3.2 Oil and Fats

There are following points to remember :

1. Oils and fats are trimesters of high fatty acids with glycerol, i.e., they are glycerol esters and glycerides. They are called triglycerides or triglycerols.

2. Oils are liquids at ordinary temperature and their molecules are basically glyceryl esters of unsaturated fatty acids. The molecules of facts are basically glyceryl esters of saturated fatty acids.

3. The fatty acids have un-branched carbon chain and their molecules normally contain even number of carbon atmos. The most abundantly occurring fatty acid in nature is *palmitric acid*.

4. The glycerides in which all the three fatty acids are identical are called simple triglycerides.

The glycerides in which the three fatty acid units are not identical are called mixed triglycerides. The mixed triglycerides more commonly occur in nature than the simple triglycerides.

3.2.1 METHODS OF EXTRACTION OF OILS AND FATS

Oils and fats can be extracted by using any of the following methods.

3.2.1.1 RENDERING

The animal tissues containing fat are heated with water, so that the fat melts and get separated out.

3.2.1.2 PRESSING

The plant seeds containing oil are crushed by rollers and then pressed under hydraulic press, so that the oil gets separated out. The remaining pressed cake is used as fodder for the milch cows, buffalos etc.

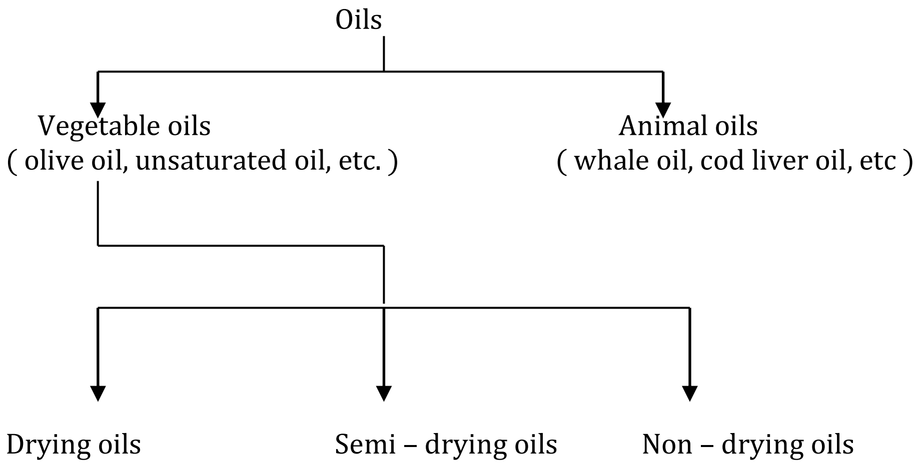
3.2.1.3 SOLVENT EXTRACTION

The oil and fats are soluble in common organic solvents, like petroleum ether benzene, CS_2 etc. Therefore , oils and fats left behind in the pressed cake can be completely extracted out by using the above solvents.

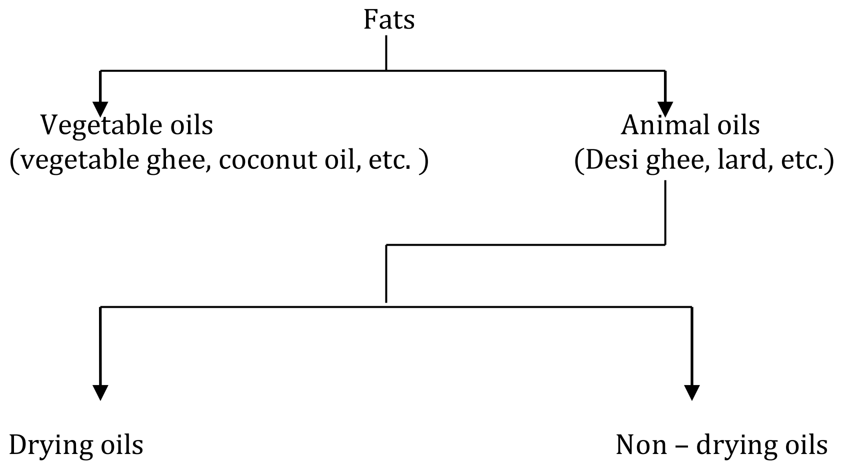
The crude oils separated by the above methods are washed with a small amount of alkali solution due to which free acids and colloidal impurities are removed. After that, the oil is subjected to bleaching by animal charcoal at about 75 to 80 °C. In the end , steam us passed through the oil for removing adhering and soluble impurities.

3.2.2 CLASSIFICATION OF OILS AND FATS

Oils can be classified as follows:



Fats can be classified as follows :



3.2.2.1 VEGETABLE OILS

Glycerol is one of the constituents of vegetable oil.

DRYING OILS

Drying oils readily dry up on exposure to air. These are commonly used in paints and varnishes. The important example of drying oils is linseed oil.

SEMI FRYING OILS

Semi drying oils dry up very slowly on exposure to air. These are also commonly used in paints and varnishes.

Example : Cottonseed oil.

NON DRYING OILS

Non drying oils do not dry up even on exposure to air.

Example : Til oil and Mustard oil.

Cholesterol ($C_{27}H_{46}O$), Which is very important animal lipid, is structurally not a fat. It is an unsaturated alicylic alcohol, which form rhombic plants, melting point 148 °C. Phytosterol ($C_{29}H_{50}O$) is a plant lipid, which forms needle like crystal, melting point 132 – 144 °C.

PHYSICAL PROPERTIES

- In pure form, these are tasteless, colorless and odorless liquids or solids.
- These are lighter than water and immiscible with water.
- These are soluble in petroleum ether, benzene, ether, chloroform , acerone, CS_2, etc.
- These are natural.
- These form emulsions on stirring with emulsifiers, like soaps, gelatins, etc.

3.2.4 REACTIONS

3.2.4.1 HYDROLYSIS

The oils and fats undergo hydrolysis by water or dilute acids to give a mixture of glycerol and fatty acids (aliphatic mono-carboxylic acids).

The mother liquor left behind after removal of the fatty acids is called sweet water, which is used for the manufacturing of glycerol.

When caustic alkalis are used for the hydrolysis of oils and fats, then glycerol and soaps (alkali metal salts of higher fatty acids) are formed. This reaction is called saponification.

$\text{Glyceride} + 3\text{NaOH} \rightarrow \text{Glycerol} + 3\text{R} - \text{COONa}$ (Soap)

Enzymes can also bring about the hydrolysis of oils and fats.
Example : emulsion of oils or fats undergoes complete hydrolysis in three or four days to give glycerol and fatty acids on using the enzyme, lipase. The fatty acids are obtained in sufficiently pure form by this method.

