**Chemical Technology**

**Polymer:** these are larger chain molecule having a high molecular weight in the range of $10^3$-$10^7$. These are made up of single unit of a molecule which is repeated several times with a chain structure.

Polymerization is of two type.

**Addition** – 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:** $\pi$-bond is broken and two new $\sigma$-bond form.

ii. **Chain reaction:** a polymer is formed within fraction as the kinetic is very fast. The chain kinetic occurs in four steps.
   i. Initiation
   ii. Propagation
   iii. Chain transfer
   iv. Termination (may or may not occur)

iii. **Ionic reaction:** these are similar to chain addition reaction but in place of free radical. They have positive or negative charge.

**Condensation polymerization:** two or more monomers combine together to form a new compound with the help of reaction between different groups. Along with elimination of simple functional molecules.

  e.g. Nylon 6, Nylon 66.

**Types of polymer: classes of polymer**

i. Homopolymer: MMMMMM

ii. Copolymer: AMAAMMM


iv. Graft: Main chain of one monomer and side chains of another
Method of polymerization

1. Bulk or mass polymerization
   i. This mode of polymerization may be employed to obtain purest form of polymer & 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 removal is main concern, heat control system are required
   ii. Very viscous difficulty in mixing.

Solution polymerization

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 mol wt.
- Some traces of solvent present in the product which need separation which further increase cost.

Difficulties
   i. Exothermic reaction, heat removal is main concern, heat control system are required

Suspension polymerization (mm):

it is the polymerization of one or more monomers by dispersion in the form of droplets of various sizes in a non-dissolving liquid. In order to control enormous amount of heat, relevant in bulk polymerization method was develop. 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 used to moulded to large.

Agitators are used to maintain specific droplet size & dispersion. It produces small sphere.
Advantage:
- Economical method water is used as suspension agent.
- Heat transfer is easily transfer good quality of polymer obtain.

Disadvantage:
- The formation and maintenance of uniform suspension of the monomer droplets are the main problem.
- Proper agitation and stability agents for maintaining the suspension.

E.g. PMMA, PVC, PE

**Emulsion polymerization (um):**

E.g. Rubber polymer and some plastic

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

**Differ from suspension polymers:**
1. Particle size in 0.1 μ in diameter.
2. Initiator is in the aqueous phase.

Agitator is not required because of emulsion agent.

Advantage:
- Heat transfer excellent.
- Low molecular weight polymers.
- Soft & tacky product can be miniature use due to agglomeration.

Disadvantage:
- The surface active agent used in all producing emulsion polymer are water soluble which result in some degree of water sensitive.
- The presence of ionic material which are introduced in the polymer by the used of surface active agents and which result poor electric property.
Elastomers

Elastomers are the resistance solid which have considerable flexibility. They are composed of polymer which have glass transition temp below room temp.

GTT: it is the temp at which glassy state convert into rubbery state.

Styrene Butadiene Rubber

Styrene butadience rubber (SBR)

\[ \text{directly from Naptha cracker or ethylene} \]

Application → tyres & tyre related product

SBR blended with styrene to increase tensile strength hard.

Polybutadiene: PB is not directly use as rubber rather as blending agent to blend with some other rubber to improve the quality of rubber.

Therefore use in making balloon inner types of tire.

Nitrile Rubber-

Acrylonitrile butadiene rubber

Uses Is as gasket (sealing purposes)

(polyisoprene)-Natural Rubber

Derived form heave tree.
Synthetically NR is manufacture in naphtha cracker
Used as rubber.

**Polychloroprene: (Neoprene) or synthetic rubber**

Raw material is chloroprene is made by acetylene.

\[ 2 \text{Acetylene} \rightarrow \text{monovinly acetylene} \]
\[ \text{HCl} \]
\[ \text{chloroprene} \]

Used in transportation industry.

**Chlorobutyl Rubber**

Isobutylene & isoprene (3%)
Making of tubeless tyre

**Polysiloxanes**, also known as silicon Rubber

Row material is siloxane

**Polysiloxanes**: exceptional mechanical performance under extreme condition of temp therefore use in electrical appliance & aerospace industry.

**Hypalon**: condensation product of chlorinated sulphur monoxide & polyethylene and therefore hypalon is known as chlorosulphorated polyethylene compound.
**Application:** convert belt.

**POLYURETHANE (rubber):** isocyanates & polyol used in making tyres of industrial tricks urethane linkage (NH-CO)

E.g. spandex it is a synthetic fiber to r its exceptional elasticity.

It is polyurethane pleurae copolymer.

**Thermoplastic:** thermoplastic are organic chain polymers usually become soft when heated and can be molded again and again under the pressure & temperature.

They can be linear or branched can have very low or no cross link.

Ex: PE, PP, PS, PVC, PC, PBT.

**Poly ethylene:** main product of petro-chemical is ethylene. Most widely use thermoplastic its every increasing demand due to availability of monomer ethylene

**Properties of poly ethylene**

i. Low price
ii. Electrical insulation
iii. Good chemical resistance
iv. Good process ability
v. Toughness flexibility in films.
vi. Transparency.

- (LLDPE) which is intermediates and structure to the high pressure and low pressure materials (50%) marker.

**Preparation of monomer**

Earlier – monomer are taken from sugar molasses which ethylene alcohol which then dehydrated to get ethylene.

