CT-
CHEMICAL
TECHNOLOGY

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Thanks to all of You :

Sept 8th 14

Chemical Technology –

Polymer	Petroleum	Petrochemical	Natural Polt
⇒ Thermoplastic	⇒ Characteristic	Products of	⇒ Sulfuric Acid
⇒ Thermosetting	⇒ Classification	⇒ Ethylene	⇒ Paper & pulp
⇒ Elastomer	⇒ Properties	⇒ Propylene	⇒ Soap & Detergent
⇒ Fiber	↓	⇒ Butylene	⇒ Sugar
	Crude oil	⇒ Benzene	⇒ Oil & Fats
		⇒ Toluene	⇒ Chlor-Alkali
			⇒ Fertilizers.

Polymer :-

Polymers are large chain molecules having a high molecular wt., these are made up a single unit or a molecule which is repeated several tym within the chain structure. This repeating unit is known as the monomer. & the process is known as polymerization.

$$n\ (CH_2=CH_2) \longrightarrow -(CH_2-CH_2)_n-$$

Ethelene → Polyethelene

Types of Polymerization :-

Addition Polymerization :-

The rxn occur by the formation of rapid change and no elimination of small molecule takes place.

Such rxn generally occur among double & triple bonded molecules. Typ

Types of addition polymerization

Step Rxn :—

A π bond is broken and two new σ bonds are formed.

$$n(CH_2=CH_2) \longrightarrow -(CH_2-CH_2)_n-$$

Chain Rxn :-

In the chain rxn, we need four things (free radical)

→ Initiation
→ Propagation
→ Termination.

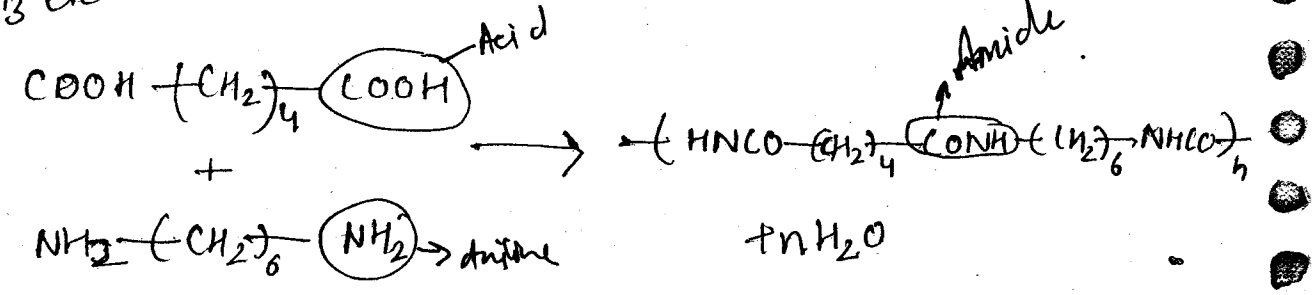
Polymer is formed in a single step within the fraction of second. the chain kinetics occur in three steps above mentioned. The chain transfer agent may be used if necessary.

Ionic Rxn :-

These are similar to the chain addition rxn wid +ve & -ve charges.

Condensation Polymerization

Two or more than 2 monomeric units combine together to form a new compound having different functional group with the elimination of small molecules like water, hydrogen, NH_3 etc.



Techniques of Addition Polymerization

Bulk Polymerization:—

» Bulk Polymerization consists of a reactor, monomer units, initiator, a chain transfer agent if neccessary and a terminator.

» This mode of polymerization may be employed to obtain the purest form of polymer.

» Pure liquid or gaseous monomer is subjected to the polymerization condition.

» The rxn is exothermic & heat removal is the main concern. Therefore heat control system is required.

» Polystyrene and many other thermoplastic compounds are made by using this technique.

Solution Polymerization:—

» An inert solvent is added to the reacting mixture in the rxn vessel in the process. The slovent enhances the heat capacity and therefore facilitates heat transfer.

» Sum of the solvent may be refluxed to remove heat from the rxn vessel.

» Compare to the bulk polymerization solution polymerization reduces both the rxn rate and the molecular wt. of the compound.

Suspensi-

Suspension/ Emulsion Polymerization:—

» In order to control an enormous amt of heat release in bulk polymerization, In suspension polymerization, rxn. mass is dispersed or suspended as minute droplets of size 1mm in dia.

⇒ Each of these droplets act as tinny bulk reactor. and the heat transfer occur from droplets to the water having large heat capacity.

⇒ Agitators are used along with the ~~stp~~ suspending agents in the aqueous phase in order to maintain a specific droplet size and the suspension.

⇒ It produces small uniform polymer sphere. These are used directly or may moulded to form large ~~spha~~ shape /desired shape.

⇒ In the emulsion polymerization, the dispersed particles are smaller in size i.e. in the range of micrometer.

⇒ In the E·P, sometimes an emulsion wid soap is used which act as stabilizing agent and no need of agitator is there for this case.

Q.) Difference btwn Suspension & Emulsion polymerization?

Q.) Action of the emulsifying agent and its name?

Classification of Polymer (based on arrangement)

Homopolymer → —MMMMM—

Co-polymer → —MMNNNMNNNMM— → Random arrangement

Block → .MMM.NNNMMMMNNN MMMM.

Graft → —MMMMM—
NNNN
NNNN

Based on branching

Linear → ——————

Branched →

Crosslinked →

Based on properties

Thermoplastic
Thermosetting
Elastomer
Fiber

Thermoplastic :—

By the application of heat & pressure this polymer becomes soft and can be moulded into any kind of shape and thus can be used again and again.

They have linear or very little branching.

eg → polyethelene, polypropylene, polystyrelene, PVC, polycarbonate.

Thermosetting :—

These consist of a network of long chain molecules i.e. cross-link which gives a polymer – a 3-D structure. By the application of heat & pressure they remain heard and can't be moulded.

eg → phenolformaldehyde, ureaformaldehyed, epoxy, melamineformaldehyde

Elastomer : —

Glassy state

Glassy state refers to the state at which the material is heard and brittle.

Rubberly state

It refers to the state at which the material is flexible & elastic

Glass transition Temp : —

The temp at which the material changes it state to from glassy state to rubbery state is known as G.T.T

Elastomer

They are resistant solids which have considerable flexibility. They are composed of polymers having GTT below room temp. All rubber comes in the class of elastomer.

eg→ Styrene butadiene Rubber, butyl Rubber, Nitrile Rubber, Polyisoprene Neoprene, Chlorobutyl Rubber, Silicon Rubber, Polyurethane Rubber. Hypalon.

Fiber:—

These are the solids which can formed thread like structure and have high tensile strength.

eg→ polyamides, polyesters, cellulosic fibers, acrylic fibers

Thermoplastic:—

It is polyethylene

Polyethelene:—

Polyethelene is most widely used thermoplastic. and its ever increasing demand is based on the availability of monomer ethelene from naptha (from petrochemical complex)

High P	Intermediate P	Low P
(1000–2500) atm	(30–100) atm	(6–10) atm.
ICI in UK	Ph. Pet. Co. in USA	Carl Zeigler Germany
Peroxide	Philips	Aluminium triethyl activated with heavy metal derivative titanium chloride. zeigler catalyst.
	MoO_3 or Cr_2O_3 on Alumina.	
Low Density Polyethelene LDPE	High Density HDPE	Linear low Density Polyethelene LLDPE

Polyethylene Uses:-

It is used as a packaging material.
eg→ cement bags.

Polypropylene:-

Monomer → propelene.
Come from the napthea cracker.

Production process:-
It is formed by the low pressure process
used as packaging material.

IPCL (Indian petrochemical Corporation Ltd) is the only manufacturer of propelene in India at the commercial scale.

Polystyrene:-

Raw Material - Styrene
Monomer of Styrene – Benzene which comes from the naptha cracker

Process
Styrene is produced by the dehydrogenation of ethyle benzene which in turn is produced by alkylation of benzene.

Use:-
Bcz of its ease of fabrication, thermal stability and low cost it finds wide application in electronics, shoe soules, wires & cables etc.

Poly Vinyl chloride

PVC is second ~~largest~~ and most versatile of all the thermoplastic,

It contains abt 56·8% chlorine and balance hydrocarbon.

A major portion of chlorine is produced in the world is used in the manufacture of PVC

Process:—

Basic monomer- Vinyl chloride which is made from ethelene produced by the petrochemical complex.

