Titanium can be used for storing chlorine gas which is sufficiently wet.

C.T

PETROLEUM INDUSTRY

Crude oil

- (st chain) Paraffin C_nH_{2n+2}
- Naphthanic C_nH_{2n} (sat ring)
- Olefinic C_nH_{2n} (unsat st chain)
- Aromatic (unsat ring) C_nH_{2n-6}

Light:
- Refinery gas (LPG, Butane, propane)
- Gasoline/Petrol
- Naphtha
- Solvent spirit
- Jet fuel
- Kerosene

Intermediate:
- diesel
- Gas oil (to make petrol)

Heavy distillate:
- Lubricating oil
- LFO
- HFO
- wax
- Tar
- Residue

1. Flash point: min temp at which oil gives sufficient vap to form an inflammable but flame is not sustain.
2. Fire point: 4-5°C more than flash point. [> 50°C → Pensky Marten; < 50°C → Abel]
3. Cloud point: temp at which oil becomes cloudy during cooling.
4. Pour point: temp below which oil refuses to flow. 4-5°C more than cloud. In hilly area we use Ethylene glycol. Used to estimate rel amt of wax & measured by pour point apparatus.
5. Octane: % by volume of Iso-octane in mixg n-heptane + Iso-octane with same knocking tendency as that of fuel.
   (2,2,4 trimethyl pentane) Octane No ↑ knocking tendency ↓ ⇒ Antiknocking ↑ (Aromatic, Olefin, Naph, para ↑)
   (tetraethyl lead, Ethanol, Iso-octane) → Branching ↑ octane No. In India O.N = 85-90, USA ≥ 95.
6. Cetane No: % by vol of n-cetane ($CH_3-(CH_2)_{14}-CH_3$) & α-methyl naphthalene that has same ignition delay.
   → Branching ↓ Cetane No. and ↑ by adding [1. Ethyl nitrate 2. Acetone 3. Amyl nitrate]
   2 stroke: Suction & Compression; Ignition & Exhaust
7. Smoke point: max height of flame w/o smoke (min 25mm)
8. Aniline point: min temp at which equal vol of oil & aniline is miscible.
   a) Low aniline → highly aromatic (Petrol) b) High aniline → high paraffinic (diesel), like dissolve like property.
9. Carbon Residue → [Conradson apparatus]
10. Acid no → no of mg of KOH req to neutralise free acid in 1gm of oil, measured by → [titration]
11. Sulphur Content → [Bomb Calorimeter], ↓ the efficiency of engine by ↓ octane no.
12. Moisture content → measured by [dean & Stark apparatus]
13. Calorific value → heat produced in kcal when unit mass of fuel completely burned with pure oxygen.
    $GCV = NCV + \lambda$

Cracking (Endothermic) (For gasoline)

- thermal 450-750°C, 1-70 atm → Vis Breaking, thermal Reforming, Pyrolysis, Coking
- Catalytic 350-650°C, 1-15 atm → FCC, HydroCracking, Hydrotreating, Reforming

Reforming: Catalytic Reforming ✱
- Fixed bed → Non Regenerative (Platforming) eg High octane gasoline from naphtha; Regenerative (Hydroforming)
- moving → TCR, Hyperforming
- fluidised → Fluidised hydroforming (Regenerative)

gasoline, petrol

Thermal Reforming

Heavy naphtha → VIS Breaking → Coking

Pyrolysis → petrochemical (olefine)

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1. Thermal Cracking

1. VIS Breaking: (Reduce viscosity) low temp, high P 500°C & 20 atm. feed is heavy naphtha, gas oil or residue from ADU unit.

2. Thermal reforming (gasoline): high T & P. Feed is naphtha & product of vis breaking (

3. Pyrolysis: high T & low P. 700°C 1 atm. It is heart of Petrochemical. Feed → naphtha, Pdt → Olef

4. Coking: Feed is converted to lighter pdt & high amt of coke produced. Use to ↓ losses

2. Catalytic Cracking: Catalyst used in form of Powder, Beds or pellets eg silica, Alumina, clay, Zeolite (mostly used). Produce good yield compare to thermal, less coke formation, less gas & more liq products.

FCC (Max profit unit) – Feed should be in vapour form. It can be used to crack VDU Residue. $\boxed{\text{Catalyst – zeolite}}$ & ZSM5 – cheap.

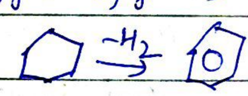
→ octane no. of gasoline produced by FCC is 95. Heat supplied by catalyst itself

Hydro Cracking: Cracking in presence of H_2. Catalyst → Tungsten sulphide (vapour), Fe (liq phase)

→ produce desired pdt with removal of S, N, O and saturates olefins.

Hydrotreating: mild opn then hydrocracking, Removal of S, N, O, No cracking (No Cracking) $\boxed{\text{Catalyst} = \text{CO, MO}}$

Reforming: Rearrangement of molecules w/o affecting m.w of feed. aromatic (Not Rxn) Feed is lies in gasoline boiling Range (Naphtha, gasoline, gas oil)

→ Preference of feed stock: 1. virgin naphtha 2. Coking naphtha 3. Catalytic naphtha eg 

→ Reforming is also thermal as well as Catalytic.

Catalytic Reforming: 2 types of Catalyst

a) Non precious metal oxide (Cromia & molybedna supported on alumina base)

b) Precious Metal oxide (Platina on silica alumina based or alumina base)

→ Halides promotes activity of platina on alumina catalyst but if silica alumina based is used, no halides are required.

(1) Polymerisation (olefins): $\boxed{\text{Catalyst} = \text{Phosphoric acid}}$, Produce gasoline boiling Range pdt

2 Isobutene → di-isobutene (GBR)

(2) Alkylation: alkyl grp is added, In Petroleum Refining it means Rxn of olefins with iso-paraffins to produced larger iso-paraffins in Range of GBR.