Now, petroleum source, steam cracking

**Polymerization of ethylene- (process)**

I. High pressure processes.
II. Ziegler process
III. Phillips process
IV. The standard oil (Indiana) process.
V. Metallocene process

1. **High pressure polymerization**

   Pressure – 1000 – 2500 atm
   Catalyst → Benzoyl peroxide, oxygen, azodi-isobutyronitrile
Density – 0.915 – 0.94 g/cm³
ICI, UK
Product LDPE

(Intermediate process)

**The Phillips process (HDPE)**
Pressure → (30 – 100) atm
Company – Phillips – pet – co.in USA
In this process ethylene, dissolved in a liquid hydrocarbon such as cyclohexane is polymerized by a supported metal oxide catalyst (CrO₃) on finely divide silica – alumina gel.

Ziegler process (low pressure process)
(5-10 atm) density (0.945s/cm³)
(HDPE)
Catalyst → titanium chloride and aluminum triethyl
Company → Ziegler process
(Intermediate)
Standard oil company process (Indiana)
Similar to Phillips but use promoter
40 – 8 atm
Molybdenum oxide is a catalyst the solvent is used hydrocarbon.
(HDPE) – 0.96 g/cm³

**Polypropylene**
Catalyst Ziegler Natta catalyst
Low pressure
In india the only manufacture of PP is IPCI (Indian petrochemical corporation limited)

**Application**: automobile parts, car battery luggage, chair, toys.
Prop: heat resistance environment stress resistance good appearance.

**Difference between PE & PP is**
Group on carbon atom so flexibility but rigidity increase

**Polyvinyl chloride (PVR)** process use emulsion & suspension
It is second largest consumed thermoplastic & more versatile.
PVR contains
56.8% chlorine & rest HC
Benzyl peroxide catalyst

Polystyrene

- Good electrical insulation
- Transparently, rigidity, low water absorption low cost good mould ability

**Technique:** mass, suspension mostly used

**Application**
- Dials, K nons, cover for domestic appliance electrical equipment car equipment.

**Process**
- Nova PS tech
- UOP PS tech

Polycarbonate: condensation polymerization of sodium salt of bisphenol and phosgene.

- Engineering plastic
- Transparent break & secretion resistant
- Flame resistance chemical resistant

**Uses:** mobile cover, laptop cover.

Fibers:

- These are the solids which can form thread like structure & have high tensile strength.
- First natural fiber is Rayon
- First synthetic fiber is Nylon

**Polyamides**

**Nylon 6, 6:** it is produce by condensation polymerization of adipic acid and hexa-methylene diammina.

- Produce from cyclohexane
Nylon 6: it is produced by polymerization of caprolactum which is in turn produce by cyclohexane

Nylon 66: low water absorption high Temp, tensile strength, chemical stable compare to nylon 6.

Properties of Nylon:

1. Good abrasion resistance.
2. Good electrical insulator.
3. Temp below then room temp so they are flexible.

Application

Parachute conveyor & seat belts, clothing, wigs, sport, equipment, bra idly outdoor upholstery, genes, bearing, Nylon tyre.

Polysters

Dacron

Terylene

- Dacron is a condensation product of DMT (Dimethyl Terephalate) & ethylene glycol.
- DMT – P-xylene & P-toluic esters with catalysts
- Terylene- PTA (purified terephthalic acid) & ethylene glycol.
- PTA – oxidation of P-xylene

Application: photography films, videos computer & magnetic tape.

Acrylic fiber: third largest class of synthetic fiber after polyester & nylon.

Commercially acrylic fibre is orlon. when some modification is done then modified acrylic fiber is known as Dynel.

In acrylic fibre monomer is acrylonitrile which is produce by amonoxidation of propylene.

While in the case of modified acrylic fibre, acrylonitrile is co-polymerized with vinyl chloride.

E.g. clothing

Celluloses fibre

Out of cellulosic fibre, Rayon is most important. one rayon is made from cellulose derived from natural occuring material. Therefore falls under the category of natural fibre.

Some of the examples are

Viscose rayon
Cupnmmonium Rayon
Acetate Rayon
Raw materials are mainly cellulose, NaOH, CS₂

Xanthation: a process in which white cellulosic fibre treated CS₂ under 20°-30°C to cellulosic xanthate also known as yellow fibre resolved with caustic solution to form viscous Rayon. Final product is viscous Rayon.

ACETATE RAYON
Raw material for acetate rayon are wood pulp, acetic anhydride and sulphuric acid

Cuprammonium Rayon
Cellulose, copper salt & ammonia

Thermosetting
Thermosetting polymers are network of long chain molecule that is cross linked. Under heat & pressure, they decompose. They can’t be re-shaped. E.g. UF, MF, PF, epoxy resin etc.

Phenol – formaldehyde resins
1. Novalic PF resin (acid catalyzed)
2. Resol PF resin (base catalyzed)
Mainly used as adhesive

Urea formaldehyde Resin
Application – textile industrial
Acid catalytic

Melamine formaldehyde resin
It is prepare form urea. When molten urea is nested to 360°C to 700°C in the presence of quartz sand. It converts into iso cyanic acid + NH₃

Iso cyanic acid $\xrightarrow{\text{Converted}}$ Melamine + CO₂
Alumina

It is used to make non breakable kitchenware
EPOXY RESIN

Bisphenol AND epichlorohydrin
Use in coating

Sulphuric Acid Industry

MP – 10.4˚C

BP – 340˚C

Contact process

Raw material → sulphur, oxygen & catalysts V₂O₅ in pellet form disperse on a porous carries.
Process – 1
1. Burning of sulphur in presence of dry atmosphere air (which is dried with help of H₂SO₄. Dry air is required to avoid corrosion problems and fumes in the product S + O₂ → SO₂ highly exothermic

2. Product is cooled to 250˚C to 400˚C with the help of a recovery boiler.
3. Then this SO₂ is fed to multistage catalytic converter having beds of V₂O₅ catalyst.
   SO₂ + ½ O₂ → SO₃
   Less exothermic
   Slowest step.
   - In the first bed, conversion of about 80% is achieved and temperature is maintained at 550-660˚C. then it is passed to achieve 98% conversion.
4. Then SO₃ product mixed with water to form 99% conc. oleum & H₂SO₄
   - H₂SO₄ + SO₃ → H₂SO₇
   SO₃ + H₂O → H₂SO₄

Advantage of V₂O₅
1. Immune to poison
2. Required in less amount (almost 10 kg in 1 ton of H₂SO₄)
3. Low initial capital investment.
4. Only 5% is to be replaced per year.