Uses:—

By the addition of plasticizers, rigid PVC can be converted into flexible PVC

Rigid PVC finds application in pipe fitting, bottles etc &

Flexible PVC " " " insulation of wire etc.

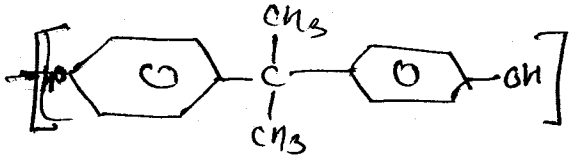
Q> Name the Plasticizers.

Q> Diff. LDPE, HDPE, LLDPE

Poly Carbonate:—

Process:—

It is produced by the condensation polymerization of the sodium salt of ~~the~~ Bis-phenol and phosgene



Bis-phenol

$COCl_2$

phosgene

used as an engg. plastic bcz they are transparent
Break Resistance
Exceptional optical clarity
Impact strength
Flame Resistance.

Thermoplastics	Monomer & Sources	Process Description	Use	Remark
Polyethylene	ethylene		Packaging Material	most widely used
Polypropylene	Propylene	low Pressure Process	Packaging Material	IPCL is only manufacturer.
Polystyrene	Styrene (Benzene)	Dehydrogenation of ethyl ⬡ which in turn produced by alkylation of ⬡	Electronics Shoe shaul wires & Cables	Ease in fabrication thermal stability low cost.
Poly Vinyl Chloride	Vinyl Chloride	VC made from ethylene prod. by petrochemical Complex.	R.P- pipe fitting bottle. F.P - insulation of wire	2nd largest & most versatile.
Poly Carbonate	Bis-phenol & Phosgene.	Condensation Polymerization		Transparent Break Resistance Exceptional optical clarity Impact strength Flame Resistance

Q.) Diff. btw LDPE, HDPE, LLDPE?

LDPE (Low Density Polyethylene) –

It has the most excessive branching.

It causes the low density to have a less compact molecular structure which makes it less dense.
It has density of 0.910–0.925 g/cm³.

HDPE (High Density Polyethylene)

It has the most ~~excessive~~ minimal branching of its polymer chain.

Bcz it is denser it is more rigid & less permeable then the LDPE.

It has density of 0.941 – 0.940 g/cm³.

LLDPE (Linear Low Density Polyethylene) more braching in compare to LDPE

It has a significant number of short branches.

Bcz of shorter & more braches its chain are able slide against each other, & long branching chains that would get caught on each ", which gives higher tensile strength & higher impact & puncture resistance.

It has a density of 0.91 – 0.94 g/cm³.
It is more transparent in comparision to other polyethylene.

Q.) Name the Plasticizer?

Plasticizer or dispersants are additives that increase the plasticity or fluidity of material.

Dicarboxylic / tricarboxylic ester-based plasticizer:–

Bis(2-ethylhexyl) phthalate (DEHP) used in construction material & medical devices

Di-n-butyl phthalate (DnBP, DBP) used for cellulose plastic, food wraps, adhesives, nail polishes, glasses, perfumes.

Di-n-hexyl phthalate (DnHP) used in flooring material, tool handles & automobile parts.

Di-octyl phthalate (DOP, DnOP) used in carpets, note book covers, high explosives.

Trimellitates

used in automobiles interiors & other application where high temp is required.

Trimethyl Trimellitates (TM TM), n-octyl trimellitates (OTM)

Other plasticizers

Benzoates, Dioctyl terephthalate, alkyl sulphonic acid phenyl ester.
Polybutene.

Biodegradable Plasticizers:—

Acetylated monoglycerides used as food additives.

Alkyl citrates used for food packaging, medical parts, cosmetics & children toys.

Triethyl citrates (TEC), Tributyl Citrates (TBC), Trihexyl Citrates (THC)

Q.) Action of emulsifing agent and its name?

Agar
Albumin
Mono & diglycerides
Monosodium phosphate
Soaps
Propylene glycol.

Emulsion (chemical) : a mixture of two or more immisible liq.

Suspension (Mechanical agitation) : a liquid containing insoluble solid particles.

A suspension can be separated and doesn't mix together but emulsion does.

for the same m.wt this process must kam ya jada hu?

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Suspension is mechanical phenomena while emulsion is a chemical phenomena.

The pdt of suspension can be separated by mechanical means but it is not same for the emulsion.

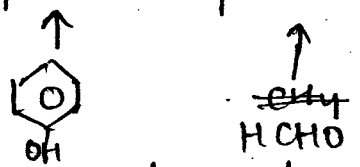
Emulsion polymerization takes place only when CMC is achived.

In suspension polymerization takes place for each droplet while for emulsion it takes place for a group of particle known as latex, having the concn greater than or equal to CMC.

Thermosetting

Phenol formaldehyde Resin

The raw material - phenol & formaldehyde



It is the oldest thermosetting polymer used as adhesive. It is of two types.

- Novalik PF (Acid catalysed)
- Resole PF (Base ")

Urea formaldehyde Resin :—

Raw material — urea which comes from ammonia & CO_2
formaldehyde " " CH_4 (Methane)

These are the pdts of condensation polymerization.
used in textile & paper.

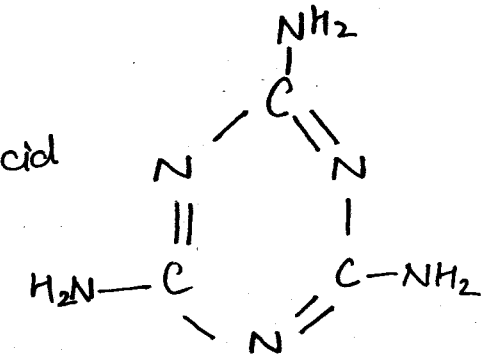
Melamine formaldehyde Resin :—

Raw material — Melamine

Melamine

It is produced from urea. When molten urea is heated to abt 360-700°C in presence of quartz, urea decomposes to isocyanic acid. Further isocyanic acid is converted to melamine in presence of alumina catalyst.

Urea
↓ Quartz
Isocyanic Acid
+NH_3
→ (Alumina)



+ CO_2

It used as non-breakable crockery in the kitchen wear and have better chemical & heat resistance compared to urea resins.

Epoxy Resin

It is made by the rxn of bis-phenol & Epichloro hydrine

It is used as coatings.

Thermosetting	Raw material	Process	Use	Remarks
Phenol formaldehyde	Phenol ← C_6H_5OH CH_4 → formaldehyde HCHO	Condensation Polymerization	as adhesive	oldest thermosetting polymer.
Urea formaldehyde	$NH_3 + CO_2$ → Urea CH_4 → formaldehyde	Condensation Polymerization	textile & paper	
Melamine formaldehyde	Urea $\xrightarrow[310-700°C]{\text{quartz}}$ Isocyanic acid + NH_3 ↓ Alumina Melamine + CO_2	"	Non-breakable crockery	Better chemical & heat resistant
Epoxy.	Bis-phenol A + Epichlorohydrin	"	Coating.	

Elastomers:-

Styrene butadiene (SBR or Buna-S) is first elastomers.

Raw material – ~~Sty~~ Styrene.

Butadiene → come directly from napha cracker or can be made from ethylene.

used for tyres & tyres Related part.

SBR + S ⟶ SBS Styrene butadiene Styrene Rubber having improved performance compared to SBR

Polybutadiene:-

Monomer - butadiene

It is not used directly as a Rubber but used as blending agent to improve the qualities of other rubber.

Butyl Rubber:- (Poly Isobutylene)

Raw material - Isobutaylene which comes from naptha cracker directly or can be made by n-butane.

$$\text{n-butane} \xrightarrow[\text{Dehydro genation}]{-H_2} \text{Isobutene} \xrightarrow[\text{Dimerisation}]{Pt} \text{Isobutylene}$$

Butyl Rubber is impermeable to gas, therefore used in making balloons.

Nitrile Rubber:- (Acrylo nitrile Butadiene Rubber)

Raw material - Acrylo nitrile
Butadiene.

Used in gaskets.

Polyisoprene (Natural Rubber)

Derived from the Hevea tree, It can be made synthetically by polymerization of isoprene which is prepared in the naptha cracker.