Iso-butane + propene → Iso-heptane (GBR)

$\boxed{\text{Catalyst} = H_2SO_4, HF}$

MTBE – methyl tertiary butyl ether   Raw material methanol + Isobutylene
has highest octane no – 118
also called oxygenates → octane enhancer

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③ **Isomerisation:** Converts n-paraffins to Iso-paraffins in presence of $AlCl_3$ promoted with HCl. also improve octane No. eg n-butane → Iso-butane (CBR)

Sweetening process: Removal of 'S', H_2S, mercaptans (it makes oil sour)   5 types

** a) doctor sweetening: $2RSH + NaPbO_2 + S \xrightarrow{NaOH} R\text{-}S\text{-}S\text{-}R + PbS + 2NaOH$
$NaPbO_2$ → Sodium Plumbite

b) Copper chloride: CuCl sol^n is used for removal of 'S'

c) Solutizer process: mostly used & Extraction process, methanol & naphthanic acid used as solvent. Methanol used → Unisol Process; Naphthanic used → Mercapsol process.

d) Catalytic desulphurisation: Catalyst = Bauxite (alumina)

e) Hydroforming: in presence of H_2.

Dewaxing: wax Remove from lubricating oil, 3 method are
a) Chilling & Pressing (Previously used) b) urea dewaxing (in presence of urea)
** c) Solvent dewaxing (mostly used) → Solvent – Methyl, Ethyl, Ketone or Propane

De-Asphalting: are high m.w comp & have high Boiling Range, remove from lubricating oil
→ done by distillation / solvent Ext Process Solvent = Propane **

# **De-Aromatisation:** (EDELENAU Process) done for purification of Kerosene
Solvent = liq SO_2

Liquid fuel from coal: gasoline, diesel, fuel oil can be produced by destructive (More severe cond^n) hydrogenation of coal (Bergius process) & liquification of coal (Fischer Tropch process)

1. **Bergius process:** Powder coal made into paste with heavy oil & heated up to 400-500°C & 200-250 atm in presence of organic comp of (Sn) in converter followed by cracking & hydrogenation to yield

2. Fischer tropch (widely used): Convert coal in water gas $CO : H_2$ (1:1) by heating at 1200°C $C + H_2O \xrightarrow{1200°C} CO + H_2$
→ convert water gas into synthetic gas (Syn gas)
** → Syngas is passed at atm pressure over Cobalt ~~too~~ thorium or Fe catalyst at 180-200°C to produce straight chain paraffin & olefins
→ Produce 20% of total energy demand of south africa.

$CO + H_2O \rightarrow CO_2 + H_2$ (CO_2 Removed by Absorption)

$nCO + (2n+1)H_2 \rightarrow C_nH_{2n+2} + nH_2O$ (paraffin)

$nCO + nH_2 \rightarrow C_nH_{2n}$ (olefin)

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Gaseous fuel: mix of paraffinic HC & methane is main constituent & occurs in gas/oil fields.

Note When natural gas contains very less recoverable condensate (< 15 gm/m³) then it is called dry Natural gas & (> 50 gm/m³) → wet natural gas.

1. CNG: To use of natural gas is tough so it is either compressed or liquify
   → LNG is easy for transportation bcz of easy to carry liq from gas.

Advantages
1. High octane no.
2. Emission of CO & other HC is very less
3. CNG fire Engine have longer life
4. It has better cold starting process

Disadvantages: CNG tanks are heavy bcz at high P heavy cylinders are req in terms of thickness.

2. LPG: mix of Propane (20%) & butane (80%), used as cooking gas & also called Bottled gas.
   → Highly volatile which expands 247 times its volume as vapour.
   → Non toxic & does not support life & odorless.
   → To detect leakage, we add Mercaptons into it.
   Advantage & disadvantage same as CNG.

3. Producer Gas: mainly contain CO & N_2 (1:2), produced by blowing air or mix of air & steam hot-bed of solid fuel (coke)
   → Bituminous coal is used, used in steel industry, calorific value = 1250–1550 $kcal/m^3$ at NTP
   CO_2 – 4 to 6%, CO – 20 to 30%, H_2 – 11 to 20%, CH_4 – 0 to 3%, N_2 – 46 to 55%

4. Water Gas: CO & H_2 (1:1), produced by action of superheated steam (~~syngas~~) or hot bed of solid fuel.
   → Anthracite coal is used, on burning it produce blue flame
   → Water gas is used in steam reforming of methane
   → Water gas is used to produce Syn gas used in fertilizer industry.

★ Calorific value preference
- CNG > water gas > Producer gas
- LPG > water gas > Producer gas
- Natural gas > Coke oven gas > Water gas > Producer gas