Disadvantage
1. Less reactive – to increase reactivity we use dilute SO₂ i.e. O₂/SO₂ → high.
2. Feed to catalytic converter is 7-10% So2 before V2O5 platinum is used as a catalyst because of high reactivity but it gets easily poison and high capital investment now, that’s why V₂O₅ is used.
Paper and pulp

Pulp: Commercial fibrous materials obtain from bamboo wood & Vegas.

Method of pulping
i. Mechanical
ii. Chemical

Pulping: disintegration of bulky fibrous material into smaller ones in 2-5 cm small size wood chips

Steps:

i. Chipper Bin: it consists of large rotary disc having knife and it cut wood into 2-5cm chips.

ii. The wood chips contain fibre & lignin and to remove lignin from the fibre, we use a solution known as white liquor which consist of NaOH & Na₂S.

iii. This two streams along with water fed into digestor

| Water – 50% | Wood chip – 25% |

Digestor: it acts as a pressure cooker and 25 to 30 m tall tower, temp is maintain at 170°C at the top & middle section and 65°C at the bottom section. In digestor under the action of white liquor & high temp, wood chips start to break & lignin starts to dissolve in white liquor and color of white from the digestor undergoes a series of bleaching & washing changes it colors changes from brown to white.

Bleaching agents are H₂O₂, O₃ & Cl₂O₂ etc.

Bleached fibre store as pulp for further use may sent to paper mill for the paper production. Blank liquor recover from the digestor undergoes recovery section and recovery is done to decrease pollution & regenerate white liquor. Black liquor obtain from digester is very dilute. Therefore it is concentrate with evaporator 10-12 % to 60-65%. Then conc. Black liquor send to mixed tank where make up chemicals are added (Na₂SO₄ & S).

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

\[
\text{Na}_2\text{SO}_4 + \text{C} \rightarrow \text{Na}_2\text{S} + \text{CO}_2
\]

Heat is so produce is use in the production of steam which in turn use in production of electricity required for mill.
The production from the boiler sent to dissolving tank where cold water is added recover green liquor.
Green liquor is then sent to causticizing tank where milk of time is added to recover white liquor.
This cycle of converting white liquor to black liquor to green liquor to white liquor known as Kraft cycle, and it is very cost effective. Because of this paper is available to us at such rate. The whole process of making pulp is known as sulfate Kraft process.
Sulfate name is given because use of Na$_2$SO$_4$ (Alkaline process)
Na$_2$S is added to NaOH to increase its performance & also help in bleaching.
The amount of Na$_2$S present in white liquor is known as sulfidity. More is sulfidity more easier to bleach fibre.

Sulfidity = \( \frac{Na_2S}{Na_2S + NaOH} \)

This paper produce from sulfate Kraft process are strong. Therefore Kraft name is given to the process as Kraft means strong.
Product from this process- strong brown bag, strong white paper
Paper can also be produce from another process known as sulfide process which acidic process gives pure white paper having less strength.

**Difference b/w sulfate & sulphide**

<table>
<thead>
<tr>
<th>Sulfate</th>
<th>Sulphid pro.</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. Alkaline process</td>
<td>I. Acidic process</td>
</tr>
<tr>
<td>II. Strength of paper is high</td>
<td>II. Low strength</td>
</tr>
<tr>
<td>III. Brown or less white paper</td>
<td>III. White paper</td>
</tr>
<tr>
<td></td>
<td>IV. Magnesium bi-sulphate &amp; sulphur dioxide in acidic medium with cooking liquor.</td>
</tr>
</tbody>
</table>

**Paper**

The fibre produces from pulping send to web forming section where they are mechanically disintegrated to a very small size & they are send to web-forming section where they are mixed with water.
Solution is 99% water and 1 % fiber. The web is reining on a belt to reduce water content and then sent through pressing section where the slurry passes though pressure reduce water content 60-65%. The production is sent to the dry section where it passed through smoothing roll, steam heated metal rolls and drying roll to reduce water content to 5%. The product is then send to finishing section where it is pass through calendaring roll for making smooth paper and winding roll to wind up the paper in the form of bundle.
**Fertilizer Industry**

Ammonia (NH₃)
- MP → - 32.7°C
- BP → - 77.7°C
- Solubility → soluble in water
- It is used in making urea.
- Raw material → N₂ & H₂
- N₂ → air
- H₂ → Synthesis gas
- Catalysts FeO

Haber’s process, temp – 500-600°C press (100-1000 atm)

\[
2N₂ + 3H₂ \rightleftharpoons 2NH₃
\]

Endothermic
- The main problem is maintaining the temp as catalyst diffuses over 620°C.