Neoprene :- (Poly Chloroprene or Synthetic Rubber)

The poly Chloroprene is made via ~~acyl~~ acetylene

$$\text{Acetylene} \xrightarrow[\text{Dimerisation}]{\text{Mono Vinyl Acetylene}} \xrightarrow{HCl} \text{Chloroprene}$$

Used in transportation industry.

Chlorobutyl Rubber :-

made by the rxn btw isoprene & isobutylene (3%)

It is used in making tubeless tyre

Silicon Rubber :- (Polysiloxanes)

Monomer → siloxanes

$$\{O-Si-O\}$$

They have exceptional mechanical & electrical performance under extreme temp conditions. Therefore used in the electrical appliances.

Polyurethane Rubber

Raw material → Polyisocyanate

→ Poly ~~hydroxyl~~ hydroxyl

Urethane linkage ← Alcohol + Isocyanate

They are used in making tyres of trucks.

Hypalon

Hypalon are chlorosulphonated polyethylene compds which is made by the rxn btwn chlorinated SO & Polyethylene

They are used in making conveyor belts.

Elastomers :-

Elastomer	Raw Material & Process	Uses
1) SBR/BUNA-S	Styrene ← Benzene Butadiene ← Ethylene	Tyre & Tyre Related pdt
2) Butyl Rubber	n-butane $\xrightarrow{-H_2}$ Isobutene Isobutylene $\xleftarrow[\text{Dimerisation}]{\text{Pt}}$	Impermeable to Gas used in Making Balloons
3) Nitrile Rubber	Acrylonitrile & butadiene.	Gaskets
4) Polyisoprene	Hevea Tree	As a Rubber
5) Polychloroprene	Acetylene $\xrightarrow{\text{Dim.}}$ Mono Vinyl Acetylene Chloroprene $\xleftarrow{HCl}$	As a Vulcanized Rubber
6) Chlorobutyl Rubber	Isobutylene + Isoprene (1-3)%	Tubeless tyres
7) Polysiloxane	Monomer with Siloxane linkage	Electrical Appliances
8) Polyurethane	Alcohol + Isocyanate → Urethane	Tyres for Trucks
9) Hypalon	Chlorinated SO + Polyethylene	Conveyer Belt.

SBS
↓
Blend of SBR & S

Polybutadiene
↓
used as a blending agent.

SPANDEX
(Polyurethane Rubber
having urethane as well as Urea linkage.

Q.) What are Curing Agents → functions & names.?

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Fibres

- Polyamides
  - Nylon-6
  - Nylon-6,6
- Polyester
  - Dacron
  - Terylene
- Acrylic
  - Orlon
  - Dynel
- Cellulosic
  - Viscose Rayon
  - Acetate Rayon
  - Cuprammonium Rayon.

Synthetic

Polyamide

Nylon-6,6

Raw material – adipic acid & Hexamethylene diamine.

both raw material containing 6-carbon atom.

∴ name as 6,6

Both the raw material can be prepared by cyclohexane

Nylon-6 :–

– ~~Capro~~ Caprolactum containing-6 carbon atom ∴ the name -6.

– Caprolactum can be produced by cyclohexane.

⇒ Nylon-6,6 has a higher melting pt in comparision to Nylon 6

⇒ Nylon-6,6 is chemically extremly very stable compare to Nylon 6.

Polyester :–

Dacron

It is a condensation pdt of dimethyl terephthalate (DMT) and ethylene glycol. On the other hand, terelene is a condensation pdt of ~~chlorified~~ purified Terephthalic acid (PTA) & Ethylene glycol.

Dimethyl Terephtalate is produced by p-xylene & p-toluic ester in the presence of Co Catalyst.

PTA is produced by the oxidation of p-xylene.

Q.) Diff btw PTA & DMT ?

Q.) " " Nylon6 & Nylon66 ?

Acrylic :-

Third largest consumed fiber.

The commercial acrylic fiber is orlon and modified acrylic fiber is Dynel.

In acrylic fiber, the monomer is acrylo nitryl while in modified acrylic " , acrylo nitrile is co-polymerized wid vinyl chloride.

Acrylonitryl is produced by propylene by amino oxidation process also known as ammoxidation

Cellulosic fibre :-

Cellulosic fibres are semi-synthetic fiber while the rest-3 are ~~poly~~ purely synthetic.

Rayon is the first fibre (naturally occuring)

Nylon is " " " (man made) Synethetic

Viscose Rayon :- (semi synth)

R.M ⇒ Cellulose, ~~CO_2~~ Carbon di sulphide, Sodium hydroxide

Acetate Rayon

R.M → wood pulp, acetic anhydride, Sulphuric acid.

Cuprammonium Rayon

R·M ⇒ Cellulose, copper salt, ammonia.

Xanthation:-

It is the process in which white cellulosic crumbs or fibres. treated wid Carbon di sulphide under 20-30°C to form cellulose xanthate. also knows as yellow crumbs. After this it is dissolved wid the caustic soln to form viscous Rayon.

Q.) Write uses of each ?

Woven/Non-woven fibre:-

Petroleum Refining

Unit Operations → Unit process

Crude oil is a multi-component mixture containing more than 10^{18} compounds. The process refinary can be viewed upon as a combination of both physical & chemical process or unit operation and or unit processes resp.

Dominant physical process is distillation while the chemical process involves alkylation, isomerization etc.

In petroleum refinary obtaining any intermediate pdt or a pdt stream with a defined characterization of several properties. Indicates that whether it is a disel, petrol or any other pdt.

This characterization involves the physical characterization lyk viscosity, density etc as well as chemical characterization in term of no. of functional groups or double or triple bond character.

Classification of crude oil :—

Paraffinic Crude oil :- (C_nH_{2n+2})

Saturated hydrocarbons.

Olefinic " " C_nH_{2n} → Aromatic

0% present in crude oil

Unsaturated hydrocarbon.

Napthenic " " C_nH_{2n}

50% present in crude oil

Saturated ring compounds lyk cyclohexane.

Aromatic " " C_nH_{2n-6}

Unsaturated Ring compounds lyk benzene.

Olefinic ~~is not present~~ in crude oil and 50% of napha

Olefinic content is not desired in final pdt bcz olefin undergo oxidation when it comes in contact wid air which affects the quality of final pdt. Therefore depending upon the pdt requirement we convert olefin either in aromatic or into paraffins.

Petrolatum:—

It is used as lubricant which is used in grease manufacture.

Gas oil is send to the cracking unit for further separation.

LFO & HFO are not used separately. There blend are used in firing the furnaces.

Properties of the petroleum pdt:—

Flash pt & fire pt:— (measured by Pensky-Martyen Apparatus)

The flash pt is a minimum temp at which an oil gives out sufficient vapour to form an inflamable mixture wid air and catches fire when flame is applied. But this flashes shud be instantaneous.

When the flashes sustain for atleast 5 sec then the temp noted is know as fire pt.

Both the temp indicates the usability of fuel or indicate the maximum limit of temp. upto which the fuel can be used safely

Generally fire pt is 4-5°c higher than the flash pt.

Cloud pt & pour pt:—

When an oil is cooled at specified rate, the temp at which it becomes cloudy or hazzy it becomes cloud pt of an oil.

The temp at which an oil just seize to flow or stops to flow. is known as pour pt. (at pour pt oil flows but above it, it freezes)

pour pt is 4-5°c lower than cloud pt.

Measured by cloud pt apparatus.

Octane number:-

This is a property of gasoline which is used in spark ignition engine and expresses its knocking characteristics.

Peterob knock:-

After the compression stroke, the spark plug will introduce the spark which produces a flame that propagates in a defined manner. But if fuel is of low quality then complete combustion of fuel is not there and fuel oil mixture will stick to the walls of the engine. This mixture also produces flame which collide with the central flame and results into an explosion which in turn produces an audible knock.

Octane no. is defined as $\frac{\%\text{ by volume of iso-octane}}{\text{IsoOctane} + \text{n-heptane}}$

IsoOctane → 100, n-heptane → 0

In India, the gasoline of octane no. 87 is sold, while in USA the gasoline of octane no. 95 is sold. Higher the octane no. lower the knocking and higher is the performance of gasoline. Octane no. can be improved by addition of TEL (tetra ethyl lead) which in turn causes air pollution. Octane no. increases in the order.

paraffins < Naphthenes < Olefins < Iso-paraffins < Aromatics.

Centane Number:-

It is a characteric property of diesel knock. Sudden combustion of high amt of charge & pre-mature combustion & high ignition delay period (post mature combustion).