$CH_3-C(H)O$

PETROCHEMICAL INDUSTRY

Products	Raw material	Process + steps	Catalyst
Formaldehyde	CH_4/Methanol	I) Catalytic conv $CH_4 \rightarrow CH_3OH$ II) Pyrolysis to HCHO	Cu-zeolite Ago/ZnO
C_1 Chloro methane	CH_4	absence of air / add^n of Cl_2	—
Vinyl chloride	Ethene OR Ethylene	I) Ethene + $Cl_2 \rightarrow C_2H_4Cl_2$ II) $C_2H_4Cl_2 \xrightarrow{-HCl} CH_2CHCl$	$FeCl_3$ Charcoal (cracking) Ago
Ethylene oxide	Ethene	Partial oxidation CH_2-CH_2 (O)	Ago
C_2 Ethanol Amine	Ethene / Ethylene oxide	$C_2H_4 + \frac{1}{2}O_2 \rightarrow CH_2-CH_2$ (O) Ethylene oxide + $NH_3 \rightarrow$ ETA	Ammonification
6. Iso-propanol	propylene	propylene + $H_2SO_4 \rightarrow$ Iso propyl sulphate IPS + $H_2O \rightarrow$ Iso propanol + H_2SO_4	Sulphation Hydrolysis
Acetone	Propylene / Iso-propanol	Iso-propanol $\xrightarrow[Cu]{-H_2}$ Acetone	dehydrogenation Cu
C_3 3. Cummene / Alkylating benzene / Isopropyl benzene / methyl ethyl benzene	Benzene + Propylene	Benzene + propylene $\xrightarrow{zeolite}$ cummene 	Alkylation Zeolite
Acrylonitrile	propylene	propylene + ($NH_3 + O_2$) $\rightarrow$ Acrylonitrile	Ammoxidation Mo-Bi
Dodecene ($C_{12}H_{24}$) $\rightarrow$	propylene		
10. Iso-prene	propylene	2 propylene $\xrightarrow{Tri\text{-}prop\ Al}$ 2methyl 1pentene 2methyl 1pentene $\xrightarrow{Acid\ med}$ 2methyl 2pentene 2methyl 2pentene $\xrightarrow{HBr}$ Isoprene	Tripropyl aluminium (dimerisation) (Isomerisation) Acidic med pyrolysis HBr
11. Butadiene	n-butane	n-butane $\xrightarrow{dehydrogenation}$ Butadiene	CrO
C_4 12. Benzene	Toluene	toluene $\xrightarrow{Hydroalkylation}$ Benzene	Cromia

Note for making Alcohol, hydrogenation of aldehyde Ni Catalyst

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	Product	Rawmaterial	Process & steps	Catalyst
13.	Phenol	Cummene	Cummene + air $\xrightarrow{NaOH}$ Cummene Hydro Peroxide	Partial oxidat
			CHP + H_2O $\xrightarrow[\text{acidic med}]{\text{Hydrolysis}}$ Phenol + acetone	Hydrolysis (acidic m
14.	Phenol	Benzene	Benzene $\xrightarrow[FeCl_3]{\text{Chlorination}}$ monochloro benzene	Chlorination ($FeCl_3$)
	C4		MCB + NaOH $\xrightarrow{\text{Causticizing}}$ Sodium Benzoate	Causticizing (NaOH)
			Sodium Benzoate $\xrightarrow[HCl]{\text{Hydrolysis}}$ Phenol + NaCl	Hydrolysis (HCl)
** 15	Phenol	Toluene	Toluene $\xrightarrow[\text{naphthanie oxidation}]{+O_2\ CO}$ Benzoic acid	Oxidation (CO-naphthan
			Benzoic acid $\xrightarrow[\text{Redn}]{LiAlH_4}$ Phenol	Reduction ($LiAlH_4$)
** 16.	Styrene	Benzene & Ethylene	Benzene + Ethylene $\xrightarrow{AlCl_3}$ Ethyl benzene	Alkylation ($AlCl_3$)
			** * Ethyl benzene $\xrightarrow[-H_2]{SnO/PbO}$ Styrene	dehydrogena... (SnO/PbO)
17	Pthalic anhydride * (Reacting system is Jacket liq phase CSTR)	Naphthalene or O-xylene	Naphthalene + O_2 $\xrightarrow{V_2O_5}$ Pthalic anhydride + H_2O + CO_2	V_2O_5
			O-xylene + O_2 $\xrightarrow{V_2O_5}$ Pthalic anhydride + H_2O	V_2O_5
** 18.	Maleic Anhydride	Benzene	Benzene + O_2 $\xrightarrow{V_2O_5}$ MA + H_2O + CO_2	V_2O_5
		(Now used) **	Benzene + O_2 $\longrightarrow$ MA (by vap phase oxidn of n-butane)	Vanadyl phosp
*** Oxo Rxn 19.	Oxo-processing (CO + H_2)	Olefins	Olefin + CO + H_2 $\longrightarrow$ Aldehyde	(Oxidation) CO-naphthanie
20.	Nitrobenzene	Benzene	Benzene $\xrightarrow{HNO_3 + H_2SO_4}$ NB	Nitrating mix $HNO_3 + H_2SO_4$
* 21	DDT (dichloro diphenyl trichloro ethane)	Chloral and Monochloro Benzene	EtOH + Cl_2 + H_2O $\longrightarrow$ Chloral	Used as pesticide (banned now)
			Monochloro benzene + Chloral $\longrightarrow$ DDT	

banned due to non biodegradable

① ② ③

Pol
Pol
1.
2.
...

Wulff process - Acetylene prodn
Sulphite → Pulp

Polymer Industry

Poly - many   Mer - unit   Polymer - many unit

Polymerisation are of 2 types

1. **Addition** - $nCH_2=CH_2 \rightarrow -(CH_2-CH_2)-_n$ no elimination

2. **Condensation** : Elimination of small molecule

Adipic acid + HMDA → Nylon 6,6 + nH_2O

$COOH-(CH_2)_4-COOH + NH_2-(CH_2)_6-NH_2 \rightarrow -(HNCO-(CH_2)_4-CONH-(CH_2)_6-NHCO)-_n + nH_2O$

types of polymer

1. Homo - MMM (single monomer)
2. ~~Hete~~ Co-polymer - MMNMM (more than 1 monomer)
3. Block polymer - $\boxed{MM}$ $\boxed{NNN}$ $\boxed{MM}$ $\boxed{NNN}$ - when monomer exists in blocks.
4. Graft polymer - M-M-M-M-M-M (side chain N-N-N-N) main chain is of one type of monomer and side chain is diff monomer.