**Urea**

NH₂CONH₂
- BP → decompose
- Soluble in water
- Raw material carbon dioxide (From Syn gas)
- Ammonia – from ammonia plant
- Urea use as nitrogen fertilizer either in solid form or liquid form

- In solid form → 40-42% N₂
- Liquid form → 45% N₂

1. Ammonia & CO₂ stream are compressed separately and fed to reactor at 185°C & 200 atm where following reaction takes place.

\[
2NH₃ + CO₂ \rightarrow NH₄COONH₂
\]

2. Urea, ammonium carbamate & unreacted reactant, water stream are heated & depressurized and sent to flash evaporator operate at 27 atm, when NH₃ & CO₂ react completely.

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

4. The 99% molten urea is then sprayed form prilling tower and temp is maintained just above Melting Point of urea to minimize the production of bi-Uriet which is undesirable.

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

Phosphorous Fertilizer

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

They are form of calcium phosphate

<table>
<thead>
<tr>
<th>SSP</th>
<th>TSP</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. Calcium phosphate</td>
<td>I. Calcium phosphate</td>
</tr>
<tr>
<td>II. Raw material is phosphate rock + H₂SO₄</td>
<td>II. Raw material Phosphate Rock + H₃PO₄</td>
</tr>
<tr>
<td>III. 16-20% content in phosphate rock</td>
<td>III. 40-45% content in phosphate rock</td>
</tr>
<tr>
<td>IV. Phosphate rocks are crushed mixed with H₂SO₄ which 60% concentrate passed through blender and passed through rotary granulator and rotary dryer to get SSP</td>
<td>IV. Same process</td>
</tr>
<tr>
<td>V. To make ammonium sulphate NH₃ is added before rotary granulator</td>
<td>V. To make ammonic phosphate NH₃ is added before rotary granulator.</td>
</tr>
<tr>
<td>VI. Final product form required 24 hr storage.</td>
<td>VI. No storage required.</td>
</tr>
</tbody>
</table>

To make SSP Now a day’s nitric acid is used as the process now gives SSP having high phosphorous content as compared to previous process.
**Chlor alkali**

*production of NaOH & chlorine*

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

\[ Na^+ + H_2O + e^- \rightarrow NaOH + \frac{1}{2} H_2 \]

\[ NaCl + H_2O \rightarrow NaOH + \frac{1}{2} H_2 + \frac{1}{2} Cl_2 \]

**Mercury cell process:**

\[ Na + e^- \rightarrow Na^0 \]

\[ Na^0 + Hg \rightarrow NaHg \]

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

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

Step 1: Brine is purified by adding Na\textsubscript{2}CO\textsubscript{3} & NaOH and H\textsubscript{2}SO\textsubscript{3} is used for drying of chlorione.

Step 2: the porine is the fed to diaphragm cell which then produces 10-12% NaOH, which is concentrated to 50% bu multi effected ersporation.

Step 3: more purified Brine is then fed to mercury cell then to denuding tower to produce 70% conc. NaOH.

Step 4: chlorine is washed dried with H\textsubscript{2}SO\textsubscript{4} and then refrigerated and stored.

**Difference b/w**

<table>
<thead>
<tr>
<th>Dia phagram</th>
<th>mercury</th>
<th>Membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Less purified brine can be used</td>
<td>More</td>
<td>More</td>
</tr>
<tr>
<td>10-12% conc. NaOH</td>
<td>70% conc. NaOH</td>
<td>33% NaOH</td>
</tr>
<tr>
<td>As bestor</td>
<td>Mercury (we use)</td>
<td>Use (membrane)</td>
</tr>
<tr>
<td>Chlorine contain oxygen</td>
<td>Chlorine is pure</td>
<td>Chlorine product contain O\textsubscript{2}</td>
</tr>
<tr>
<td>Energy contain very less indiapha</td>
<td>Energy consummation high</td>
<td>Energy consumes 77% of Hg.</td>
</tr>
</tbody>
</table>

End users of paper & pulp, soap & detergent, fertilizer pharmaculates etc
Oil & fats

These are of two types:

i. Essential oil
ii. Veg oil

Oil used for the nutrient of animal, plant or human are vegetable oil
Oil use in cosmetic, soaps are known as essential oil
Oils are generally of glycerides of fatty acid.
Generally having the form

\[
\text{R1: Co} \quad \text{O} \quad \text{CH}_2
\]

\[
\text{R2: Co} \quad \text{O} \quad \text{CH} \quad \text{tri-glyceride}
\]

\[
\text{R3: Co} \quad \text{O} \quad \text{CH}_2
\]

Stearic \( \text{C}_7 \text{H}_{35} \) double ↑
Oleic \( \text{C}_{17} \text{H}_{33} \) bond ↓
Linbleic \( \text{C}_{17} \text{H}_{31} \) MP reactivity
linolenic \( \text{C}_{17} \text{H}_{29} \) towards oxygen

Therefore problem of rancidity occurs.
To avoid this problem oils & fat undergoes hydrogenation to yield saturated compound in presence of nickel or Raney Nickel (Alloy of Ni & Al) process description.
Either by digestion process used in pulp & paper or by extraction
Oil coming from both the process sends to purification.

i. Alkali or \( \text{Na}_2\text{CO}_3 \) is added to remove the impurity by coagulation in the form of foots then foot is send to the so in industries.
ii. Then bleaching is done with the help of feller earth.
iii. At least the finish oil is sent for hydrogenation to ↑ the MP and ↓ the reactivity.
iv. Ghee based oil is hydrogenated at low pressure & high temp to yield a product with MP similar to pro butter.
v. Vanaspati oil is produced by hydrogenation ↑ (high) press and low temp to yield s product having high MP, max stability and use for cooking temp.
Temp should not be exceeding 200°C to avoid side r × n.
Sugar industry

Sugarcane it gives sucrose \( \text{C}_{12}\text{H}_{22}\text{O}_{11} \)
Soluble in water
Process step:

i. It is crushed and pressurized by three pressure roll & water is added to its yield.
ii. The juice is treated with calcium hydro phosphate followed by lime to precipitate the colloids.
iii. \( \text{SO}_2 \) bubble through the juice to H the PH reach 7 and it also help in beaching.
iv. Juice is then filter with cake filter, and a kes obtain use as manage.
v. Juice is sent to malt effect evaporator for enporation.
vi. Then the crystallization is done and the soln of crystal and syrup is known as mass cite.
vii. Finally crystals are separated by centrifugaration and white sugars are made by carbonation.