Cetane no. increases in the order

paraffins > Naphenes > Olefins > Iso-paraffins > Aromatics

The cetane no. is defined as $\frac{\%\text{ by volume of cetane}}{\text{Cetane} + \alpha\text{-methyl Naphthalene}}$

(Cetane: I no; α-methyl Naphthalene: 0)

It can be increased by addition of ~~ethyl acetate and~~ ethyl nitrate & acetone.

High cetane no. facilitates easy starting of engine specially in cold weather

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Smoke pt:-

This is the property of kerosine and it determines the suitability of kerosene as a fuel. higher the smokept → higher the quality.

Kerosene sample is burnt in a standard lamp wid a specified wick for 5 minutes and the height of the flame is recorded when it leaves no smoky tail.

* "This is the maximum height of flame in mm wid out smoke formation when the kerosene in burnt in a standard lamp under closely controlled condition."

Aromatic content is undesirable in kerosene

Smoking of kerosene is mainly due to the presence of aromatic hydrocarbons.

A good quality kerosene used for the domestic purpose, Should have high smoke pt. 25 mm

paraffins are desirable in kerosene as it has got the highest smoke pt as the aromatic have got lowest smoke pt.

Carbon Residue:-

⇒ It is a %age of carbonaceous residue left after distillation of crude oil or its pdts in the absence of air.

→ Carbon deposites ~~feel~~ foul the surface, results in wear and affects the regeneration of cracking catalyst.

→ Carbon residue gives an indication of relative ~~fog~~ coke forming tendency. on evaporation and pyrolysis of an oil.

→ It also tells the carbon depositing tendency of fuel oil in the engines.

→ It is determine by the *Conradson Apparatus*.

→ For a good fuel it should be less than 0.1%.

Aniline pt:-

→ It is the lowest temp at which an oil completely missible wid an equal volume of aniline.

→ It is a the measure of aromatic content of the oil, More is the aniline pt, lesser will be the aromatic content, or higher is the paraffinic content.

→ It is a characteristic property of diesel.

→ The aromatic content in the oil as a tendency to dissolve rubber which cause detoriation of rubber sealings and packing. Thus aniline pt gives an indication of the possible detoriation.

→ Aniline for cetane is 95.6°C and for hexyl benzene is -12°C

Acid number:-

Acid value or acid no. determine the acidity of an oil. It is defined as no. of mg of KOH, required to neutralize the free acid present in 1g of oil.

→ Acid value of petroleum pdts should be less than 0.1.

→ Increase in acid no. indicates the sludge formation & corrosion problems.

Distillation Range

→ This is the characteristic of crude oil, diesel, gasoline etc.

→ In a distillation test, a measured volume of the oil is distilled at the specified rate which is suitably increased as the distillation proceeds.

→ The initial boiling pt i.e IBP is the temp when first drop of condensed liquid drops from the condensor.

→ Final boiling pt i.e FBP is the maximum temp recorded at the end of distillation.

→ Mid boiling pt is the temp at which 50% of the distills off.

→ This data used for making T-xy curve which is used to design the distillation column.

Sulphur Content :-

→ Presence of sulphur decreases the octane no. produces SO_x in the environment and decreases the efficiency of a engine and make the oil sour. (oil content S) (oil free of S) sweet)

→ S content in the oil is determine by Bomb Calorimeter.

Moisture :-

→ Water in a fuel is undesirable, bcz it causes flame failure

→ Water content is removed by the preheating.

→ It is present in the ~~oil~~ fuel oil upto 1%.

→ It is measured by the Dean & Starc method.

Calorific Value :-

→ Total heat produce when a unit mass of fuel is Completely burnt wid pure oxygen. It is determined by The Bomb Calorimeter.

Q.) Diff btw gross calorific Value & Net calorific Value ?

Cracking :-
(Thermal / catalytic)

→ Cracking means heating of higher boiling petroleum fractions lyk heavy oil at high temp and pressure to produce lower boiling petroleum fractions.

→ Main application of cracking for production of gasoline from gas oil.

→ It is also done to produce olefins, for petrochemical prodn from the gas oil and the naptha.

→ They are also used to lower the viscosity of oil.
eg→ visbreaking * also to produce coke eg→ coking process

Thermal cracking process is carried out at high pressure from 1-70 atm (general pressure range) and temp of 450 to 750°C while catalytic cracking the pressure range is 1-15 atm & the temp range 350 - 650°C

→ Catalytic cracking compared to thermal cracking produces less gas, less coke but more liquid pdts.

→ Catalyst used in cracking are used in the form of powder, pellets and beds and include silica, alumina, natural clay, zeolite etc.

→ The pellets and beds of catalyst are used in fixed bed while the powder form are used in the fluidized bed.

→ Higher temp. gives higher yield of gasoline where as higher pressure reduces the octane no. of gasoline.

Types of Thermal Cracking :-

Vis-breaking :-

It is the low temp and high pressure thermal cracking process. The temp is 500°C and pressure is 20 atm. Feed is the mainly the residue from adu atmospheric distillation unit.

Thermal Reforming

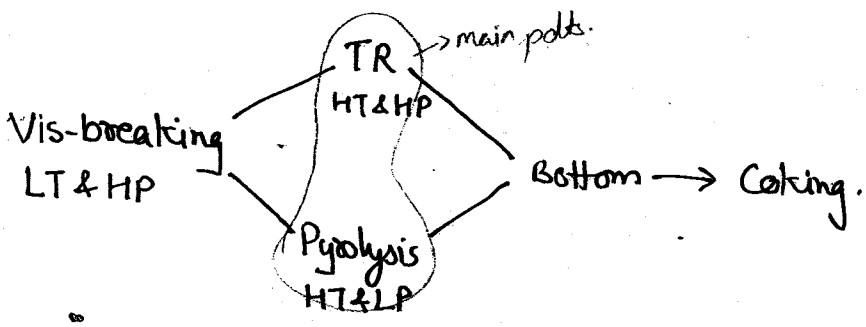
High temp & high pressure process. Temp 530°C & pressure bw 50-70 atm. Feed is mainly naptha.

Pyrolysis :-

High temp & low pressure process. Pressure 1 atm & temp 700°C. Pdt is mainly aromatic compd. feed is naptha. It is also used to produce olefins.

Coking :-

In this process more severe rxn condition are used then Vis-breaking so that feed is completely converted to lighter pdt lyk gasoline. Feed to coking is thermal cracking residues.



Cracking rxns. are endothermic in nature while regeneration rxn are exothermic in nature.

Catalytic Cracking:—

It is most efficient unit of the refinery producing gasoline of very high ~~no~~ octane no.

Fluidized catalytic Cracking:—

→ It produces the gasoline of very high octane no almost 95
→ It most efficient process of refinery and run at almost no operating cost.
→ The residue of each of the unit can be cracked in FCC unit.
→ It consist of two units reactor (endothermic) and regenerator (exothermic)
→ The temp. required for the rxn is btwn 820-550°C which is achieved by regenerated catalyst in regeneration unit.
→ Catalyst used is zeolite - powder

Hydrocracking :—

→ Cracking in the presence of hydrogen is known as hydro-cracking
→ Catalyst used - Tungsten sulphide for vapour phase & Iron catalyst for the liquid phase.
→ Rxn condition — 400-500°C, mild press.- 70—700 kgf/cm²
→ It produces desired pdts with lower molecular wt. then the feed stock and completely removes sulphur nitrogen and oxygen. and also saturates the olefins.

Hydrotreating –

This processes is comparatively done at mild condition at 300 – 350°C and press 15–170 kgf/cm².

→ It aims at removal of impurities lyk S, N, O, hallides and the traumetals.

→ It is also used for the stabilization of petroleum pdt. by saturating the olefins present in them.

→ Catalyst use → Cobalt, molybdena.

*** Both the above process possible due to the availability of the surplus hydrogen rich gases which comes from the catalytic reforming of naphtas.

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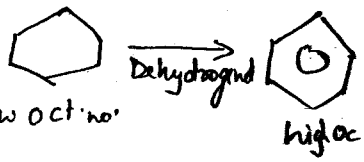
Reforming :–

Reforming means rearrangement of molecules w/o much affecting the avg. molecular wt. of feed. for ex → dehydrodegenation of naphtene to aromatic.