3.2.4.2 HYDROGENATION

The oils are liquids at ordinary temperatures, because they are glyceryl trimesters of higher unsaturated fatty acids. In order to convert the oils (liquids) into fats (solids) , the oils are subjected to hydrogenation under pressure in the presence of finely divided nickel catalyst. This process results in saturation of the double bonds present in the fatty acid units to form single bonds by addition of hydrogen.
Example : The oil triolein (a liquid having b.p 17 °C) on hydrogenation gives a fat tristerin (a solid having melting point 60°C).
The above process of hydrogenation is called hardening of oils and is used in the manufacture of vegetable ghee and margarine.

3.2.4.3 Hydrogenolysis

When excess amount of hydrogen is passes through an oil or a fat, then glycerol and higher alcohols are obtained. The breaking up of an organic molecule by excess of hydrogen is called Hydrogenolysis.
Example: Tristearin undergoes Hydrogenolysis to give glycerol octadecyl alcohol.

$\text{Tristearin}\ \overrightarrow{6\ \text{H}_2}\ \text{Glycerol} + C_{17}H_{35}CH_2OH$ (Octadecyl alcohol)

3.2.4.4 RANCIDIFICATION

When an oil or a fat is kept exposed to air and humidity for a very long period of time, Then it (especially fat) starts giving an unpleasant smell. This change is called rancidification and it involves oxidation and hydrolysis. Oxidation at the double bond results in the formation of aldehides, which undergo oxidation to form lower fatty acids, The unpleasant taste and smell is actually due to these acids and aldehydes. Pure oils and fats can be stored in good condition when they are kept away from air and humidity.

3.2.5 USES

- As important food materials.
- In the manufacturing of soaps, candles and glycerol.
- As lubricants.
- In the manufacture of paints and varnishes.
- As illuminants.

As medicines, e.g. croton oil and Castrol oil used as purgatives.

3.2.6 MANUFACTURING OF VEGRETABLE GHEE

HYDROGENTAION OF OILS

Oils are liquids at ordinary temperatures, because unsaturated glycerides are present in them in high amounts. Therefore, in order to conevert them to fats (solid at ordinary temperature), they are subjected to hydrogenation under pressure in the presence of finely divided nickel catalyst. Thus, solid saturated glycerides, i.e., fats are obtained. This process is called hydrogenation of oils or hardening of oils.

Manufacturing of vegetable oil involves the following steps.

(i) SEPARATION OF FREE ACIDS:

The oil first heated and a calculated amount of NaOH is added to it, so that the free acids undergo neutralization. The salts and suspended impurities so formed get separated out in the form of scum.

(ii) BLEACHING:

The oil filled in one tank is then decanted out to the other tank. The oil is bleached or decolorized at 70 to 80 °C with the help of animal charcoal and then filtered.

(iii) DEODORISATION:

In order to deodorize the oil, superheated steam is passed through it.

(iv) HYDROGENETAION :

The oil purified by the aforesaid processes is taken in a iron tank, where it is heated to 150 to 200 °C by steam coils. A small amount of nickel format is added to it and then hydrogen gas is passed through it under 12 to 15 atm pressure. Hydrogen gas converts nickel format to finely divided nickel, which acts as a catalyst hydrogenation is carried out till the fat having desired hardness is obtained. The catalyst is removed by filtration and desired flavors are then added to the fat.

3.2.7 ANALYSIS OF OILS AND FATS

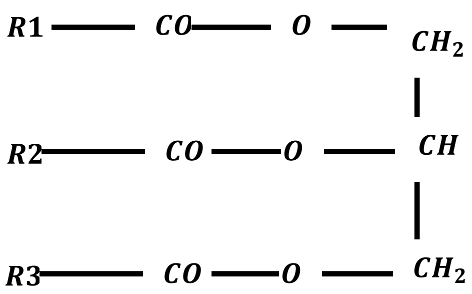
These are of two types:

(i) Essential oil

(ii) Vegetable oil

Oil used for the nutrition of animal, plant and human are vegetable oils.
Oil used in cosmetics, soaps or commercial purpose is known as essential oils.
Oils are generally glycerides of fatty acids.

Generally having formula



Stearic ………………….	$C_{17}H_{35}$
Oleic ………………….	$C_{17}H_{33}$
Linoleic ………………….	$C_{17}H_{31}$
Linolenic ……………….	$C_{17}H_{29}$

As we go from stearic to linolenic, double bond character increases. As double bond increases, tendency of oils and fats to react with oxygen increases. This in turn introduces the problem of rancidity.

To avoid this problem, oils and fats undergoes hydrogenation to yield saturated compound in presence if nickel or Rany Nickel (Alloy of Ni and Al).

PROCESS DESCRIPTION

i. Either by digestion process which is used in pulp and paper or by extraction of oil seeds. Oil coming from both the process send to purification.
ii. Alkali or Na_2CO_3 is added to remove the impurity by coagulation in the form of foots then foots is sent to the soap and detergent industries.
iii. Then bleaching is done with the help of fuller earth.
iv. At last the finish oil is sent for hydrogenation to increase the M.P and decrease the reactivity.
v. Ghee based oil is hydrogenated at low pressure and high temperature to yield a product with M.P similar to butter.
vi. Vanaspati oil is produced by hydrogenation at high pressure and low temperature to yield product having high M.P. maximum stability and use for cooking temperature.

Temperature should not be exceeding 200 °C to avoid side reaction.

3.3 PULP AND PAPER

PULP : Commercial fibrous material obtain from bamboo, wood and baggage.

METHOD OF PULPING

(I) Mechanical

(II) Chemical

Pulping : Disintegration of bulky fibrous material into smaller ones in 2 to 5 cm small size wood chip.

STEPS :

i. Chipper Bin : it consist of large rotary disc having knife and it cut wood into 2 to 5 cm chips.
ii. The wood chips contain fiber and lignin and to remove lignin from the fiber, we use a solution known as white liquor which consist of NaOH and Na_2S.
iii. This two streams along with water fed into digester , Water → 50 % , Wood chips → 25 % , White liquor → 25 %.

DIGESTOR

It acts as a pressure cooker and 25 or 30 m tall tower, temperature is maintained at 170 °C at the top and middle section and 65 °C at the bottom section. In digester under the action of white liquor and high temperature, wood chips starts to break and lignin starts to dissolved in white liquor and color of white liquor changes to black. Fiber obtained from the digester undergoes a series of bleaching and washing which changes its color from brown to white.

Bleaching agents are H_2O_3, O_3 and Cl_2O_2 etc.

Bleaching fiber is stored as pulp for further use or may sent to paper mill for the paper production.
Black liquor recover from the digester undergoes recovery section and recovery is done to decrease pollution and regenerated white liquor. Black liquor obtained from digester is very dilute, therefore, it is concentrated with multi effect evaporator 10 to 12 % to 60 to 65 %. Then concentrated Black liquor sent to mixed tank where make up chemicals are added (Na_2SO_4 and S).

Mixture is then sent to a boiler where carbon content present in the form of lignin burns.

$$Na_2SO_4 + C \rightarrow Na_2S + CO_2$$

Heat is so produce is use in the production of steam which in turn used in production of electricity required for mill.