The mother liquor the left is known black strap molcess with in the send to alcohol industry.

Soap & detergent

Soaps are the compounds of the type \( \text{RCOOM} \) where \( \text{M} \) is any alkali metal where \( \text{RCOO} \) tatty acid.
Detergents can anionic & cationic
Anionic detergents are those which give \( \text{R}^- \) negative in water and have detergent characteristic.
For e.g. sulphates, sulphonets and
\( \text{ABS} \rightarrow \text{alkyl Benzene sulphonate} \)
Linear alkyl benzene suphonate
- Cationic detergents are those which give \( \text{R}^+ \) in water and have germicidal properties.
  - E.g. \( \rightarrow \) ammonium compounds such as pyridium derivatives.

Soap manufacturation

Two steps is important in the manufacture, one is fat splitting it is used to produce fatty acids & glycerin from vegetable oil or other fatty oil.
Soaponification \( \rightarrow \) it is used to produce soap by reacting the fatty acid with alkali P.e. \( \text{NaOH} \).
Raw materials required veg oil
Other fatty oils
\( \text{NaOH} \)
Metal oxide with \( \text{Zn} \) (\( \text{Zno} \))
Producer gas
It comprises mainly \( \text{Co}: \text{N}_2 \) in 1:2, it is made from solid fuel mainly bituminous coal.
Calorific value – 1250-550 Kcal/m\(^3\)
It is used in gas finances.
<table>
<thead>
<tr>
<th>CO₂</th>
<th>Co</th>
<th>N₂</th>
<th>H₂</th>
<th>CH₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-6%</td>
<td>20-30%</td>
<td>46-55%</td>
<td>11-20%</td>
<td>0-3%</td>
</tr>
</tbody>
</table>

Water gas Co: H₂

1: 1

Calorific value – 2800 Kcal/Nm³

Produce from anthracite

<table>
<thead>
<tr>
<th>CO₂</th>
<th>Co</th>
<th>N₂</th>
<th>H₂</th>
<th>CH₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-5%</td>
<td>40-42%</td>
<td>3-6%</td>
<td>48-51%</td>
<td>0.1 to 0.5%</td>
</tr>
</tbody>
</table>

Application

i. Fuel in furnaces.

ii. Use in fertilizer industry to produce ammonia & urea.

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

Petrochemicals

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

\[
C_xH_y + H_2O + O_2 \rightarrow \text{Methane, ethane + ethylene + propane + propylene + butane + butylenes + Co + CO}_2 + \text{benzene + toluene + C + heavy oils}
\]

Steam cracking is the heart 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 temp (800°C) to yield following product.

2. Quench section or Zone: Product produce 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)

Separation section
(Methane) + (Ethane + Ethylene) + (Propane Propylene) + (Butane + Butylenes) + (Co + Co₂) + (Benzene + Toluene)
(C+ Heavy Oil)

Products of petrochemicals

1. Formaldehyde →
   i. Process → catalytic conversion of methanol to methanol using cu- zeolite catalyst
   ii. Methanol convert to form formaldehyde
      \[ \text{CH}_3\text{OH} \rightarrow \text{HCHO} + \text{H}_2 \]

2. Chloromethane →
   \[ \text{CH}_4 + \text{Cl}_2 \rightarrow \text{CH}_3\text{Cl} + \text{HCl} \]
   \[ \text{CH}_3\text{Cl} + \text{Cl}_2 \rightarrow \text{CH}_2\text{Cl}_2 + \text{HCl} \]
   \[ \text{CH}_2\text{Cl}_2 + \text{Cl}_2 \rightarrow \text{CHCl}_3 + \text{HCl} \]
   \[ \text{C}_4\text{Cl}_3 + \text{Cl}_2 \rightarrow \text{CCl}_4 + \text{HCl} \]

   Not catalyst used. absence of O₂ and photochemical process

3. Vinyl chloride → raw material is ethylene
   Chlorination of ethylene
   \[ \text{C}_2\text{H}_4 + \text{Cl}_2 \xrightarrow{\text{FeCl}_3} \text{C}_2\text{H}_4\text{Cl}_2 \]
   \[ \text{HCl} + \text{CH}_2\text{CHCl} \xrightarrow{\text{charcoal}} \text{CH}_2\text{OCH}_2 \]

   Vinyl chloride

4. Ethylene oxide → Partial oxidation of ethylene in presence of silver oxide or alumina.
   \[ \text{C}_2\text{H}_4 + \frac{1}{2} \text{O}_2 \rightarrow \text{CH}_2\text{OCH}_2 \]
   Ago
   Or
   Alumina
5. Ethanol amine →

\[ \text{C}_2\text{H}_4 + \frac{1}{2} \text{O}_2 \xrightarrow{\text{Ago, Alumina}} \text{mono ethanol amine} \]