*** → In order of preferance the feed stocks used are Virgin naptha, Coking naptha & Catalytic naptha.

→ Catalytic naptha is not too desirable bcz of high olefinic content.

→ lyk the cracking reforming is also of two types
→ Thermal
→ Catalytic.

→ In the catalytic cracking two types of catalyst are used. non-pricious metal oxide lyk Molybdena or Chromia on alumina bas.

Precious oxide platinum on a silica alumina or silica base Hallides promotes the activity of a platinum on alumina catalyst and it some conc in the catalyst is neccessary for good operation.

But if silica alumina base is used no hallides are required.

Types of catalytic Reforming :—

Fixed Bed	Moving Bed	Fluidised Bed
1) Non-regenerative Process. eg → Platforming	1) TCR (Thermofor Catalytic Cracking)	Fluidised Hydroforming Process
2) Regenerative Process eg → Hydroforming	2) Hyperforming	

Polymerization :—

Gases ~~used in~~ produced in cracking are rich in C_2 & C_4 compds (olefins) these gases undergo polymerization in the presence of a catalyst (mainly phosphoric acid) to give pdts of gasoline boiling range.

for eg → 2 Isobutene undergo polymerization to form di-isobutene, which is a branched chain polymer.

The gasoline so produced is known as polymer gasoline.

Its main aim is to increase the branching or to convert the feed into iso-paraffin.

Alkylation :—

In petroleum refining alkylation means rxn of an olefin wid iso-paraffin to produce a larger iso-paraffin having higher octane no.

for ex → isobutane + propene to give isoheptane.

The catalyst used in either Sulphuric acid or hydrogen fluoride and the acid consumption of ~~more~~ H_2SO_4 is more than HF.

Isomerization:-

This process aims at converting n-paraffins to iso-paraffins in presence of aluminium chloride as catalyst.
for eg → the isomerization of n-butane to form iso-butane.
Sometimes aluminium trichloride is also promoted with HCl to increase the efficiency.

Asphalt:-

Petroleum wid high content of napthanic compds are known as asphalts.

Properties & yield	Paraffinic Crude	Asphaltic Crude oil
*Density	low	high
yield of gasoline	high	low
*Octane no. of petrol	low	high
*Sulphur Content	low	high
*Smoke pt. of kerosene	high	low
*Cetane no. of diesel	high	low
Freezing pt of fuel oil	high	low
*Yield of lubricants	high	low
Yield of wax	high	low
Colour	light	dark
Odour	sweet	pungent

Purification of petroleum pdts

Purification is done mainly bcz of 3 reasons.

→ Minimising

→ Improving

→ Recovery

Minimising	Improving	Recovering
Acid & Corrosion	Smoke pt	Hydrogen sulphide
Carbon Residue	Octane no.	Alkyl phenols
Gum formation	Cetane no. for kerosene, petrol & diesel.	Sulphonates.
Catalyst deactivation		

Sweetening Process :-

Removal of sulphur and its compounds lyk hydrogen sulphide mercaptan etc. from the petroleum pdts is called sweetening.

Five process for sweetening.

1) Doctors test
2) Copper chloride sweetening process
3) Solutizer process
4) Catalytic desulphorization
5) Hydrofining process.

Solutizer :-

An agent for promoting solubility. When methanol is used as solutizer the process is known as unisol process. When napthanic acid is used as solutizer then it is know as Mercapsol process.

In the catalytic desulphorization catalyst used is bauxite.

Hydrofining is same as catalytic desulphurization process but in the presence of hydrogen.

Dewaxing :-

Removal of wax from petroleum pdts :

→ Chilling & Pressing :-

At lower temp, waxes crystallise and ppt out from oil

→ Solvent dewaxing Process :-

Two types of solvent are used methyl ethyl ketone, propane.

→ Urea dewaxing :-

→ Deasphalting of petroleum pdts. (This separation is done for lubricating oil).

Asphalts readily oxidises and form Carbanious sludges and hence must be removed from lubricating oil. They are also undesirable in the catalytic cracking as they produce Coke.

They are removed by solvent deasphalting process. Solvent used is propane.

Deaeromatization Process :-

It is mainly done for the kerosene. It is also known as EDELENAU

Presence of ~~kerosene~~ aromatic in kerosene makes it smoky hence they have to be removed. It is removed by solvent dearomatization process.

Solvent - Liq. sulphur di oxide.

Demerit of using this solvent is that, moisture content cannot be tolerated in the system bcz the solvent then become highly corrosive.

Liquid fuels from Coal :-

Bergius Process

Finally powdered coal is made into a paste wid heavy oil and then heated upto 400–500°c under 200–250 atm pressure in the presence of organic compounds of tin. in the convertor followed by cracking and hydrogenation. to yield

i> Gasoline
ii> Middle oil
iii> heavy oil

Fischer-Tropsch Process :-

This method involve the conversion of coal into water gas wid the help of water at 1200°C

$$C + H_2O \xrightarrow{1200°C} \underbrace{CO + H_2}_{\text{water gas}}$$

From a part of water gas CO is removed and converted to CO_2 which is again removed by absorption.

$$CO + H_2O \underset{}{\overset{Fe}{\rightleftharpoons}} CO_2 + H_2$$

Hydrogen so obtained is mixed with the rest of the water gas in a ratio of synthesis gas. i.e ratio of 2:1 for $H_2 : CO$

The synthesis gas is passed at atmospheric pressure ~~for~~ over cobalt co thorium catalyst at 180–200°c to yield straight chain paraffins and olefins.

The only large commercial plant of Fischer-Tropsch process in the world is located in South Africa known as SASOL plant. It supplies more than 20% of South Africa total requirement of liquid fuel bcz of availability of cheap coke and lack of crude oil resources.

defin series of Undcop & -
pdts of distillatn in one line
Properties - def, apparatus, mean is (low or high), pro...
cracking - def, endothermic, stream of thermal conditions

hydrocracking & hydro treating in single line.
... 1 line
def ref, pref of feed, types of cat
types of catalytic reforming, 2 lines
def of poly, alkyla, isomerization, table

Purification → Name of sweetning process & sweetening
def of desulphurization process
" " dearsphalting & " (name & solvent)
" " dearomatization & "
Bergius & Fischer tropsch (process)

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Gaseous Fuel :-

1) Natural Gas :- It is a mixture of paraffinic hydrocarbon in which methane is the main constituents.
They are available in the oil fields as well as in the gas field.

a) Dry Natural Gas :-
When the natural gas contains very less recoverable condensable ($<15 gm/m^3$), NCV is high

b) Wet Natural Gas :-
When the Natural gas contains ($>50 gm/m^3$) of recoverable condensate then known as same.
, Gross calorific value high

2) Compressed Natural Gas :-
To use natural gas in its pure form is tough hence to use it as a alternative fuel for an engine. It has to be compressed at a high press. 200 atm. for the transportation purposes. Natural gas is liquified at a temp of 160°C (cooling).

Advantage of CNG over petrol :-

⇒ O.N of C.N.G → 130 & hence It does not PEL which cause pollution.

⇒ The emition of CO & unburned hydrocarbon is very less in the exhaust.

⇒ It has better cold starting property.

Disadvantage of CNG :-

→ CNG storage tank ha weight bcz heavy engine are req. for the storage of natural gas at high pr.

3) Liquified Petroleum Gas :- (C_3-C_4) Streams are liquified at low pr. & supplied in the light cylinder. Generally a mix. of abt 80% butane & 20% propane is used for filling in LPG cylinder & also known as botteled gas.

It is prepared by
a.) Wet natural gas
b) Refinary gases
c) Pure butane & propane.

** LPG is a highly volatile liquid which expands to 247 times its volume as vapour.

1 LPG liq = 247 lt. of LPG vapour.

* It is non toxic,
* doesn't support life.
* Heavier then air,
* Odourless.

therefore mercaptan are added for the detection of leakage from the cylinder.

4.) Producer Gas :-

It comprise mainly of CO & Nitrogen. In the ratio 1:2 ($CO:N_2$ 1:2). & produced in a furnace known as producer by blowing air or a mix of air & steam through hot bed of solid fuel.

⇒

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

→ It's calorific value is 1250-1550 kcal/Nm^3
→ Low temp favours high production of CO_2
→ High temp favours high production of CO.
→ Water in the coal bed & steam in the air increases the proportn of H_2 & CO in the gas thus raising its calorific value.