The production from the boiler sent to dissolved tank where cold water is added recover green liquor.

Green liquor is then sent to causticzing tank where milk of lime is added to recover white liquor.

This cycle of converting white liquor to black liquor to green liquor to white liquor is known as kraft cycle, and it is very cost effective. Because of this, paper is available to us at such price. The whole process of making pulp is known as sulfate kraft process.

Sulfate name is given because we use a_2SO_4 . It is an Alkaline process.

Na_2S is added to NaOH to increase its performance and also help in bleaching.

The amount of Na_2S present in white liquor is known as sulfidity. More is sufficient more easier to bleach fiber.

Sulfidity = $Na_2S/(Na_2S + \text{NaOH})$

This paper produce from sulfate kraft process are strong. Therefore kraft name is given to the process at Kraft means strong.

Product from this process strong brown bag, strong white paper.

Paper can also be produced from another process known as sulfate process which is acidic process gives pure white paper having less strength.

Difference between sulfate and sulfite

SULFATE	SULFITE
I) Alkaline process	I) Acidic Process
II) Strength of paper is high	II) Low strength
III) Brown or less white paper	III) White paper
IV) White liquor is NaOH with little Na_2 S to enhance bleaching effect.	IV) White liquor is Magnesium bi-sulfate and sulphur dioxide in acidic medium.

Paper

The fiber produces from pulping sent to web forming section where they are mechanically disintegrated to a very small size and mixed with water.

Solution is 99% water and 1% fiber. The web is running on a endless conveyor belt to reduce water content and then sent through pressing section where the slurry passes through pressure rolls to reduce water content to 5%. The product is then sent to finishing section where it is pass through calendaring roll form making smooth paper and winding roll to wind up the paper in the form of bundle.

3.4 SUGUR INDUSTRY

Raw material is sugarcane. It gives sucrose ($C_{12}H_{22}O_{11}$), it is soluble in water.

PROCESS STEPS :

i. It is crushed and pressurized by three pressure rolls and water is added to increase the yield.
ii. The juice is treated with calcium hypo phosphate followed by lime to precipitate the colloids.
iii. SO_2 is then bubbled through the juice to decrease the PH to 7 and it also help in beaching.
iv. Juice is then filtered with cake filter, and the filter cloth obtained is used as manure.
v. Juice is then to multi effect evaporator for evaporation.
vi. Then the crystallization is done and the solution of crystal and syrup is known as massecuite.
vii. Finally crystals are separated by centrifugation and white sugar is made by carbonation.

The mother liquor, left is known as black strap molasses which is then sent to alcohol industry. The major engineering problem in sugar industry in inversion of sugar which means sucrose reacts with the moisture present in the atmosphere to from glucose and fructose. To avoid this, angle of polarimeter is checked for sugarcane befor using it as the raw material. If the angle comes out to be - 97% , then it means no inversion but if it comes out to be 20 °C then it means full inversion.

3.5 SOAPS AND DETERGENTS

Soaps are the compounds of the type RCOOM where M is any alkali metal and RCOO is fatty acid.

Detergent can be anionic and cationic.

Anionic detergents are those which give R negative in water and have detergent characteristics.

For example : Sulfates , sulphonates and ABS → alkyl Benzene sulphonate, linear alkyl benzene sulphonate.

Cationic detergents are those which give R positive in water and having germicidal properties.

Examples : Ammonium compounds such as pyridinium derivatives.

SOAP MANUFACTURING

Two steps is important in the soap manufacturing , one is fat splitting, it is used to produce fatty acids and glycerin from vegetable oil or other fatty oil.

Second is Soapnification, it is used to produce soap by reacting the fatty acid with alkali i.e., NaOH.

Raw materials required are vegetable oil and other fatty oils. Catalyst is ZnO.

CHAPTER 4

PETROCHEMICALS

Petrochemicals based on only one reaction i.e., steam cracking or Pyrolysis

$$C_xH_y + H_2O + O_2$$
$$\downarrow$$

Methane, ethane + ethylene + propane + propylene + butane + butylenes +
Co + CO_2 + benzene + toluene + C + heavy oils

Steam cracking is the heat of petrochemical. The product produces are used in manufacturing of polymers.

Ethylene is the main product zones in steam cracking.

1. Hot zone or Hot section

Hydrocarbon feed is preheated and mixed with steam at high temperature (800 °C) to yield following product.

2. Quench section or Zone

Product produced by hot zone are quench by water to recover heat. The hot water so produce is use in generation of steam.

3. Cold section → (recovery section)

Separate section
(Methane, ethane + ethylene + propane + propylene + butane + butylenes +
Co + CO_2 + benzene + toluene + C + heavy oils)

PRODUCTS OF PETROCHEMICALS

1. Formaldehyde

i. Process

Catalytic conversions of methane to methanol using Cu-zeolite catalyst.

Ii Methanol convert to form formaldehyde

$CH_3OH \rightarrow HCHO + H_2$

2. Chloromethane

$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$

$CH_3Cl + Cl_2 \rightarrow CH_2Cl_2 + HCl$

$CH_2Cl + Cl_2 \rightarrow CHCl_3 + HCl$

$C_4CL_3 + Cl_2 \rightarrow CCl_4 + HCl$

No catalyst is used. Absence of O_2 and photochemical process

3. Vinyl chloride

Raw material is ethylene

Chlorination of ethylene to produce ethylene dichloride which in turn undergo Pyrolysis to form vinyl chloride.

$C_2H_2 + Cl_2\overrightarrow{FeCl_3}\ C_2H_4Cl$

HCl + $CH_2CHCl \overleftarrow{\text{charcoal}}$ Vinyl chloride

4. Ethylene oxide

Partial oxidation of ethylene in presence of silver oxide or alumina.

$C_2H_4 + \frac{1}{2}O_2 \rightarrow CH_2OCH_2$
(ago or alumina)

5. Ethanol amine $\rightarrow CH_2OCH_2 + NH_3 \rightarrow$ Mono ethanol amine.

It is produced by the ammonification process of ethylene oxide.

6. Iso-Propane

It is produced by the sulfation of proylene followed by the hydrolysis to form iso-propanol.

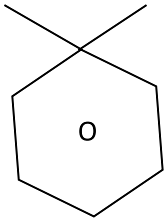
Propylene + H_2SO_4
↓
Iso-propyl sulfate
↓ (Hydration)
Iso-propanol + H_2SO_4

7. Acetone

Isopropanol so formed undergo dehydrogenation in the presence of copper catalyst to form acetone.

Propylene + H_2SO_4
↓
Iso-propyl sulfate
↓ (Hydration)
Iso-propanol + H_2SO_4
$(-H_2)$ ↓ (Cu)
Acetone

8. Cumene or Isopropyle Be



Benzene + Propylene $\xrightarrow[\text{(Alkylation)}]{\text{(Zeolite)}}$ Cummene

Benzene and propylene in the presence of Zerolite to form Cumene by the help of alkylation

9. Acrylonitrile

Propylene + $NH_3 + O_2 \xrightarrow[\text{(ammoxidation)}]{\text{(MO-Bi)}}$ Acrylonitrile

It is produced by the ammoxidation process of propylene in the presence of MO-Bi as catalyst.