By the ammonification process of ethylene oxide

6. Iso-Propanol →

\[ \text{Propylene} + \text{H}_2\text{SO}_4 \rightarrow \text{Isopropyl Sulfate} \]

Hydration

\[ \text{Iso Propanol} + \text{H}_2\text{SO}_4 \]

7. Acetone →

\[ \text{Propylene} + \text{H}_2\text{SO}_4 \rightarrow \text{Isopropyl Sulfate} \]

Hydration

\[ \text{Iso Propanol} + \text{H}_2\text{SO}_4 \rightarrow \text{Acetone} \]

8. Cumene Or Isopropyl Benzene

\[ \text{C}_4 \]
Raw materials

Benzene & Propylene in the presence of Zeolite to form cumene by the help of alkylation

9. Acrylonitrile → it produces by the amination of propylene.

10. Iso perene → three steps

Dimerisation

\[
\text{Tripropyl / Aluminium} \quad 2 \text{Propylene} \rightarrow 2-\text{methyl 1- pentene}
\]

Isomerisation

\[
2-\text{methyl 1- pentene} \rightarrow \text{Acid catalyst} \quad 2\text{methyl 2- pentene}
\]

Pyrolysis

\[
2-\text{methyl 2- pentene} \rightarrow \text{HBr} \rightarrow \text{Isoprene}
\]

11. Butadiene →

\[
n-\text{butane} \rightarrow \text{dehydrogenation} \quad \text{cromium oxide} \rightarrow \text{Butadiene}
\]

12. Benzene → Toluene goes hydrogenation in the presence of chromium oxide to form Benzene.

13. Phenol from cumene (2 steps)

a. Per oxidation

\[
\text{Cummene} + \text{Basic} \rightarrow \text{Cummene hydro} \rightarrow \text{Acid} \quad H_2SO_4
\]

No - Phenol +
14. Phenol from Toluene (2 steps)
   a. Oxidation.
      \[ \text{Toluene} + \frac{1}{2} \text{O}_2 \rightarrow \text{Benzoic acid} \]
   b. Reduction.
      \[ \text{Benzoic acid} \rightarrow \text{phenol} \]

15. Phenol from Benzene (3-steps)
   a. Chlorination.
      \[ \text{Benzene} + c_2 \rightarrow \text{Benzyl chloride} \]
   b. Causticization.
      \[ \text{Benzyl chloride} + \text{NaOH} \rightarrow \text{Sodium Benzoate} \]
   c. Hydrolysis in acidic medium.
      \[ \text{Sodium benzoate} \rightarrow \text{phenol} \]

16. Styrene:
   a. Alkylation of benzene to form ethyl benzene in presence of \( \text{AlCl}_3 \).
   b. Dehydrogenation of ethyl benzene in the presence of \( \text{Sno}/\text{Feo} \).

17. \( \text{PPthalic anhydride} \)

\[ \text{Napthalene} + \text{O}_2 \xrightarrow{\text{V}_2\text{O}_5} \text{PA} \]
\[ \text{O-xylene} + \text{O}_2 \xrightarrow{\text{V}_2\text{O}_5} \text{PA} \]

18. \( \text{MMaleic Anhydride} \)

\[ \text{Benzene} + \text{O}_2 \xrightarrow{\text{V}_2\text{O}_5} \text{MA} \]

19. \( \text{DDT} \rightarrow \text{Dichloro Diphenyl Trichloro ethane} \)
    Monochloro + chloral 1
Benzene

Oxo-processing – it is the technique used for making aldehyde

General reaction

\[ \text{Olefins} + \text{Co} + \text{H}_2 \rightarrow \text{Aldehyde} \]

- Aldehyde may be oxidizing to give acid or may undergo hydrogenation in the presence of nickel form alcohol.

Petroleum Industry

The crude oil is multi-component mix of more than $10^6$ compounds.

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

Classification of crude oil

i. Paraffinic crude oil containing saturated hydrocarbon.

ii. Olefinic crude oil containing unsaturated compound.

iii. Naphthenic crude oil containing saturated ring compound.

iv. Aromatic crude oil $C_nH_{2n-6}$

v. Olefinic content in crude oil is least present

vi. Naphthenic presence is maximum – 50%

Products of distillation

- Refinery gas
- Gasoline
- Naptha
- Jet fuel
- Kerosene
- Diesel
- Gas oil
- Lubricating oil
- Petrolatum
- Fuel oil
- Tar/bitumen
- Wax casphalt
- Light fuel oil
- Heavy fuel oil

Residue/Coke
Petrolatum – it is used in the grease manufacture.
Fuel oil – it is used to ignite the furnace.
Gas oil - send to cracking unit to extract fraction of gasoline.

**Properties of petroleum:**

1. **Flash points** → it is minimum temp at which an oil gives out sufficient vapour to form an inflammable mixture with air and catches fire that is vapour flash when flame is applied.

   **Note** – the flashes should be instantaneous this temperature is known as flash point.

   **Fire point** → same definition
   Flame at least sustain at 5 sec
   The difference between two is 4-5°C
   They tell us upper limit of temperature up to which fuel can be use safely.
   They measure by instrument
   Pensky-martyn apparatus
   
<table>
<thead>
<tr>
<th>Flash point</th>
<th>fire point</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gasoline</td>
<td></td>
</tr>
<tr>
<td>Diesel</td>
<td></td>
</tr>
</tbody>
</table>

2. **Cloud point and pour point**

   When an oil is cooled at specified rate of the temp at which it becomes cloudy or hazy is known as cloud point of oil.
   The temp at which oil just seized to flow is known as pour point.