① **Bulk polyn** : ~~Purity~~ Purest form of polymer, large amt of heat released which may not be controlled by cooling jacket. Involves only monomer molecules. eg polystyrene, polyethylene, poly propylene, ~~poly~~ PET.

↓ purity ↑ heat control ↑

② **Solution** : Inert solvent is added to enhance heat capacity and product contain some traces of solvent (M.W of compound ↓)

③ **Suspension and Emulsion polyn** : large amt of heat control. Each droplet act as tiny bulk reactor and H.T from droplet ~~of~~ solvent and better heat control bcz of reduced size. Agitator is used to maintain droplet size in dispersion (suspension) while Emulsifying agent used in Emulsion polyn which convert Rxn mass into stable emulsion so no agitation is req ⇒ high MW polymer. eg SBR, Chloroprene, Acrylic Rubber.

(MM) physical mix   (tiny) chemical Rxn

Emulsion eg Styrene Butadiene elastomer (SBR) & teflon

Suspension → 90% PVC produced

Olefins including styrene and methyl methacrylate.

Ammoxidation – Acrylonitrile from propylene
Nitration – Aniline from benzene
Oxidation – Benzoic acid from toluene

Calcium Ammonium nitrate – fertilizer
$CaCl_2$ – NaCl – Rope Pump
Black liquor – sugar
Activated silica alumina – Petroleum

Thermoplastics

Thermoplastics	Monomer	Process	Use	Remark
① Polyethylene	ethylene Low P' → 6-10atm → Carl Zeigler in Germany → Zeigler catalyst (Aluminium triethyl activated with heavy metal derivative like $TiCl_4$) → LLDPE → high branching with both short & long chain	High P' → 1000-2500atm → developed by Imperial Chemical Industry (ICI in UK) → catalyst = Peroxide ~~Eg~~ LDPE → ~~LDPE~~ → short & regular branches	Packaging material Intermediate P' → 30-100atm → Philips petroleum corporation in USA → Cr2O3/MoO3 on alumina → HDPE → very few branches	Most widely used
② Polypropylene	Propylene	low pressure Zeiglar process	packaging material	IPCL & BCPL is only manufacturer
③ Polystyrene	Styrene (Benzene)	dehydrogenation of Ethylbenzene which in turn produced by alkylation of Benzene	Electronics, Shoe sole, Wire & cables	Thermal stability, low cost, Ease in fabrication
④ Polyvinyl Chloride (PVC)	Vinyl Chloride	Vinyl Chloride made from Ethylene	Rigid PVC – pipe fitting Flexible PVC – Cable & wires, insulation	2nd largest consu... & most versatile

R.M.: Ethylene + 1-butene → LLDPE

With addn of plasticizer Rigid PVC can be converted into flexible PVC.

★★ $\boxed{\text{plasticizers used in PVC = Hydrogenated phthalic}}$

★ $\boxed{\text{Catalyst = Butyl lithium}}$

★★ V.Imp ★

Thermoplastics	Monomer	Process	Use	Remark
⑤ Poly Carbonate (Engineering Plastic)	Bis-phenol & phosgene ($COCl_2$)	Condensation Polymerisation (Presence of Organic Solvent)	Optical clarity, Impact strength, flame resistance,	—

Thermoplastic
Rasayani

Product
Phenol Formaldehyde
Urea Formal...
Melamine Formal...
★★ Ep... Re...
Pe...
Poly...
(a)
(b)
Pl...
Te...

Deacon's process – chlorine
Modified solvay – soda ash
Vacuum, evap – common edible salt
Beck – caustic soda

Thermosetting → Condensation
formaldehyde like

Product	Raw material	Process	Use	Remarks
Phenol Formaldehyde	Phenol + Formaldehyde → CH_4	Condensation Polyn	Adhesive, making glass fibres	Oldest thermosetting Polymer
		Acid catalysed – Novalik PF Resin		
		Base catalysed – Resole PF Resin		
Urea Formaldehyde	Urea → $NH_3 + CO_2$ Formaldehyde → CH_4	Condensation Polyn	textile + paper	$NH_2-\overset{O}{\overset{\|}{C}}-NH_2$
Melamine Formaldehyde	Urea $\xrightarrow[360\text{–}700°C]{\text{Quartz}}$ Isocyanic acid + NH_3 → (Alumina Catalyst) → Melamine; Formaldehyde → CH_4	Condensation Polyn	Kitchen wear & Non breakable crockery	Better chemical & heat resistant
Epoxy Resin	Bis-phenol Epichloro Hydrin	Condensation Polyn	Coatings	

FIBRES

Product	Raw material	Process	Uses	Remark
Polyamide → 2nd Largest used				2nd largest used
(a) Nylon 6	Caprolactum	Polymerisation →	Parachute, Clothes, Ropes, Nets, garments	
(b) Nylon 6,6	Adipic acid and Hexamethylene diamine	Condensation → from Cyclohexane	tyre ropes, gear wheels, friction bearing, Conveyor belts, Parachute	Nylon 6,6 is chemically stable than Nylon 6 and high m.p than Nylon 6
Polyester (Polyethylene terepthallic)	Paraxylene + O-xylene → (Co Catalyst)			1st largest among fibres
(a) Dacron	DMT (Dimethyl terepthalic)	Condensation	packaging of food + beverages	100% Recyclable, soft + light wt.
(b) Terylene	Purified terepthalic acid and Ethylene glycol	Condensation	PET Bottle	

Antimony catalyst (Sb) in both dacron + terylene process as both are PET

BCPL is
manufacture
stability
t,
breakdown

most widely used
mark

t conserve
satile

Q Catalytic cracking is Carbon Rejection process

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Product	Rawmaterial	Process	Uses	Remark
(3) Acrylic fibre				3rd largest Consumed
(a) Orlon	Acrylonitryl → acrylic fibre			
(b) dynel	Acrylonitryl and Venyl chloride → modified acrylic fibre			
At 2018 (4) Cellulose fibre				
Rayon: made from Cellulose dried from natural occuring material.				
(a) Viscous Rayon	Cellulose NaOH, CS_2 (Carbondisulphide)	Xanthation		
(b) Acetate Rayon	Wood Pulp, acetic anhydride, 4 H_2SO_4			
(c) Cupraammonium Rayon	Cellulose, Copper salt + ammonia			

Xanthation: Greeek word means yellowish, golden.