→ Best fuel for the producer gas manufacture is bituminious coal

Uses

Firing in furnaces.

5) Water Gas :—

→ It comprising mainly CO & H_2

→ It is prepared by the action of superheated steam on a bed of hot coal.

H_2	CO	CH_4	CO_2	N_2
48-51%.	40-42%.	0.1-5%.	3-5%.	3-6%.

Calorific Value → 2800 Kcal/NM^3

→ Water gas is also called as blue gas as it burns with a bluish flame.

Uses :— Use for firing in furnance.

Fertilizer Industry.

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Petrochemical Industry:—

→ It has wide application in manufacture of polymer.
→ Ethylene & propylene are main pdts:
→ Steam cracking is heart of petrochemical Complex.

$$C_xH_y + H_2O + O_2 \xrightarrow[800^\circ C]{} \text{Pdts}$$

Pdts C_2H_4, C_2H_2, H_2, CO, CO_2, C_3H_8, C_3H_6, C_4H_{10}, CH_4, C_4H_8, C_6H_6, Toluene, C & heavy oils.

Steam cracking
↳ Hot Section
↳ Quench Section
↳ Cold Section.

In the fist one, hydrocarbon feed stock is preheated & mixes wid steam heated to a temp of 800°C and thermal cracking results. (Pyrolysis rxn)

In the quench section, the pdts are quenched by water to recover the heat and to generate steam, which is used in plant (Recovery section)

1) H_2 Separation take place
2) Ethylene " " "
3) Propylene " " "
4) Aromatics " " "
5) Removal of CO & CO_2

Formaldehyde :—

Formed in two steps
i) Catalytic conversion of CH_4 to CH_3OH in the presence of Copper zeolite.
ii) CH_3OH is cracked to form formaldehyde in presence of (Silver or Zinc) oxide.

$$CH_3OH \longrightarrow HCHO + H_2$$

Chloro methanes:—

$$CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$$
$$CH_3Cl + Cl_2 \longrightarrow CH_2Cl_2 + HCl$$
$$CH_2Cl_2 + Cl_2 \longrightarrow CHCl_3 + HCl$$
$$CHCl_3 + Cl_2 \longrightarrow CCl_4 + HCl$$

These exothermic rxn, takes place in the gas phase.

Vinyl Chloride :—

Vinyl chloride CC

formation takes place in two steps.

i) $C_2H_4 + Cl_2 \xrightarrow[FeCl_3]{} C_2H_4Cl_2$ (liq phase, Exothermic)

ii) $C_2H_4Cl_2 \xrightarrow[Charcoal]{} CH_2CHCl + HCl$ (gas phase

Ethelene Oxide :— (pdt of C_2)

$C_2H_4 + 0.5O_2 \xrightarrow[Ag\,O\ on\ alumina]{} CH_2OCH_2$ (past. oxidation

Ethanolmine :—

$CH_2OCH_2 + NH_3 \longrightarrow CH_2OCHNH_2$

Monoethanol Amine $+ NH_3$

↓

$H_2NCH_2OCHNH_2 + NH_3$

Diethanol Amine

$H_2N\,CHOCH(NH_2)_2$

Triethanol Amine

Isopropanol :—

i) sulphation (addition of S)

propylene $+ H_2SO_4 \rightarrow$ Isopropyl sulfate

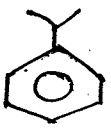
ii) ~~hydrolysis~~ hydration.

Isopropyl Sulfate $+ H_2O \longrightarrow$ Isopropanol $+ H_2SO_4$.

Acetone

Isopropanol $\xrightarrow[Copper]{-H_2}$ Acetone

Cumene :— (Isopropyl benzene)



+ propylene $\xrightarrow{Zeolite}$ Cummene.

; Process i) alkylation.

Acrylo Nitrile :—

By ammoxidation of propylene

$C_3H_6 + NH_3 + O_2 \xrightarrow[Mo\text{-}Bi]{} Acrylonitrile + H_2O$

Isoprene :- $CH_3-C(CH_3)=CH-CH_2$ isoprene.

i) Dimerization :-

2 Propylene $\xrightarrow[\text{Aluminium}]{\text{Tripropyl}}$ 2-Methyl-1-pentene.

ii) Isomerization :-

2-Methyl-1-pentene $\xrightarrow[\text{Medium}]{\text{Acid}}$ 2-Methyl-2 pentene
(H_2SO_4 or HF)

iii) Pyrolysis :-

2-Methyl-2-pentene $\xrightarrow{HBr}$ Isoprene + CH_4

Oxo-processing

for the making of aldehydes and also known as hydroformylation.

$C_3H_6 + CO + H_2 \xrightarrow[\text{Naphthenate}]{\text{Cobalt}}$ aldehyde
(olefines)

main pdt is aldehyde, for the making of alcohol, aldehydes undergo hydrogenation in a nickel catalytic bed reactor to produce butanol.

Buta-diene :- (C_4)

n-butane $\xrightarrow[\text{Cromium oxide on alumina}]{-H_2}$ Butadiene ; dehydrogenation.

Benzene pdtn :-

Hydro-dealkylation of toluene to produce benzene.

Toluene + $H_2 \xrightarrow{\text{Cromia}}$ Benzene + CH_4

Phenol :- (from cummene)

i) peroxidation :-

Cummene + Air $\xrightarrow[\text{medium}]{\text{Basic}}$ Cummene hydroperoxide
($CNaOH$)

ii) Sulphation :-

Cummene hydroperoxide + $H_2SO_4 \longrightarrow$ Phenol + Acetone.

phenol from toluene:-

i> Oxidation of toluene to benzoic acid.

$$\text{Toluene} \xrightarrow{\text{Cobalt naphthanate}} \text{Benzoic acid}$$

ii> Benzoic acid is reduced to give phenol.

$$\text{benzoic acid} \xrightarrow[\text{reducing agent}]{LiAlH_4} \text{phenol}$$

phenol from benzene

i> Chlorination :-

$$\text{Benzene} + Cl_2 \xrightarrow{FeCl_3} \text{Mono chloro benzene}$$

ii> Caustisizing

$$\text{Mono chloro benzene} + NaOH \longrightarrow \text{Sodium benzoate}$$

iii> Hydrolysis in acidic medium

$$\text{Sodium benzoate} \xrightarrow[(aq.)]{HCl} \text{phenol} + NaCl.$$

Styrene:-

i> alkylation of benzene to form ethyl benzene

catalyst - $AlCl_3$

ii> Dehydrogenation of ethyl benzene

catalyst - FeO or SnO

Pthallic Anhydride:-

i> $\text{Napthalene} + O_2 \xrightarrow{V_2O_5} \text{Pthallic Anhydride} + H_2O + CO_2$

ii> $\text{O-xylene} + O_2 \xrightarrow{V_2O_5} PA + H_2O$

Maleic Anhydride:-

i> $\text{Benzene} + O_2 \xrightarrow{V_2O_5} \text{Maleic Anhydride} + H_2O + CO_2$

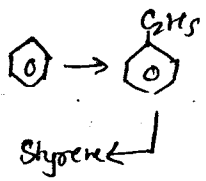
DDT (Dichloro, Diphenyl trichloro ethane)

Mono chloro benzene + Chloral ⟶ DDT

Chlorination of ethanol.

$EtOH + Cl_2 + H_2O \longrightarrow$ Chloral.