10. Iso-prene

It is formed by three steps

- Dimerisation
- 2 Propylene $\xrightarrow{\text{(Tripropyl Aluminium)}}$ 2 – methyl 1 – pentene

- Isomerisation
- 2-methyl 1-penetne $\xrightarrow[\text{(Iso – merisation)}]{\text{(Acid catalyst)}}$ 2 – methyl , 2 – pentene

- Pyrolysis
- 2 – methyl 2 – pentene $\xrightarrow{\text{(HBr)}}$ Isoprene

11. Butadine

n – butane $\xrightarrow[\text{(Cromium Oxide)}]{\text{(dehydrogenation)}}$ Butadine

12. Benzene

Toluene goes hydrogenation in the presence of chromium oxide to form benzene.

13. Phenol from cummene (2-steps)

a) Peroxidation

Cummene + air $\xrightarrow{\text{(Basic medium)}}$ Cumene hydro peroxide

↓ (Acid H_2SO_4)

No-catalyst

Phenol + Acetone

14. Phenol from toluene (2-steps)

a) Oxidation

Toluene + O_2 $\xrightarrow{\text{(Co-Napthanate)}}$ Benzoic acid

b) Reduction

Benzoic acid $\xrightarrow{(LiAlH_4)}$ Phenol

15. Phenol from Benzene (3-steps)

a) Chlorination

Benzene + Cl_2 $\xrightarrow{(FeCl_2)}$ Benzyl Chloride

b) Causticization (Basis medium)

Benzyl Chloride + NaOH → Sodium Benzoate

c) Hydrolysis in acidic medium

Sodium benzoate + HCl → Phenol

16. Styrene

a) Alkyation of benzene with ethylene to form ethyl benzene in presence of $AlCl_3$.

b) Dehydrogenation of ethyl benzene in the presence of SnO/ FeO to form styrene.

17. Pthalic

$$\text{Napthalene} + O_2 \xrightarrow{(V_2O_5)} \text{PA}$$

$$\text{O-xylene} + O_2 \xrightarrow{(V_2O_5)} \text{PA}$$

18. Maleic Anhydride

$$\text{Benzene} + O_2 \xrightarrow{(V_2O_5)} \text{MA}$$

19. OXo – processing

It is the technique used for making aldehyde
General reaction

$$\text{Olefins} + \text{CO} + H_2 \xrightarrow[\text{(Hydroformylation)}]{\text{(Co – napthanate)}} \text{Aldehyde}$$

CHAPTER 5

POLYMERS

These are large chain molecule having a high molecular weight in the range of 10^3 to 10^7. These are made up of single unit of a molecule which is repeated several times with a chain structure.

Polymerization is of two types :

ADDITION PILYMERIZATION

An addition polymerization occur by the formation of rapid chain, and no elimination of small molecule occurs.

It is formed by mainly unsaturated monomer.

These are of three types

i) Step reaction : π-bond is broken and two new σ-bond form.

ii) Chain reaction : a polymer is formed within fraction as the kinetic is very fast. The chain kinetic occurs in four steps.

- a) Initiation
- b) Propagation
- c) Chain transfer (If polymer with different molecular weights are required)
- d) Termination (May or may not occur)

iii) Ionic reaction : These are similar to chain addition reaction but takes place in the presence of free radical. They have positive or negative charge.

Example : Polyethylene , PVC , Polystyrene etc.

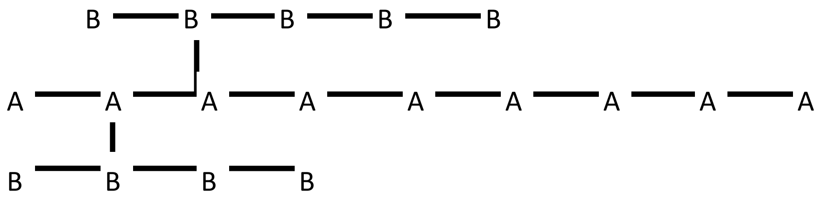
Condensation Polymerization :

Two or more monomers combine together to form a new compound with the help of reaction between different functional groups. Along with elimination of simple molecule like H_2, H_2O , CO_2 etc.

Examples : Nylon 6, Nylon 6 6 .

Types of polymer

i) Homopolymer : MMMMMM
ii) Copolymer : AMAAMM
iii) Block Polymer : A-A-A-A-B-B-B-B-A-A-A-A
iv) Graft : Main chain of one monomers and side chains of another.



METHOD OF POLYMERIZATION

1. Bulk or mass polymerization

In a reactor , a monomer and initiator is added. Initiator initiates the reaction propagates and when a large molecular weight compound is formed, we add a chain terminating agent to terminate the chain. Polymer obtained by this mode is known as bulk polymer and is pure.

i) This mode of polymerization may be employed to obtain purest form of polymer and greatest yield of polymer.

ii) Pure liquid or gaseous monomer is subjected to polymerization condition to get liquid or gas polymer.

iii) Small amount of catalyst modifier may be added.

Bulk polymerization is used generally for :

i) Extremely high molecular weight
ii) Maximum clarity (Purity)

Difficulties

i) Exothermic reaction, heat remove is main concern heat control system are required.

ii) Very viscous difficult in mixing.

Solution polymerization

It is same as bulk polymerization but an inert solvent is added to the reaction vessel for reducing the viscosity and facilitate heat transfer.

Compare to bulk polymer. It reduces both reaction rate and molecular weight.

Solvent used is of high heat capacity and it is also refluxed from time to time to increase heat control.

Some traces of solvent present in the product which needed separation which further increase cost.

Difficulties

i) Heat control is better than bulk polymerization but still is the main concern.

Suspension polymerization (mm) :

It is the polymerization of one or more monomers by dispersion in the form of droplets or various sizes in a non-dissolved liquid. In order to control enormous amount of heat, the reaction mass is dispersed as minute droplet of size (0.01 to 1mm) diameter in continuous phase. It produces small polymer sphere which can be used to moulded to large polymers having high molecular weight.

Agitator are used to maintain specific droplet size and dispersion. It produces small sphere.

Advantage :

- Economical method water is used as suspension agent.
- Heat transfer is easy.
- Separation cost are higher as solvent is present in newly formed small polymer spheres.

Emulsion polymerization (um)

In this type of polymerization one or more monomers are polymerized and emulsion is formed with the solvent. Monomers are brought together in the form of an aqueous emulsion with help of soap, detergent and emulsifying agent. The polymer obtain is in the form of latex which can be used as such or it is isolated by adding acids or salts or by centrifuging to form lumps for the final production.

Difference form suspension polymerization:

1) Particle size is 0.1 um in diameter.

2) Initiator is in the aqueous phase.