→ Xanthate salts are produced by Rxn of alcohol with KOH/NaOH and CS_2 (Carbon disulphide)

→ Cellulose react with CS_2 in presence of NaOH, to produce Sodium Cellulose Xanthates which upon neutralisation with H_2SO_4 gives Viscous Rayon.

NaOH → not Recover

CS_2 → Recover

(A) Biodiesel are triglycerides ✗

(B) Biodiesel is essentially mix of ethyl esters ✓

(C) " is highly aromatic ✗

(D) " has low aniline point ✗

production involves transesterification that yields glycerol as by product.

Performance No – Aviation gasoline
Drop point – grease
Smoke – kerosene
Viscosity index – Lubricating oil

Elastomer

Product	Raw Material	Process	Uses	Remark
Styrene Butadiene SBR (BUNA-S)	Styrene and Butadiene	Rxn takes place in presence of Na.	tyres, tyre related product	
Poly-butadiene	Butadiene (from naphtha cracker)	—	blending agent with SBR to improve properties	not used directly as product
Poly-Isobutylene (Butyl Rubber)	Isobutylene	n-butane $\xrightarrow{-H_2}$ Isobutene $\downarrow$ Pt Catalyst Isobutylene	Making of balloons, air tight purpose	2% Isoprene add to ↑ properties
Chlorobutyl Rubber	Butyl Rubber and Cl_2	$BR + Cl_2 \rightarrow$ Chlorobutyl Rubber	Tube less tyre	greater flexibility
Nitrile Rubber (ABR) Acrylonitrile Butadiene Rubber	Acrylonitrile and butadiene	Acrylonitrile + Butadiene $\downarrow$ ABR	Seals and gasket.	R.M from petrochemical
** Poly-Isoprene (Natural Rubber)	Hevea tree	Natural elastomer from hevea tree and made synthetically from propylene	As a Rubber	—
** Neoprene (Polychloroprene) or synthetic Rubber	** Acetylene	Acetylene $\xrightarrow{dim}$ mono vinyl acetylene $\downarrow HCl$ chloroprene	Transportation Industry, ** Vulcanised Rubber → Neoprene	—
* 8) Silicon Rubber (Poly Siloxanes) $-(O-Si-O)-$	monomer with siloxane linkage; R.M = Siloxane	→	Electrical appliances, Aerospace industry	Extreme temp condn
9) Polyurethane **	Alcohol + Isocyanate $\downarrow$ Urethane	Isocyanate + polyols + Metal complex → Poly urethane; RNCO → Isocyanate ($RNH_2 + COCl_2 \rightarrow RNCO + 2HCl$) ROCO (Cyanides)	tyres for truck, seat for automobile	
** 10) Hypalon	Chlorinate and Polyethylene	Chlorinate + Polyethylene $\downarrow$ Free Radical Catalysed Rxn Hypalon	Conveyor Belt	

INORGANIC INDUSTRY

Potassium sulphate

① H_2SO_4 (Sulphuric acid) 6.2 to 6.5% V_2O_5 on silica + 1% K_2SO_4

R.M = Sulphur + O_2 MP = 10.4, BP = 340°C (decomp)

Catalyst = V_2O_5 (DCDA process)

- ★ Sulphur from salt domes by Frasch process → from mining
- ★ Sulphur from Pyrites by Finish process
- ★ H_2S conversion from natural gas by Claus process → from Refinery

Liquified O_2 obtained by Linde process or Cryogenic liquification

Chamber process	Contact process
1. Previously used	1 Presently used
2. Conc H_2SO_4 < 80%	2 H_2SO_4 Concⁿ > 98%
3. Homogeneous (HNO_2)	3. Heterogeneous (V_2O_5 solid catalyst)

V_2O_5	Pt
1. Presently used	1. Previously used
2. less reactive	2. more reactive
3. Immune to Poison	3. Reactivity of V2O5 can be ↑ by using dilute SO_2 and feed to Catalytic Conv is (7–10%) SO_2 + 90% O_2
4. req in very less amt (10kg per 1 ton prodⁿ of H_2SO_4)	

Paper and pulp

Fourdrinier process

White liquor ($NaOH + Na_2S$)

Make up Chemicals (Na_2SO_4, Na_2S)

Green liquor (Na_2CO_3)

Causticization : milk of lime added to green liquor to recover white liquor

White black

green white

$Ca(OH)_2 + Na_2CO_3 \rightarrow NaOH + CaCO_3$

White

also called Sulphate Kraft process

white

$NaOH + Na_2S \xrightarrow{\text{lignin}}$ black liquor $\xrightarrow[\text{water}]{\text{cold}}$ green liquor

Kraft cycle ⇒ White → Black → green → White

↓ milk of lime $Ca(OH)_2$

White liquor (NaOH)

Fourdrinier

	web forming	→ Pressing	→ drying	→ finishing
% H_2O	50-82%	60-65%	5-6%	5-6%

★ Diatomaceous earth coating 10% aluminium nitrate to avoid explosion

Bleaching of pulp: To Remove brown color which is due to presence of lignin. Bleaching done with the help of (H_2O_2, Cl_2O_2, Cl_2), before using

Sulfite process ★ ($NaHCO_3$, Na_2SO_3)

Cooking liquor → mg bisulphite + mg bicarbonate / mg bicarbonate } doubt — SO_2 in acidic medium

★ paper are held together by H-bonding.