Products	Raw Material	Process & steps	
1) Formaldehyde	CH_4/methanol	i) Catalytic conversion $CH_4 \rightarrow CH_3OH$ ii) Pyrolysis of to HCHO	Cu-zeolite Ag or Zn oxide
2) Chloromethane	CH_4	Absence of air/photochemical xxn addition of Chlorine.	
3) Vinyl chloride	Ethene	i) Ethene + $Cl_2 \rightarrow C_2H_4Cl_2$ ii) $C_2H_4Cl_2 \longrightarrow CH_2CHCl$	$FeCl_3$ charcoal
4) Ethylene Oxide	Ethene	Partial oxidation	Silver oxide
5) Ethanol Amine	Ethene/ Ethylene oxide	Ethylene oxide + $NH_3 \rightarrow$ Ethanolamine	
6) Isopropanol	Propylene	Propylene $\xrightarrow{\text{Sulfation}}$ Isopropyl Sulphate; Isopropanol $\xleftarrow{H_2O}$	
7) Acetone	Propylene/ Isopropanol	Isopropanol $\xrightarrow{-H_2}$ Acetone	dehydrogenation Cu 6
8) Cumene	Benzene & Propylene	Benzene + propylene ⟶ Cumene	Zeolite alkylation.
9) Acrylonitrile	Propylene	Propylene ⟶ Acrylonitrile	Ammoxidation. Mo-Bi
10) Isoprene	Propylene	propyline ⟶ 2-Methyl 1-pentene; 2-Methyl 2-pentene ⟶ Isoprene	Dimerization (Tripropyl Aluminium) Isomerization (H_2SO_4 or HF) Pyrolysis (HBr)
11) Butadiene	n-butane	n-butane ⟶ Butadiene	Dehydrogenation Cromium oxide on Alumina

12.) Benzene	Toluene	Toluene → Benzene	Hydrodealkylation (Chromia)
13.) Phenol ↑ (Cumene)	Cumene	Cumene $\xrightarrow{Base}$ Cumene peroxide Phenol + Acetone ← $\xrightarrow{A}$	Peroxidation (NaOH Sulphation
14.) Phenol ↑ (Benzene)	Benzene	Benzene → Monochloro benzene Sodium benzoate ← ↳ phenol	Chlorination ($FeCl_3$) Causticizing ($NaOH$) Hydrolysis HCl(aq)
15.) Phenol ↑ toluene	toluene	toluene → Benzoic acid phenol ←	Oxidation Cobalt naphthanate Reduction $LiAlH_4$.
16.) Styrene	Benzene & Ethylene	 Styrene ←	alkylation $AlCl_3$ Dehydrogenation (FeO & SnO)
17.) Pthallic Anhydride	Naphthalene O-xylene	Naphthalene $+O_2 \xrightarrow{V_2O_5}$ PA $+H_2O+CO_2$ o-xylene $+O_2 \xrightarrow{V_2O_5}$ PA $+H_2O$.	
18.) Maleic Anhydride	Benzene	Benzene $+O_2 \xrightarrow{V_2O_5}$ MA $+H_2O+CO_2$	
19.) DDT	Chloral & Monochloro Benzene	Etoh $+Cl_2+H_2O$ → Chloral DDT ← Monochloro Benzene +	used as insecticide

Oxo-Processing / Hydroformylation

Olefins $+CO_2+H_2$ → Aldehyde (cobalt Naphthenate) aldehyde)

Alcohol (Butanol) ← Nickel Oxide (hydrogenation)

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Natural product Industry :-

Sulphur Industry :-

» H_2SO_4 ~~<=> RM~~

» M.P = 10.4°C

» B.P = 340°C (Decomposes)

» Raw material - Sulphur & Oxygen (Air)

» Catalyst — V_2O_5 (solid catalyst) (in Pellet form on a porous carrier)

* Rxn steps

$$S + O_2 \longrightarrow SO_2 \quad \text{(Highly Exo)}$$

$$SO_2 + \tfrac{1}{2}O_2 \longrightarrow SO_3 \quad \text{(Slowest step less Exo)}$$

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

$$H_2SO_4 + SO_3 \longrightarrow H_2S_2O_7$$

i.) S is burnt in the presence of dry atmospheric air which is dried wid the help of H_2SO_4.
The dry air is required to avoid corrosion & fumes in the final pdt.

ii.) It is filtered and cooled to 250°C from 400°C wid the help of a boiler. Resulting stream is feed to a multistage catalytic convertor having the beds of catalyst on which rxn take place.

iii.) The SO_3 pdt is cooled and mixed wid H_2O to form 99% conc^n Oleum.

iv.) DCDA process step involves the absorption of gases in the two towers.

Catalyst advantage & disadvantage :-

Advantage

1.) Immune to Poison,

2.) Require in very less amount (10 kg for 1 ton prod^n of H_2SO_4)

3.) low initial capital investment

4.) It is easily regenerated and only 3% is to be replaced per year.

Disadvantage

1.) less Reactive
use dilute SO_2 or O_2/SO_2 → High. for making the V_2O_5 less reactive catalyst to reactive 1..

Chamber Process	Contact Process
⇒ Previously Used	⇒ Now Used.
$H_2SO_4 < 80\%$.	$H_2SO_4 > 98\%$.
⇒ Homogeneous (HNO_2)	⇒ Heterogeneous (V_2O_5) (solid)

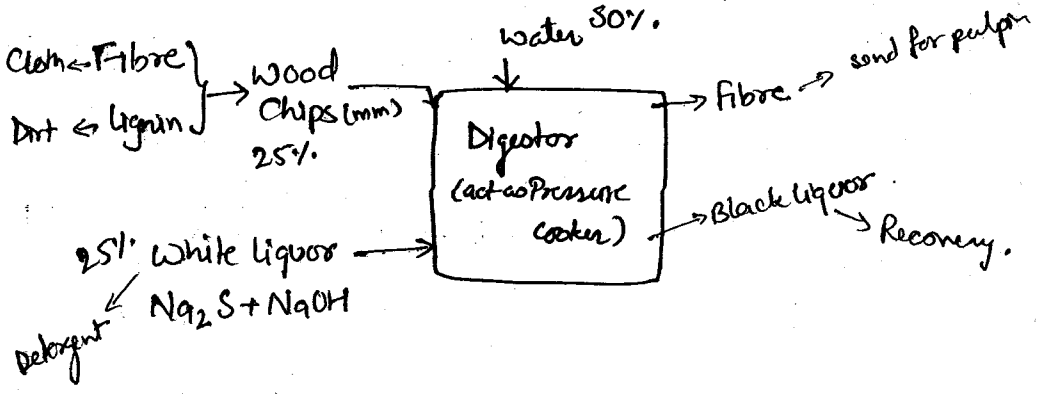
* Pt is used as Catalyst in contact process but it is replace. bc2 it is very reactive, required in large amount & costly.

Feed to Catalytic ($7-10\%$) SO_2 | ratio of feed before sending to Catalytic chamber

Paper & Pulp:-

Pulp:- Commercial fiberous material obtained from bamboo, wood & beggase

Pulping:-
The disintegration of bulky fiberous materials into the smaller



Chipper Bin It consist of a large rotary disc wid heavy knifes to cut the wood to 2-5 cm size

Digestor (Pressure Cooker)

It is a 25-30 m tall tower and the temp is maintained 170°C at the top & 65°C at the bottom. The temp at the bottom is less to avoid the mechanical of water. A mixture of 50% water; 25% WC & 25% WL is present in the digestion under the effect of high temp & pressure, wood chips starts to break and lignin start to dissolve in the white liquor. The residence tym is 1-5 hrs which is also known as cooking tym. After this the which

White liquor along with lignin is removed which is now known as black liquor. This black liquor is send to a recovery section for regenati of white liquor. The fibre material which is free from lignin is send to the bleeching section Then it undergo the series of washing & bleaching to produce white pulp. Thes pdt can be stored for the further use or ~~they~~ may send to the production mill for production of paper.

The bleaching of pulp is done to remove the pulp.
It is done wid help of H_2O_2, Cl_2, Cl_2O_2. This whole process is known as Sulphate ~~kraft~~ Process which is an alkaline processes. Bcz (NaOH) is used. Na_2S is added to NaOH to increases its efficiency as a white liquor and its presence also helps in bleaching. Sulphate name is given to this process bcz we use Na_2SO_4 in the recovery section.

Chemical Recovery from Black liquor

Recovery is done to decrease the pollution and regenerate the white liquor.

1.) Multi-effect ~~evaporation~~ and disc evaporator are used to increase the concn from 10-12% to 60-65%.

2.) Black liquor is then sent to mixing tank where the make-up chemicals (Na_2SO_4 & S) are added to the black liquor.

3.) Boiler Section:- The organic C present in black liquor is burnt in the presence of air to produce Na_2S. The heat generated is used for production of steam & electricity for the mill. The remaing chemicals are mixed wid the cold water in the dissolving tank to yield green liquor.

Milk of lime is added to the green liquor to convert this to white liquor

$$Na_2SO_4 + C \longrightarrow Na_2S + CO_2$$

$$Ca(OH)_2 + \underset{\text{Green liquor}}{Na_2CO_3} \longrightarrow \underset{\text{white.}}{NaOH} + CaCO_3$$

Kraft :→ white → Black → Green → white.

white liquor are sometimes known as cooking liquor.