<table>
<thead>
<tr>
<th>Petrol diesel</th>
<th>Diesel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cloud point</td>
<td></td>
</tr>
<tr>
<td>Pour point</td>
<td></td>
</tr>
</tbody>
</table>

   Difference 4-5°C

3. **Octane Number**

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

   Knocking characteristics – sudden explosion of fuel air mixture and collisions of flame wave which hit the engine and produce audible knocking.
   The octane No defined as the % by volume of iso-octane with same knocking tendency as that of fuel.
\[ OCN = \frac{\text{% by volume isoctane}}{\text{iso} - \text{octane} \& \text{n} - \text{heptane}} \]

- Higher the octane No, the min\textsuperscript{m} the knocking.
  In India octane No – 87 is sold
  USA octane No – 94
  OCN can be improved by the addition of tetraethyl lead which acts as anti knocking agent.
  OCN increase in the order paraffin \textsuperscript{N}apthenes < olefins < Iso paraffin < Aromatocs
  Octane No of 80 indicate that fuel is equivalent to the performances characteristic in a fuel engine fed with 80% by volume of iso-octane and 20% by volume n-neptane.
  Branching increases the octane number. Higher is the branching, higher is the octane number.

**Cetane NO\textsuperscript{N} characteristic property of diesel**
Cetane no is defined as percentage by volume of cetane to the mixture of cetane & α- methyl Naphthalene.
Paraffin > Naphthalene > olefins > iso – paraffin > Aromatics
Ethyl Nitrate or Acetone to increase cetane number
Branching Decreases the cetane number. Higher is the branching, Lower is the cetane number
  - high cetane number facilitated easy starting of engine especially in cold weather

**Smoke point**\textsuperscript{N} it is the characteristic property of kerosene.
It is the min\textsuperscript{m} height of flame (in mm) without smoke formation when the kerosene is burn in a standard lamp under closely controlled condition.
Smoking is mainly due to only presence of aromatic content. Therefore aromatic content is undesirable in kerosene higher the smoke point higher the paraffinic content lower is aromatic content.
For good quality of kerosene smoke point should be 25 mm.

**Aniline point**\textsuperscript{N} it is the characteristic property of diesel.
It is lowest temp at which oil completely miscible with aniline.
It is the measure of aromatic content in the oil.
More will be aniline point lesser will be aniline content, higher will be paraffinic content.
Aniline point give an indication of the possible deterioration of rubber ceiling, packing etc in contact have tendency to dissolve rubber.

**Acid No**\textsuperscript{N} it is defined as no of milligram of KOH required to neutralizing the free acid in 1 gm of oil.
It indicates the oxidation of oil & 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 product in the absence of air. Carbon deposits force the surface resulting in wear and affect the regeneration of cracking catalyst. It is measured by Conradson apparatus.

Sulphur content → the presence of sulphur decreases the octane number, produces SO\textsubscript{x} in the environment and decreases the efficiency of the engine. Instrument for measurement by Bomb calorimeter.

Calorific value → the calorific value of fuel can be defined as the total heat produced when unit mass of fuel is completely burned with pure oxygen. Instrument Bomb Calorimeter.

Moisture content → water in fuel is undesirable because it causes flame failure. It is measured by Dean & Stark apportion.

**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 (1-70 atm), temp (450-550°C)
2. Catalytic – pressure (1-15 atm), temp (350-650°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 processes by which heavy fractions of petroleum are decomposed at high pressure and temperatures between 450°C and 550°C for producing light hydrocarbons. Crude petroleum contains only 10-15% of gasoline. This content reaches as much as 20-30% or over when crude is thermally cracked. 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 asphalts and these converted to coke at the cracking temp. 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-breaking
2. Thermal Reforming
3. Pyrolysis
4. Coking

Vis-breaking → it is the low temp; high pressure process (500°C & 20 atm) product min" gasoline max" furnace feed is generally from ADU.

Thermal reforming → high temp & high pressure, feed is mainly naphtha used to produced gasoline.

Pyrolysis → high t, low pressure (1 atm, 700°C), it produce olefin, benzene & toluene etc.

Coking → low T, high pr more seiver condition than Vis-breaking, so, feed is coke is mainly use as electrodes in aluminum industry.
Feed from thermal reforming residue.

Catalytic cracking → catalytic cracking compare to thermal cracking produce less coke, less gas with high performance octane no of gasoline.
- Catalyst used in the catalytic cracking in the form of bed, powder or pellets include silica, alumina, natural clay, zeolite etc.
- Pellets & beds are used in fixed bed catalytic cracking but powder catalyst used in fluidized catalytic cracking gives higher yield of gasoline where higher pressure reduces octane no of gasoline.

Fluid catalytic cracking:
Products: higher yields of motor gasoline wit octane no 80-85. Iso-butane and light olefins are available for pukylation, polymerization LPG, most efficient unit of refinery, in the regenerator reaction is exothermic and in the reactor is endothermic.
No need to supply heat because in regenerator catalyst has desired temperature.
Catalyst is Zeolite in powder form the cost of makeup catalyst is also very low. Residence time is two low only 3-5 sects.

**Hydro cracking** → this is combination of catalytic cracking & hydrogenation. Cracking is done in the presence of hydrogen is known as hydro cracking, the catalyst used as tungsten sulphide for vapour phase & Iron (Fe) for liquid phase. High pressure & temp (400-500°)

**Product** → gasoline, Jet fuel and diesel oil

It completely removes sulphur, nitrogen, oxygen & also help in saturating separated of olefin.