Fertilizer Industry

Mixed fertilizer / primary nutrients:
- Nitrogen – req to development of seed and leaves. (early stage)
- Phosphorous – accelerate seeding or food formation (early growth)
- Potassium – development of starch of potatoes + grains.

① Ammonia NH_3 (Haber's process)

Comp^n of fresh feed to high T & P • urea autoclave is excess liq NH_3 + compressed CO_2 gas

soluble in water — MP = 77.7°C, BP = −32.7°C

used in making HNO_3, ammonium nitrate

N_2 (from air) + $3H_2$ (from syngas) $\xrightarrow{\text{FeO alumina ★, promoted by alkali } (K_2O)}$ $2NH_3$

Engg problem: Catalyst diffuse over 620°C

Temp 500–600°C

P. 100–1000 atm

② Urea ($NH_2\overset{O}{\overset{\|}{C}}-NH_2$)

liq NH_3 → Urea synthesis (← compressed CO_2) → flash evaporator → flash drum → vacuum evaporator → prilling tower

MP = 132.7°C, BP = decomposes

→ soluble in water

→ In solid form, N_2 = 40–42%

→ In liq form, N_2 = 45%

$2NH_3 + CO_2 \longrightarrow NH_4COONH_2$ (AC)

Ammonium carbamate ★ $\xrightarrow{-H_2O}$ NH_2CONH_2

→ 99% molten urea sprayed to Prilling tower

★★. $\boxed{2NH_2CONH_2 \xrightarrow{\text{dimerise}} \text{Biuret}}$

If we ↑ temp then Biuret formation will occur >1%. Residence time (1–2 sec) only

★★ product is obtained in form of prils (प्रिल्स)

★★ Uses as nitrogen fertilizer

200 atm
↓
27 atm
↓
1 atm
↓
60 cm Hg

conv ?

★ $\boxed{\text{Biuret decomposes into } CO_2, N_2, H_2O}$

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③ Phosphate Fertilizer

Single super phosphate (SSP) ($3CaH_4(PO_4)_2 \cdot 7CaSO_4$)	Double super phosphate (DSP) $10CaH_4(PO_4)_2$
1. also Form of Calcium phosphate	1. also form of Calcium phosphate
2. R.M : Phosphate Rock + H_2SO_4 (16-20%) (60%)	2. R.M : Phosphate Rock + 'H_3PO_4' (40-45%) (75%)
3. Ammonium sulphate can be produced if we add NH_3 before rotary granulator	3. Ammonium phosphate can be produced
4. Final fertilizer not ready to use and some storage is req	4. Ready to use
5. Mix of R.M sent to blender then rotary granulator then rotary drier to get SSP (Single super phosphate)	5. Same as SSP to get DSP.

NOTE Nowadays, for making 'SSP' we are using HNO_3 instead of H_2SO_4 as amt of HNO_3 is req less and final pdt has high 'P' content ④
high phosphorous

(Phosphoric acid)

H_3PO_4 ① Wet process → Strong H_2SO_4 leaching
→ HCl acid leaching

② Blast furnace

③ Electric furnace process.

★ # Nitric acid (HNO_3) (Pt, Rh Catalyst used)

produced ① From nitrate

② Arc process

③ Ostwald Process → oxidⁿ of NH_3 to NO

→ oxidⁿ of NO_2

→ absorption of NO_2 in water

→ Concⁿ of HNO_3

→ 52-67% Commercial grade

→ if ≥95% technical grade HNO_3 (by using H_2SO_4)

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1. Soda ash - Leblanc (Salt cake → sodium sulphate) + $CaCO_3$ → Soda ash + gypsum ($CaSO_4$)
Na_2SO_4 Limestone (Na_2CO_3) side product
↓ not used
2. Solvay process - Ammonia soda process → NH_3 recycle NH_4Cl
3. Modified process → dual process → recovery of NH_4Cl
4. Natural soda ash from deposits

White fuming Nitric acid (WFNA)

→ WFNA is storable liq oxidizer used with (Kerosene) and Hydrazine of fuel
→ WFNA is commonly specified and not contain > 2% H_2O + < 0.5% dissolved NO_2 or N_2O_3.
→ WFNA used with inhibitor compound (HF)

HF → Less oxidizing performance than RFNA (Red fuming nitric acid)
→ toxic + volatile
→ Used in making of nitroglycerine

Red fuming Nitric acid (RFNA)
(84% HNO_3)

→ It is Rocket storable oxidizer used as rocket propellent
→ Contain 84% HNO_3, 12% N_2O_4, 1-2% H_2O
** → Color of Red fumes due to ($N_2O_4 \longrightarrow NO_2$) **
→ RFNA used in Inhibitor (HF)

Uses: dye, fertilizer, pharma, explosives

(4) Chlor-alkali → Prod^n of ① Soda ash (Na_2CO_3) (Solvay process) (salt + limestone) and ② Caustic soda (NaOH), Cl_2 ③
~~Solvay process~~
→ Sodium carbonate + slaked lime

NaOH process:

Diaphragm	Mercury	Membrane
1. 10-12% Conc NaOH so further conc is req	1. Produce 70% Conc NaOH	1. Produce 33% Conc NaOH. Can tolerate Ca + mg ions in feed brine.
2. Cl_2 produced contain O_2	2. Cl_2 produced pure	2. Cl_2 produced contain O_2
3. Less purified brine (NaCl) used	3. Highly purified brine used	3. Int purification req
4. It uses asbestos (silicate material)	4. It uses mercury	4. It uses membrane
5. Energy cons is very less	5. Very high	5. 77% of mercury
6. disposing asbestos prob	6. disposing Hg problem	6. Pollution free but costly and short life

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

Uses of NaOH: paper pulp, textile, as blending agent, Petroleum

OIL & Gas Industry

Oil used for nutrition of animal or plant called Vegetable oil.
Used in perfume, soap, medicine

Oil & fats are mix of glyceride of fatty acid

$$\left.\begin{array}{l} R_1-CO-O-CH_2 \\ R_2-CO-O-CH \\ R_3-CO-O-CH_2 \end{array}\right\} \text{glyceride}$$

R_1, R_2, R_3 may be same or diff.