Sulphate kraft process is used to produce strong paper (paper shows resistance) & strong brown bags. alkaline process

Sulphite — acidic process / read own

Sulfidity :—

More the Sulfidity, more easier will be bleaching & fiber strength is more.

$$\text{Sulfidity} = \frac{Na_2S}{NaOH + Na_2S}$$

Paper production

Beater :—

Pulp fiber is mech. disintegrated wid the help of metal blades attached wid rotating drum.

Web forming :—

99.5% (H_2O - fibre) slurry

Pressing :—

In this step, pressure rolls & Suction rolls are used. H_2O content reduces to 65%.

Drying :—

Smoothening rolls, drying rolls & steam heated rolls and the water content reduces to 5-6%.

Finishing :—

Calendering rolls, Winding rolls and finally paper is produced.

Fertilizer Industry –

i) Ammonia (NH_3) :–

Haber process

$$N_2 + 3H_2 \underset{\text{Crude}}{\overset{Fe}{\rightleftharpoons}} 2NH_3$$

- N_2: Source is Air (By help of Air separation Unit)
- $3H_2$: from Syn Gas
- Fe: Promoted with Alkali
- at 100–1000 atm & 500–600°C

The main problem is that catalyst diffuses over 620°C, so temp should be maintained.

The NH_3 is used for making for urea, ammonium nitrate & HNO_3 (Pt, Rh as catalyst)

ii) Urea NH_2CONH_2 :–

Contain 40–42% N and used as Nitrogen fertilizer. It can also be used to make ureaformaldehyde resin.

Main raw materials are NH_3 from ammonium plant & CO_2 from Syn Gas

Process Step :–

i) NH_3 & CO_2 are compressed separately under 200 atm & 185°C

ii) They passed on to a reactor under the same condition & rxn will take place.

$$2NH_3 + CO_2 \rightarrow \underset{\text{Ammonium Carbamate}}{NH_4COONH_2}$$

Urea, Ammonium Carbamate, unreacted NH_3 CO_2 & H_2O streams are then heated & depressurized ~~to~~ and sent to flash evaporator operating at 27 atm

$$AC \xrightarrow{-H_2O} NH_2CONH_2$$

iii) The carbamate & urea are then fed to atmospheric flash drum and after that to vaccum evaporator which gives 99% of urea.

iv) The 99% molten urea is then sprayed to a prilling tower and temp is maintained jst above the M.P of urea to avoid the prodn of Biuret

$2NH_2CONH_2 \rightarrow$ Biuret.

Vaccum :—
60cm of Hg.

Super phosphate & Triple Super phosphate

SSP	TSP
form of a Calcium phosphate	form of a ~~eta~~ calcium phosphate
Raw mat → Phosphate Rock (16-20% P_2O_5) + H_2SO_4	Raw material → Phosphate Rock (40-45% P_2O_5). + H_3PO_4
Phosphates rocks are crushed & mixed wid 60% H_2SO_4 & passed to a blender and then rotary glanulater. and then rotary drier to get SSP	Phosphates rocks are crushed & mixed wid 75% H_3PO_4 & passed to a blender and then rotary granulater & then rotary drier to get SSP.
Ammonium Sulphate can be produced if we add NH_3 before rotary glanulater	Ammonium phosphate can be produced if we add NH_3 before rotary granulater

* for making of SSP nowa day nitric acid is used in place of H_2SO_4 as the final pdt is rich in phosphorus content.

Chlor-Alkali Industry :—

Diaphragm Process

$$Cl^- \longrightarrow \tfrac{1}{2}Cl_2 + e^-$$

$$Na^+ + H_2O + e^- \longrightarrow NaOH + \tfrac{1}{2}H_2$$

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

Mercury Cell Process

$$Cl^- \longrightarrow \tfrac{1}{2}Cl_2 + e^-$$

$$Na^+ + \underset{+e^-}{Hg} \longrightarrow NaHg$$

Takes place in Denuding tower

$$NaHg + H_2O \longrightarrow NaOH + \tfrac{1}{2}H_2 + Hg$$

$$NaCl + H_2O \longrightarrow NaOH + \tfrac{1}{2}H_2 + \tfrac{1}{2}Cl_2$$

Diaphragm Process	Mercury Cell Process	Membrane Process
less purified brine (NaCl) can be used.	More purified brine is required	More purified brine is required.
10–12% concn NaOH is produced which requires further concentration	70% NaOH (conc) is produced directly.	In between both Process production of NaOH is used.
It uses asbestos	It uses mercury	It uses a membrane
Produce Cl_2, that contain oxygen.	Produce pure Cl_2	Membrane Produce Cl_2, contain Oxygen.
Energy consumption is very less	Energy consumption is very high	77% of energy consumption to that of mercury cell process.
Problems of disposing asbestos	Problems of disposing mercury	short lyf tym of membrane

Oils & fats Industry :—

- Oils mainly are of two types → vegetable oil & essential oil.
- Oils used for the nutrition of animals, plants & human beings are known as vegetable oil.
- Oils which are used in cosmatics, perfumes, soaps, medicines etc are known as essential oil.
- Oils & fats are mixtures of glycerides of fatty acids having the general formula

$$\begin{aligned} R_1-CO-O-CH_2 \\ R_2-CO-O-CH \\ R_3-CO-O-CH_2 \end{aligned}$$

R_1, R_2 & R_3 may be same or different.

They may be

			No of Double bonds
Stearic	$C_{17}H_{35}$		— 0
Oleic	$C_{17}H_{33}$	unsaturation increases	1
Linoleic	$C_{17}H_{31}$		2
Linolenic	$C_{17}H_{29}$		3

» M.P also decreases and reactivity towards O_2 ~~also~~ increases as no. of double bond increases

» As the no. of double bond increases, reactivity towards oxygen increases and therefore the problem of rancidity occur.

» To decrease the double bond character and decrease the reactivity, oils undergo hydrogenation in presence of nickel or reny nickel (nickel-aluminium alloy)

Process

» Oils & fats are produced by seeds either by the digestion method (as used in pulp industry) or by an extractor (extraction process)

» Oil produce from both the steps is send for purification.

Purification

» Alkali or Na_2CO_3 is added to remove the free fat present in the oil which is known as FOOTS & is supplied to soap industry.

» Then bleaching is done with FULLER EARTH.

» Atlast, finished oil is seperated.

The separated oil is hydrogenated ~~with~~ in presence of hydrogen to decrease the reactivity & and increase the M.P.

** Ghee based oil is hydrogenated at <u>low pressure</u> and <u>high temp</u> to yield a pdt having <u>M.P similar to butter</u>

** Vanaspati oil is produced by hydrogenation at high pressure and low temp ~~of~~ to yield pdt of high melting pt, which can be used for cooking purpose (max^m stable)

Soaps & Detergents :-

⇒ Soaps are the compound of the type → RCOO+M where RCOO is fatty acid & M is any alkali metal (Na, K) and

⇒ The detergents are mainly of two types cationic & anionic

Anionic Detergents :-

They are those which gives R^- in water ; they posses detergent characteristics.

Sulphates, Sulphonates, ABS (Alkyl benzene sulphonate) —

Cationic Detergent :

They gives R^+ in water , they posses germicidial characteristics

Ex→ ammonium compds.

In the manufacture of soaps two pts are imp. → Fat splitting
→ Saponification.

Fat splitting
This step is used to produce fatty acid & glycerine from oils

saponification
This step is used to produce soap from fatty acid by the introduction of alkali.

Main Raw materials used are vegetable oils, other fatty oils, NaOH in the presence of metal oxide, lyk ZnO.

Sugar Industry

Raw material - Sugar Cane

Final pdt - Sucrose $C_{12}H_{22}O_{11}$

Process

⇒ Sugar Cane is crushed & pressurized by 3 pressure rolls. Water is added for the good yield.

⇒ The juice is then treated wid Calcium hypo phosphate followed by lime to ppt colloids.

» SO_2 is bubbled through the juice till the pH reach 7 or 7.1. It also helps in bleaching. The juice is then sent to cake filteration. The cake produced is used as manure

» The filtered juice is then sent to multieffect evaporator followed by the crystallization. Where the soln of crystal & syrup is known as Massecuite

» Finally crystals are separated by centrifugation & the mother liquid which is know as black strap mollasses sent to the alcohol industry.

» Sugar particles can be made white from carbonation process.