Agitator is not required because of emulsion agent.

Advantage

- Heat transfer and control is excellent.
- Low molecular weight polymers.

Disadvantage

- High separation cost.
- Emulsion formed chemically, so separation is also done chemically.

TYPES OF POLYMERS ON THE BASIS OF THEIR COMMERCIAL APPLICATIONS

Thermoplastic

Thermoplastics are organic chain polymers which usually become soft when heated and can be molded again and again under the effect of pressure and temperature.

They can be linear or branched having very low or no cross linking.
Example : Polyethylene, polypropylene , polystyrene, poly vinyl chloride etc.

Polyethylene

Main product of petro-chemicals is ethylene. Most widely use thermoplastics is ever increasing demand is due to availability of monomer ethylene

Properties of polyethylene

i) Low price
ii) Electrical insulation
iii) Good chemical resistance
iv) Good process ability

Preparation of monomers

Earlier-monomer are taken form sugar molasses which forms ethylene alcohol which then dehydrated to get ethylene.

Now, from steam cracking of Naptha, ethylene is produced.

Process of making polyethylene

i) High pressure processes.
ii) Ziegler process (Low pressure process)
iii) Phillips process (Intermediate pressure process)

Process of making polyethylene

High pressure process	Intermediate pressure process	Low pressure process
Pressure 1000 to 2500 atm.	Pressure 30 to 100 atm.	Pressure 5 to 10 atm.
Catalyst Benzoyl peroxide, oxygen	Catalyst Metal oxide catalyst (CrO_3) on finely divide silica-alumina gel.	Catalyst Titanium chloride and aluminum triethyl. Also known as zeigler Natta catalyst.
Developed by ICI in UK	Developed by Phillips petroleum corporation in USA	Developed by KarL Zeigler in Germany
It produces LDPE	It produces HDPE	It produces HDPE

Polypropylene

It is manufactured by using low pressure Zeigler process as discussed above. Raw material used is propylene which is obtained from Naptha cracker. It is used as packaging materials same as polyethylene.

Polyvinyl Chloride (PVC)

It is second largest consumed thermoplastics and more versatile.

PVC contains 56.8% chlorine and rest hydrocarbon.

Butyl lithium is used as catalyst for the making of PVC.

PVC

Rigid uses	Flexible addition of plasticizer hydrogenated phthalate plasticizer converts rigid PVC into flexible PVC.
i) Fittings	i) Wires and cable
ii) Bottles	ii) Tubes
iii) Water proof sheeting	iii) Packaging films shrink wrap.

Polystyrene

Raw material is styrene which id obtained from Naptha cracker. Polystyrene exhibits good electrical properties and that is why used in electronic packaging.
Transparently , rigidly , low water absorption , low cost and good mould ability.

Polycarbonate

It is a condensation polymer of sodium salt of bisphenol and phosgene (also known as carbonyl chloride) . It is also known as engineering plastic , it has high optical clarity , impact strength , breaking resistance, flame resistance, chemical resistance.

It is used in labs to look out the experiments that were initially took place under glass wall.

Thermosetting

Thermosetting polymers are network of long chain molecule that are crossed linked. Under heat and pressure, they decompose. They cannot be re-shaped.

Example : UF, MF, Epoxy resin etc.

1. Phenol-formaldehyde resins

Raw materials used are phenol and formaldehyde which are obtained from Naptha cracker. It is used as adhesive , composites etc.

2. Urea formaldehyde Resin

Raw materials used are urea and formaldehyde which are obtained for Naptha cracker. It is used as adhesive composition etc.

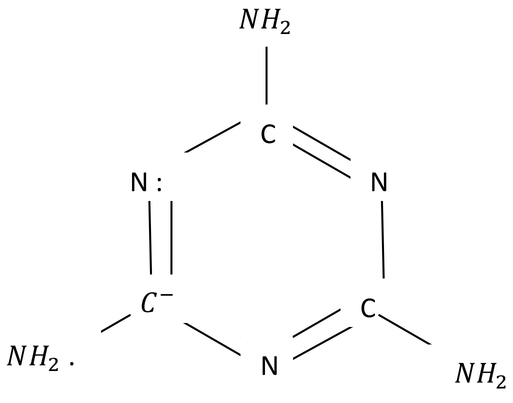
Melamine formaldehyde resin

Raw materials used are melamine and formaldehyde which are obtained from naptha cracker. It is prepared form urea.

When molten urea is heated to 360°C to 700°C in the presence of quartz sand. It converts into iso-cyanic acid + NH_3.

(Converted Alumina)
Iso cyanic acid → Melamine + CO_2

It is used to make non-breakable kitchenware.



Melamine

4. Epoxy resin

Raw materials used are bisphenol and epichlorohydine which are obtained from Naptha craker.

Used as adhesive and thermoset specially for the experimental purposes.

Elastomers

Elastomers are the resistance solids which have considerable flexibility. They are composed of polymers having glass transition temperature below room temperature.

GTT : It is the temp at which glassy state convert into rubbery state.
Glassy state : The state at which the material is hard and brittle .
Rubbery state : The state at which the material is flexible and elastic.

Types of elastomers

1) Styrene butadiene Rubber

Source or butadiene is petrochemical complex where it is manufactured by dehydrogenation of n-butane.

Source of styrene is also same and it is manufactured by alkylation followed by dehydrogenation of benzene with ethylene.

Styrene butadiene rubber is a condensation polymer if styrene and butadiene and is also known as BUNA-S where BU stands for Butadiene and S stands for Styrene.

NA represent sodium that is required for the manufacturing of SBR.

SRB is used for making tyres and tyres related products specially for the industrial purpose.

2) Poly-butadiene

PB is not directly used as rubber rather as blending agent to blend with some other rubber to improve the quality of rubber. It helps in increasing the cracking resistance of 5BR.

3) Nitrile rubber

Nitrile rubber is also known as Acrylonitrile butadiene rubber. Acrylonitrile is made by ammoxidation process of propylene. Used as gasket (Sealing purpose)

It is also known as BUNA-N where N stand for Acrylonitrile.

4) Polyisoprene – (Natural rubber)

Derived from hevea tree. Synthetically NR is manufacture in naphtha cracker used as rubber.

5) Polychloroprene : (Neoprene) or synthetic rubber

Raw material is chloroprene which is made by acetylene. Used in transportation industry.

$$\text{2 Acetylene} \xrightarrow{\text{(dimerization)}} \text{Monovinly acetylene}$$
$$\downarrow \text{HCl}$$
$$\text{Chloroprene}$$

6) Poly-Isobutylene

It is made by the polymerization of isobutylene where isobutylene can be obtained by the isomerization of butadinene. It is impermeable to gas which means it does not allows the gas to pass through it and that’s why used in making balloons, parachutes etc.