Alkyl group attached Carbe			No. of double bond
Stearic	$C_{17}H_{35}$	M.P ↓	0
Oleic	$C_{17}H_{33}$		1
Linolic	$C_{17}H_{31}$		2
Linolenic	$C_{17}H_{29}$		3

** ⇒ Reducing double bond Ni catalyst or (Ni + Al) uses
→ Raney nickel

Method of Production : Oilseeds are feed and crushed.

** (a) if digestors is used : they are fed to digestor with water & steam
** (b) if Extraction is used : Seeds fed to Extractor & solvent recovers oil.

Purification

(I) Alkali or Na_2CO_3 used to remove free fat in form of foots which is supplied to soap industry.

(II) After bleaching is done to remove unwanted color of oil (Fuller earth → provide physical surface)

(III) Oil separated is Hydrogenated with H_2 to ↑ M.P and ↓ reactivety

2 types

(a) Ghee based oil : Hydrogenated at low P & high T to yield fat with M.P same as butter
↑ like idealgas ☺

(b) Vanaspati based oil : Hydrogenated at high P & low T to yield fat of high mp and max stability and used for cooking purpose.
(वनस्पति)

① oils with oleic (1dB) is more suitable than linolenic (3dB) (false)
② Prodn of Syngas from coal & steam is endothermic (true)
③ use of Cl_2 for bleaching of wood pulp results in release of dioxin (true)
④ manufacture of urea, intermediate is ammonium dicarbonate (false) — ammonium carbamate होता है

Soaps and detergents

Soaps are compound of (RCOO)M — RCOO: fatty acid; M: alkali metal (Na, K)

Raw material → vegetable oil or other fatty acid and NaOH → Caustic soda

★★ $\boxed{\text{Catalyst = Metal oxide like ZnO}}$

Process

Fat splitting - produce fatty acid + glycerine

Saponification - Soap can be produced by Reacting fatty acid with alkali

Detergents

(a) Anionic → which gives $R^{\ominus}$ in water and posses detergent characteristics
eg sulphates, sulphonates, linear Alkyl benzene sulphonate (LABS).

(b) Cationic → gives $R^{\oplus}$ in water and posses germicidal characteristics
eg Ammonium compounds

Sugar Industry

$\boxed{CaHPO_4 / \text{lime treatment} \rightarrow \text{multistage evaporator} \rightarrow \text{Crystallizer}}$

R.M = Sugar Cane

Chemical name: Sucrose $C_{12}H_{22}O_{11}$

Process

① Crushing : sugar cane is crushed then pressure by 3 Rolls and add water to ↑ yield.

② Precipitation (Coagulation) : juice treated with Calcium Hypo phosphate ($CaHPO_4$) then by lime to precipitate.

③ Neutralization : SO_2 provide in juice till PH reach 7. also helps in bleaching

2005 ★★ Sulphation when SO_2 is used

★★ Carbonation when CO_2 is used.

④ Filtration : filtered with cake filter and cake is used as fertilizer.

also used in fats

(5) Evaporation: juice sent to multi effect evaporator for evaporation

(6) Crystallization: done in vacuum pan crystallizer and final soln of crystals and syrup is known as massecuite and seprate by centrifuge

(7) Molasses: Crystals are sep from mother liquor and mother liquor is known as molasses. It can be used in alcohol industry. ** (48-55%)

Engg problem Inversion of sugar (Write angle)

$$C_{12}H_{22}O_{11} + H_2O \longrightarrow \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

** Inversion can be checked by angle of polarisation in polarimeter

* For no inversion, Angle $= 97^\circ$
For completely inversion, Angle $= -20^\circ$

Cement Industry

R.M = Limestone, Clay, Sand, fly ash

Material formed in kiln is called clinker

Limestone, Clay, Sand → Blending → Kiln → Clinker → Clinker store → Cement mill

* Portland Cement is mix of Calcium silicates, Calcium Aluminates etc.
→ lime stone, clay, gypsum + coal.

*** # Steam Reforming of Methane (SMR Reactors)

Used for prod^n of syngas and H_2

(1) Reforming of Natural gas:

$$\underbrace{CH_4 + \overset{\text{steam}}{H_2O} \xrightarrow[700-800^\circ C]{Ni/Al} CO + 3H_2}_{\text{SMR Rxn}}$$

! main aim is prod^n of H_2

** Syngas is not used for manufacture of ethanol

Syngas → Lurgi process

(WGSR) → CO produced in 1st step is reacted with steam to produce H_2

(2) Water Gas shift Rxn $CO + H_2O \rightarrow CO_2 + H_2$ (WGS Rxn)

→ This step takes place in 2 stage called HTS (high temp) & LTS (Low temp shift Rxn)

** In HTS, Rn/Ni catalyst

** In LTS, Cu catalyst

→ After these steps, H_2 produces include small qty CO, CO_2, H_2S as impurity so purification is req.