**Hydro treating** → mild operation compare to hydro cracking, it removes the sulphur, nitrogen and halides and trace metals and also use to stabilize the olefin, the catalyst use in cobalt molybdenum.

- Temp - low
- Press - high
  - Type of hydro treating
    - Aro fining
    - Auto fining

**Reforming**

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

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

Feed is naphtha, preference of feed is virgin naphtha > coking naphtha > catalytic naphtha.

Foreign dehydrogenation of naphthenic to aromatic

- Cyclohexane → benzene

**Like cracking, reforming is also of two types.**

i. Thermal
ii. Catalytic reforming

**Catalytic reforming**

**Two types of catalyst are used**

i. Precious metal oxide like paltimum or alumina or silica-alumina base.

ii. Non-precious like molybdenum chromium or chromina or calamine bed pellets and powder.

  Generally reforming is done at 450-550°C and 15-45 kg/cm²

iii. In the precious metal oxides, catalysts halides promote the activity of platinum on alumina based, but if silica aluminas are used then no halide are required.
1. Fixed
   i. Non regenerative process -> plugging
   ii. Regenerate process – hydro forming.

2. Moving Bed
   i. TCR (thermo catalytic reforming)
   ii. Hyper forming

3. Fluidized
   Hydro forming process

**Polymerization**

Gases produce in cracking are rich in C2 and C4 compounds (olefin). Therefore undergoes polymerization in the presence of phosphoric acid to give product of gasoline product range.

E.g. 2 Iso-butanec → Di-iso butane

Gasoline produce names as polymer gasoline.

**Alkylation**

In petroleum refining alkylation means reaction of an olefin with iso-paraffin to produce a larger iso-paraffin having higher octane number.

E.g. Iso-butane reacts with propene to give iso – heptanes catalyst H2So4, HF.

**Isomerization**

In petroleum refining isomerization is done to state chain paraffin to iso-paraffin in the presence of aluminum chloride as catalyst.

Ex;

\[
\text{n-butane} \xrightarrow{\text{AlCl}_3} \text{iso-butane}
\]

**Purification of petroleum products:**

Removal of sulphur & its component like H2S, mercaptan from petroleum product is known sweetening.

Sour crude → sweetening

Sweetening process
   i. Doctor’s process
ii. Solutizer
iii. Catalytic
v. Copper chloride.

Solutizer process $\rightarrow$ it is same as extraction process, solution use methanol or naphthenic acid.

Unisol process  mercapsol process

De-Waxing
The removal of wax from petroleum product specially from lubricating oil
a. Chilling & pressing (Old process)
b. Solvent De-waxing (same as extraction, solvent used is methyl ethyl ketone or propane).

De- asphalting
Asphalt are high molecular wt compound, the readily oxidizes and form carbonaceous sludges. Therefore they must be remove from lubricating oil.
Solvent use – propane

De – aromatization
Removal of aromatic compound from kerosene is called as de-aromatization.
Solvent use- liquid $\text{SO}_2$
Condition for using this solvent moisture should not present in the feed. If moisture presents solvent become highly corrosive.

Q. Production of sulphur
Claus Process
Linde process $\rightarrow$ oxygen
Lurgi $\rightarrow$ syn gas

Process

Liquid fuel from solid fuel
Process (I) Bergius process
   (II) Fisher tropshch process

Bergius process $\rightarrow$ coal is converted into finally powder form and made into a paste with heavy oil and then heated upto 400$^\circ\text{C}$ to 500$^\circ\text{C}$ under 200-250 atm in presence of organic compound of tin in a converter (Reactor followed by cracking & hydrogenation to yield).
i. Gasoline
ii. Middle oil
iii. Heavy oil

Middle oil + hydrogenation give gasoline.
It is efficiency lower than fisher – Tropshch process.
Fisher Tropsch process
This method involves converting coal into water gas by heating it to 1200°C.

\[ C + H_2O \xrightarrow{1200°C} Co + H_2 \]  
\[ \text{Water gas} \]

Form a part of water, Co is converted to Co\(_2\) and Co\(_2\) is removed by absorption.

\[ Co + H_2O \xrightarrow{} CO_2 + H_2O \]

So, H\(_2\) obtain mixed with rest of the water gas in the ratio of Syn gas 1:2.

CO:H\(_2\)

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

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

Fischer Tropsch plant located in 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 the main constituent.

It occurs in gas field and oil field.

Dry natural gas ➔ when the concentration of removal condensate is less than 15 g/m\(^3\).

Wet natural gas ➔ when the concentration of removal condensate is more than 15 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 raw form is tough hence, to use it as an alternative fuel for engines. 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 transported in cylinders.

Advantage of CNG or LNG
1. Octane number of CNG is very high (130).
2. It has an octane number > 100 then it is called performance number.
3. Long life of engine, better cold starting property.
4. Less emission of unburned HC.
5. No need to add lead which increases the temperature.

Disadvantage
Large tanker for storage, heavy cylinder is required (highly press).

LPG
1. It is a mainly mixture of propane and butane used only as cooking gas.
2. \(C_3\) & \(C_4\) are easily liquefied at low pressure, supplied in light cylinder generally mixture of 80% butane and 20% propane is known as LPG.

It is prepared by pure butane & propene distillation of crude oil and wet natural gas.
LPG is a volatile liquid which expands 247 times its volume as vapor.
1L of LPG in liquid = 247 L of LPG in vapor.

**Advantages**

1. Non-toxic
2. Doesn’t support life.
3. Odour less
4. Heavier than oil.

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