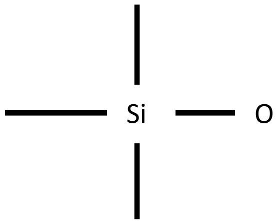
7) Butyle rubber

It is manufactured by adding little isoprene (1 to 3 %) with isobutylene. Addition of isoprene helps to improve the impermeable nature of isobutylene. Uses same as poly-isobutylene but performance is better.

8) Chlorobutyle rubber

It is made by adding chloride with butyl rubber to improve the performance and characteristics. It is used in making of tubeless tiers.

9) Polysiloxanes or silicon rubber



Raw material is siloxanes which are compound having Si-O linkage. It exhibits exceptional mechanical performance under extreme condition of temperature therefore used in electrical appliance and aerospace industry.

10) Hypalon

Condensation product of chlorinated sulphur monoxide and polyethylene and therefore hypalon is known as chlorosulphorated polyethylene compound (derivatives).

It is used in making conveyor belts.

11) Polyurethane (runner)

It is the condensation polymer of compounds having RNCO (Isocyanates) and polulol like ethylene glycol. Polyurethane are the compounds having NHCO linkage . It is used for making luxurouis cushions, seats and by some modification can be used in making flyover, bridgesm dam, etc. It is the only6 polymer that can be-used as fibre as well as thermoset

Fiber

These are the solids which can form thread like structure and having high tensile strength .
Fist natural fibers is Rayon
Fist synthetic fiber in Nylon.

1) Polyamides

It is the most used fiber having amide linkage . It is of two types.

Nylon 6, 6

It is produced by condensation polymerization of adipic acid and hexamethylene diamine.

Adipic acid an hexa-methylene diamine are manufactured form cyclohexane low water absorption, high temperature, high strength , chemically stable compare to nylon 6.

Nylon 6

It is produced by polymerization of caprolactum which is in turn produced by cyclohexane

Properties of Nylon :

1) Good abrasion resistance.
2) Good electrical insulator.
3) Chemically inert to weak acids.

Application

Parachutes, conveyor and seat belts, clothing , sport equipment, bearing , Nylon tyre etc.

2) Polyesters

It is of two types

- Dacron is a condensation product of DMT (Dimethyl Terephalate) and ethylene glycol.
- DMT – can be obtained from P-xylene and P-toluic esters with catalysts.
- Terylene-PTA (Purified terepthalic acid) and ethylene glycerol .
- PTA-can be obtained from oxidation of p-xylene

Application: It is used in beveraging for liquor and as well as used as fibre.

3) Acrylic fiber

Third largest class of synthetic fiber after polyester and nylon.

Orlon

Commercially acrylic fiber is orlon. In a acrylic fiber, monomer is acrylonitrile , which is produced by ammoxidation of propylene.

When some modification is dome then modified acrylic fiber is known as Dynel.
In the case of modifies acrylic fiber, acrylonitrile is co-polymerised with vinyl chloride.

It is used as clothing purposes.

4) CELLULOSIC FIBER

Out of cellulosic fiber, Rayon is most important. Rayon is made from cellulose which is derived from naturally occurring materials . Therefore it falls under the category of natural fibre.
Some of the examples are

VISCOSE RAYON

- Raw materials are mainly Cellulose, NaOH , CS_2
- Xanthation : a process in which white cellulosic fiber treated CS_2 under 20 to 30 °C to cellulosic xanthate also known as yellow fiber resolved with caustic solution to form viscous rayon. Final product is viscous rayon.

ACETATE RAYON

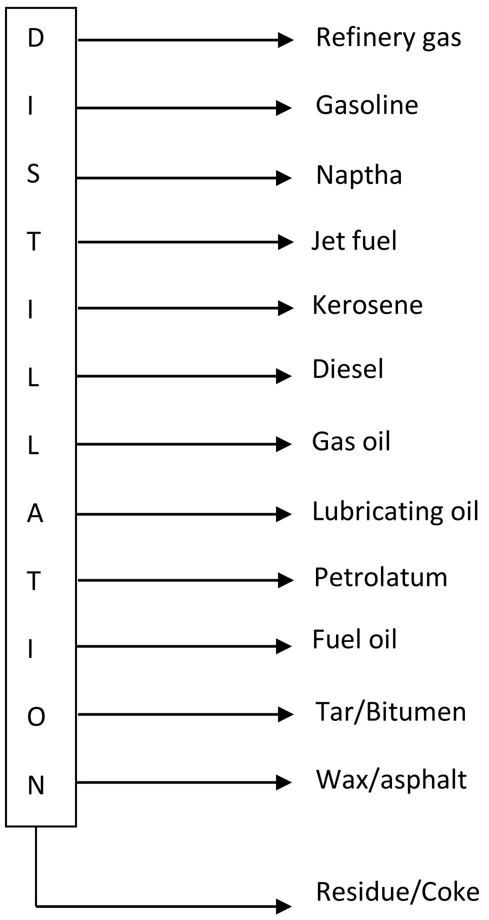
Raw materials for acetate rayon are wood pulp, acetic anhydride and sulphuric acid.

A process refinery can be view upon as combination of physical or chemical process or unit operation and unit process respectively.

Classification of crude oil

i. Paraffinic crude oil contains linear or ling chain saturated hydrocarbons.
ii. Olefinic crude oil containing unsaturated compound.
iii. Naphthenic crude oil containing saturated ring compound like cyclohexane.
iv. Aromatic crude oil C_nH_{2n-6} unsaturated ring compound. For example benzene.
v. Olefinic content in crude oil is least present.
vi. Naphthenic content present is maximum i.e., 50%.

Products of distillation



Petrolatum – it is used in the grease manufacturing.
Fuel oil – it is used to ignite the furnace.
Gas oil – Send to cracking unit to extract fraction of gasoline.

Properties of petroleum and its products :

1. Flash point

It is minimum temperature at which an oil gives out sufficient vapor to form an inflammable mixture with air and catches fire that flashes when flame is applied.

Note : The flashes should be instantaneous this temperature is known as flash point.

Fire Point → Same definition

Flashes at laser sustain for 5 seconds.

The difference between the two is 4 to 5 °C.

They tell up upper limit of temperature up to which fuel can be safely.

They are measured by instrument called pensky-martyen apparatus or Able's apparatus.

2. Cloud point and pour point

When an oil is cooled at specified rate, the temperature, at which it becomes cloudy or hazy is known as cloud point of oil.

The temperature at which oil just seized to flow is known as pour point.

Difference between cloud point and pour point is 4 to 5 °C

Pour point is lower than cloud point.

3. Octane number

This is the property of gasoline which is used in spark ignition engine to express its knocking characteristics.

Knocking characteristic – sudden explosion of fuel air mixture and collisions of flame wave which hit the engine and produce audible knowledge.

The octane number defined as the % volume of isooctane with same knocking tendency as that of fuel.

O.C.N = (% by volume isooctane)/(Isooctane and n – heptanes)

Higher the octane number, the minimum the knocking.

In India octane number – 87 is sold.

USA octane number – 94

OCN can be improved by addition of tetraethyl lead which acts as anti knocking agent.