→ CO_2 can removed by Pressure swing Adsorption (PSA) to produce 99% H_2

→ H_2S can be removed by desulphurisation process

** SMR → HTS → LTS → PSA → desulphurisation → Hot K_2CO_3 cycle ($CO \rightarrow CO_2$)

Some Important Rxn

(1) Gasification $C + H_2O \rightarrow CO + H_2$ (syngas)

(2) Water Gas shift Rxn $CO + H_2O \rightarrow CO_2 + H_2$

(3) POUROUAD Rxn ~~CO_2~~

$C + CO_2 \rightarrow 2CO$

(4) Methanation Rxn $CO + 3H_2 \xrightarrow{Ni} CH_4 + H_2O$

→ to remove CO as it is catalyst poison

1. Glauber salt – $Na_2SO_4 \cdot 10H_2O$
2. Niter cake – $NaHSO_4$
3. Gypsum salt – $CaSO_4 \cdot 2H_2O$
4. Epsum salt – $MgSO_4 \cdot 7H_2O$
5. Limestone – $CaCO_3$
6. Quick lime – CaO
7. Slaked lime – $Ca(OH)_2$
8. Caustic soda – $NaOH$
9. Bleaching powder – $CaOCl_2$
10. Baking soda – $NaHCO_3$

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(1) Phenol formaldehyde – solution Polyn
Nylon – Bulk
High Purity PVC – Suspension
Sytrene Butadiene Rubber – Emulsion Polyn or suspension

(2) methanol to gasoline – Z
Edible Hydrogenation oil – R
Methanation – Nickel
Butyl acetate – Cation Ex

(3) Edible oil – Gear pump
Crude oil from oil – Airlift Pump
98% H_2SO_4 – Centrifugal Pump
Liq contain suspension of solid – Diaphragm pump

(5) Conc H_2SO_4 – lead
Caustic soda – Aluminium
Ammonia – Fe

Q
Perspex – Polysacch

(4) H_2 from light Petroleum stock – steam reforming naptha
High octane gasoline from naptha – Platforming
Gasoline from gas oil – catalytic cracking
Petroleum coke from Residue – Pyrolysis

(7) chemical — Indu Use
Lithium stearate – grease
mg stearate – cosmetic
Al sulphate – paper

Ins fol pur

(6) Fischer tropsch synthesis – CO
Formaldehyde from methanol – Ag
dehydrogenation of ethyl benzene – Fe_2O_3

(9) In contact process, Eqm of SO_2 ↓ with ↑ in temp & ↑ with ↑ in mole ratio of SO_2 to air.

$SO_2 + \frac{1}{2}O_2 \rightleftharpoons SO_3$

(8) Oxidn of o-xylene to Pthalic anhydride – V_2O_5
Oxidn of Ethanol to acetaldehyde – Ag
Oxidn of Ammonia to oxides of N_2 → Pt

(10) sulphite process, cooking liquor – mg bisulphite + ~~[illegible]~~ (SO_2 in acidic medium) = ??

SO_2 in acidic me.

(11)

Reactor	Products
Arc furnace	Calcium Carbide
Fermenter	Citric acid
Hydrogenator	Saturated fats

(12) Ammonia synthesis – Fe/M
Steam reforming of methane – Ni/Al_2O_3

(13) Lignin > coking > catalytic naph

(14) process sequence in sugar industry is
$CaHPO_4$/lime treatment → multistage evaporation → crystallization

(15)

Chemical	Function
styrene	monomer
tert. dodecyl mercaptan	modifier
Potassium pyrophosphate	Buffer

(16) Rayon – Cellulose
Orlon – acrylic
Dacron – Polyester

dodecane → propylene Polyamide → adipic acid
NH_3 – methane
acrylonitrile → propylene

Q FCC, nature of Rxn occuring in reactor and regenerator.
Reactor – Endothermic
Regenerator – Exothermic

Q Nitration → explosives
Sulphonation → detergent
Carbonation → pulp + paper

Q → cylindrical storage tank can have self supported conical roof if its dia is more than 50 m.

Q Saponification → soap + detergent
Calcination – cement
Alkylation – Petroleum refinery

Q Styrene – monomer
tert-dodecyl mercaptan – modifier
Potassium pyrophosphate – Buffer

In sugar, addn of hydrated lime followed by carbonation for purpose of adjust pH of syrup.

Q Steam cracking → Petrochemicals
Hydrocracking → Petroleum refinery
Condensation → Polymer

Propylene–butanol = Hydroformylation
Cumene–phenol = Peroxidation
Butane–butadiene = dehydrogenation
ethylene dichloride–vinyl chloride = pyrolysis

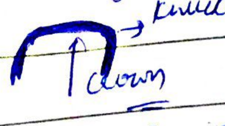
Q Bulk → Heat removal is crucial but very difficult
Solution → Polymer with high Mw can be obtained
Suspension →
Emulsion →

Q a) F in membrane in membrane cell → allow selective transfer of Na+ and retards the back transport of OH^-. This result of high purity NaOH.
b) Nylon general formula – Polyamide
c) Commonly used for process of polym of nylon – fischer tropsch for multi stage compressor
d) change in design of synthesis gas compressor for ammonium manufac → Interstage cooling
e) Kraft paper → high Tensile strength with high purity.

Q Correct sequence for process equipment for H_2SO_4.
Burner, catalytic converter, oleum absorption column, 98% H_2SO_4 acid absorption tower

Q Hydrotreating used for removal of sulphur & Nitrogen from petroleum fern.

Q Torispherical head → Crown rad, Knuckle rad and length of St. flange.



Q B.P order, lubricating oil > AGO > diesel > gasoline
Automotive gas oil.

knuckle/crown < 0.06

Q Decomposition efficiency of electrolytic cell used in NaOH = $\left(\frac{\text{gm equiv of NaOH produced}}{\text{gm equiv of NaCl charged}}\right) \times 100$