OCN increase in the order paraffin < Napthenes < Olefins < Iso-paraffin < Aromatics Octane number of 80 inddicate that the fuel is equivalent to the performances characteristic in a fuel engine fed with 80% by volume of iso-octane and 20 % by volume n –heptane.
Branching increases the octane number. Higher is the branching, higher is the octane number.

Cetane Number

Characteristic property of diesel

Cetane number is define as percentage by volume of cetane to the mixture of cetane and α – methyl Naphthalene .

Paraffin > Naphthalene > Olefins > Iso-Paraffin > Aromatics , order of octane number .

Ethyl Nitrate or Acetone to increase cetane number. Branching decreases the cetane number. Higher is the branching lower is the cetane number , higher cetane number fascilitate easy starting of engine especially in cold weather.

Smoke Point

It is the characteristic property of kerosene.

It is minimum height of flame (in mm) , without smoke formation when the kerosene is burnt in a standard lamp under closely controlled condition.

Smoking is mainly due to presence of aromatic content. Therefore aromatic content is undesirable in kerosene. Higher is the smoke point, higher the paraffinic content and lower is the aromatic content.

For good quality of kerosene smoke point should be 23 mm.

Aniline point

It is the characteristic property of diesel.

It is lowest temperature at which oil is completely miscible with equal volume of aniline.

It is the measure of aromatic content in the oil.

More will be aniline point, lesser will be aromatic content, higher will be paraffinic content.

Aniline point give an indication of the possible deterioration of rubber ceiling, packing etc. in contact as aniline have tendency to dissolve rubber.

Acid number

It is define as number of milligram of KOH required to neutralize the free acid present in 1 gram of an oil.

It indicates the oxidation of oil and its acidic property which will cause corrosion and also result in sludge formation.

Carbon residue

It is the percentage of carbon residue left after the distillation of crude oil or its products in the absence of air.

Carbon deposits fouls the surface resulting in wear and also affect the registration of cracking catalyst.

It is measured by conradson apparatus.

Sulphure content

The presence of sulphure decreases the octane number, products SO_x in the environment and decrease efficiency of engine.
Instrument for measure is Bomb calorimeter.

Calorific Value

The calorific value of fuel can be defined as total heat produced when unit mass of fuel is completely burnt with pure oxygen. Two types of calorific values are used named as gross calorific value and net calorific value.
GCV is always greater than or equal to NCV.

Instrument is Bomb calorimeter.

Moisture content

Water in fuel is undesirable because it cause flame failure. It is measured by Dean and Stark apparatus.

Cracking

Cracking is the process by which heavy petroleum fraction (higher boiling petroleum) is converted into lighter petroleum fraction (Low boiling petroleum) Under high pressure and temperature.

It is an endothermic reaction.

Two types of cracking

1. Thermal – pressure (1 to 70 atm), temperature (450 to 750 °C)
2. Catalytic – pressure (1 to 15 atm), temperature (350 to 650 °C)

Cracking is done to produce gasoline from gas oil.
It is also used to produce olefin (Pyrolysis)
It is also used to produce coke (coking)

Thermal cracking

It is one of the secondary refinery process by which heavy fraction of petroleum are decomposed at high pressure and temperature between 450 °C and 750 °C for producing light hydrocarbons.

The cracked gasoline is an excellent motor fuel.

Coke is one of the products of cracking process. This is because of the fact that the heavy raw petroleum contains resins and asphaltnes and these converted to coke at the cracking temperature. The coke is also produced due to the polymerization of olefin hydrocarbon formed in the process of cracking of heavy petroleum fractions.

Thermal cracking are of 4 types :

1. Vis-braking
2. Thermal Reforming
3.Pyrolysis
4.Coking

Vis-braking

It is the low temperature, high pressure process 500°C and 20 atm. Feed is generally from ADU (Atmospheric Distillation Unit). The product vis-breaking comes in the intermediate boiling range from high boiling rang and is sent to thermal reforming for the production of gasoline.

Thermal reforming

It is high temperature and high pressure process, feed us mainly gas oil. It is used to produce gasoline.

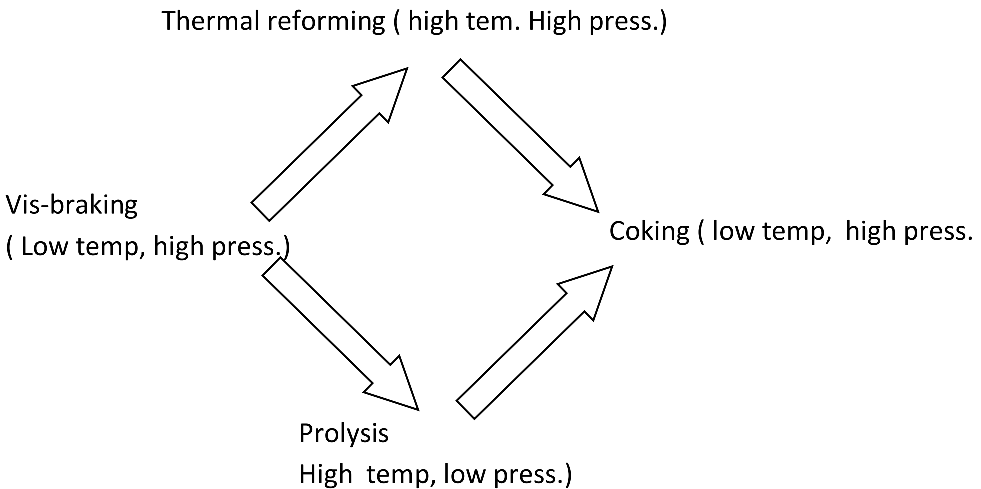
Pyrolysis

It is high temperature, low pressure (1 atm , 700 °C), it produces olefin, benzene, and toluene etc. feed is mainly naptha.

Coking

Low temperature, high pressure. More severe condition that vis-breaking feed is the residue left from thermal reforming or Pyrolysis. Coke is mainly used as electrodes in aluminum industry.

Feed from thermal reforming residue.



Catalytic cracking

Catalytic cracking compare to thermal cracking produces less coke, less gas with high performance and octane number of gasoline.

Catalyst used in the catalytic cracking are in the form of bed. Power or pellets that includes silica, alumina, natural clay, zeolite etc.

Pellets and beds are used in fixed bed catalytic cracking but powder catalyst used in fluidized catalytic craking gives higher yield of gasoline where high pressure reduces octane number of gasoline.

Fluidized catalytic cracking

It is the most important catalytic cracking that uses a reactor in series with a regenerator. In the reactor catalyst of zeolite ZSM-5 is used which helps in the cracking of hydrocarbon oil vapors into products that lies in the gasoline boiling range. As the process continues, catalytic active sites get coked and hence, regeneration is required. For regeneration purpose, catalyst are fed to the regenerator in which there is supply of air or oxygen.

Carbon deposits on the catalysts active site undergoes combustion reaction to form carbon dioxide and released enormous amount of heat which also increases the temperature of the regenerated catalyst which then enter into the reactor. Hence, no need to supply heat because in regenerator catalyst has desired temperature.

Catalyst is zeolite in power form. The cost of makeup catalyst is also very low. Residence time is too low only 3 to 5 sec.

Hydro cracking

This is combination of catalytic cracking and hydrogenation. Cracking is done in the presence of hydrogen and is known as hydro cracking. The catalyst used as tungsten sulphide for vapour phase and iron (Fe) for liquid phase.

It completely removes sulphur, nitrogen, oxygen and also help in saturating the olefinic character.

Hydro treating

Mild operation compare o hydro cracking, it removes the sulphur, nitrogen and halides and trace metals and also used to stabilized the olefin. The catalyst used is cobalt molybdenum.

Reforming

This is a process by which octane rateing of gasoline blend is increase by rearranging the molecular structure of a petroleum fraction.

The predominant reaction during reforming is the dehydrogenation of naphthalene to form high octane aromatic.

Feed is neptha , preference of feed ois coking naptha > Virgin naptha > Catalytic naptha.

Dehydrogenation of naphthenic to aromatic.

Cyclohexane – benzene

Like cracking, re-forming is also of two types

i) Thermal

ii) Catalytic reformer

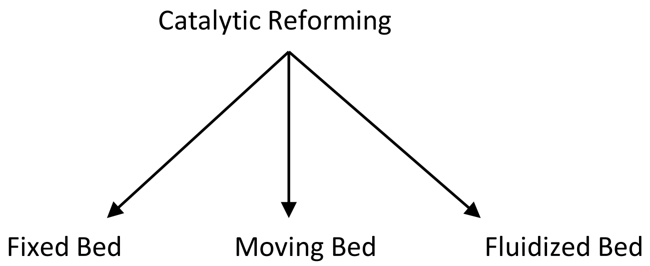
Catalytic reforming

Two types of catalyst are used

i) Precious metal oxide like platinum on alumina or silica-alumina base.

ii) Non-precious like molybdenum chromium or chromia. Generally reforming is done at 450-550 °C and 15-45 Kg/cm^2

iii) In the precious metal oxides, halides promote the activity of platinum on alumina based, but if silica alumina base is used then no halide are required.



Removal of sulphur and its component like H_2S , mercaptan from petroleum product is known sweetening

Sour curd → Sweet crude

Sweetening process

i) Doctors process
ii) Solutizer process
iii) Catalytic desulfurization process
iv) Catalytic desulfurization hydrogen process
v) Copper chloride process

Solutizer process

It is same as extraction process, solvent used are methanol or naphthenic acid.

(i) Unisol (ii) Mercapsol process

De-Waxing

The removal of wax from petroleum products specially from lubricating oil.

Process for de-waxing are :

a) Chilling and pressing (Old process)

b) Solvent De-waxing (same as extraction , solvent used in methyl ethyl ketone or propane).

De-aromatization

Removal of aromatic compound from kerosene is called as de – aromatization.

Solvent use liquid SO_2

Condition for using this solvent moisture should not present in the feed. If moisture present solvent becomes highly corrosive.

Liquid fuel from solid fuel.

Process (i) Bergius process
(ii) Ficher tropsch process

Bergius process → Coal is converted into finally power form and made into a paste with heavy oil and the heated up to 400 °C to 500 °C under 200 to 250 atm in presence of organic compounds of tin in a converter (Reactor followed by cracking and hydrogenation to yield)

(i) Gasoline

(ii) Middle oil

(iii) Heavy oil

Middle oil + hydrogenation gives gasoline.

It is efficient lower than fisher-Topssch process

Ficher Tropsch Process.

This method involve convent coal into water gas by heating 1200 °C.

$$C + H_2O \xrightarrow[\text{(water gas)}]{\text{(1200 °C)}} CO + H_2O\ (1:1)$$

Form a part of water, CO is converted to CO_2 and CO_2 is removed by absorption.

$$CO + H_2O \rightarrow CO_2 + H_2O$$

So, H_2 obtain mixed with rest of the water gas in ration of Syn gas (1: 2)

$$CO : H_2$$

Synthesis gas is passed at atmospheric pressure over a cobalt thorium oxide catalyst at 180 to 200 °C.

To increase the yield of cobalt catalyst are now replaced with iron oxide catalyst.

Ficher tropsch plant located south Africa, produces 20% of fuel of south Africa as availability of cheap coal.

Gaseous fuel

Natural Gas

It is the mixture of paraffinic hydrocarbon in which methane is main constituent.

It occurs in in gas field and oil field.

Dry natural gas : When the concentration of removal condensate is less than $15\,\frac{g}{m^3}$

Wet Natural gas : When the concentration of removal condensate is more than $50\,\frac{g}{m^3}$

Gross calorific value is more for wet net calorific value is for dry.

LNG (Liquid natural gas)

To use natural gas in its pair form is tough hence, to use it as an alternative fuel for engine. It is compressed to high pressure of 200 atm to transport natural gas; it is coated to – 160 °C to convert it into LNG which is transport in Cylinder.

Advantage of CNG or LNG

1) Octane number of CNG is very high (130)
   If Octant number > 100 then it called performance number.

2) Long life of engine, better cold starting property.

3) Less emission of unburned HC.

4) No need add lead which increase the temperature.

Disadvantage

Large tanker for storage, heavy cylinder is required (Highly press)

LPG

1) It is mainly mixture of propane and butane is used only as cooking gas.

2) C_3 and C_4 are easily liquefied at low pressure , supplied in light cylinder generally mixture of 80% butane and 20 % propane is known as LPG.

It is prepare by pure butane and propane distillation of crude oil and wet natural gas.

LPG is volatile liquid which expand 247 times its volume as vapour.

1L of LPG in liquid = 247 L of LPG in vapour.

Advantages

1) Non-Toxic

2) Does not support life.

3) Odour less

4) Heavier than oil.

Methyl Mercatan are added to detect the leakage of LPG from cylinder.

Producer gas

It comprises mainly of CO_2: N_2 in 1: 2, it is made from solid duel mainly bituminous coal.

Calorific value – 1250 to 550 $\frac{Kcal}{m^3}$

It is used in gas furnaces.

CO_2	CO	N_2	H_2	CH_4
4 to 6 %	20 to 30 %	46 to 55 %	11 to 20 %	0 to 3 %

Water Gas

It comprises mainly of CO : H_2 in 1:1, it is made from solid fuel mainly anthracite coal.

Calorific value – $\frac{2800 Kcal}{Nm^3}$

CO_2	CO	N_2	H_2	CH_4
3 to 5 %	40 to 42 %	3 to 6 %	48 to 51 %	0.1 to 0.5 %

Application

i) Fuel in furnaces

ii) Used in fertilizer industry to produce ammonia and urea.

iii) It is also known as blue gas because it burns with blue flame.