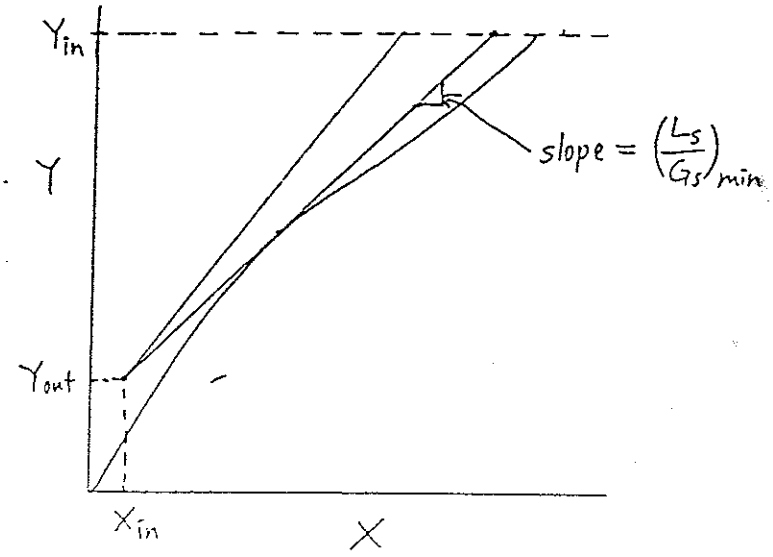
PROCESS DESIGN (Different set of questions)

(2) Design an acetone-air absorber (solvent = water) with twice the minimum flow rate.



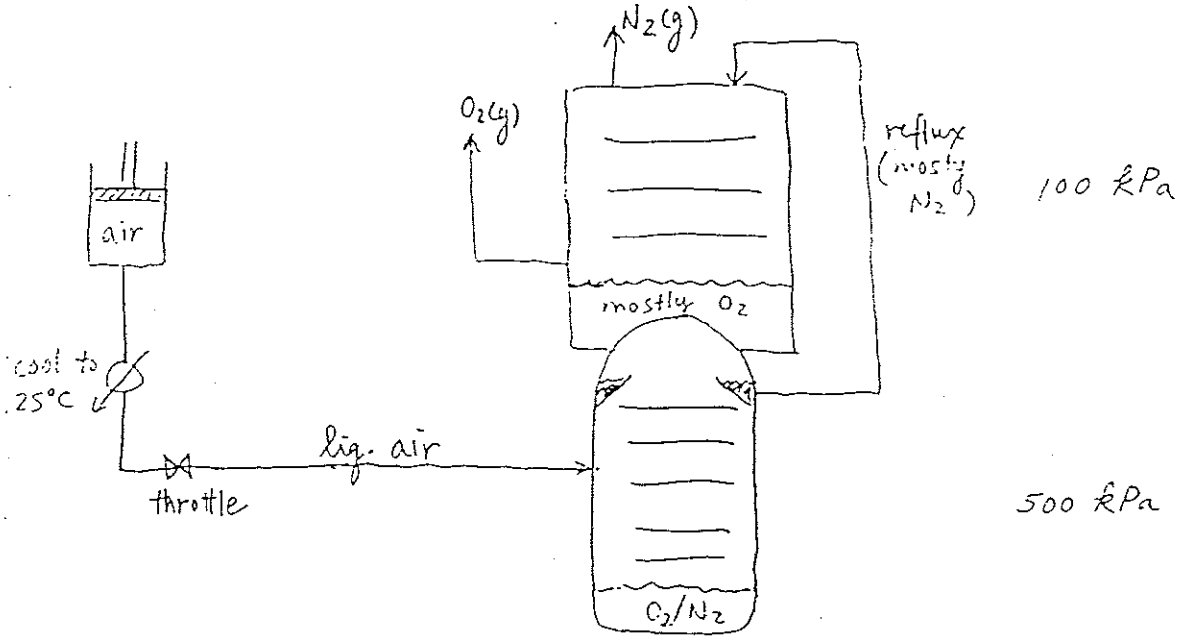
Simply multiply $\left(\frac{L_s}{G_s}\right)_{min.}$ by 2. Then draw new operating line and count steps.

(8). How could you remove water vapor from Ar gas to a level of 1 ppb if the water is initially present at a quantity of 200 ppb?

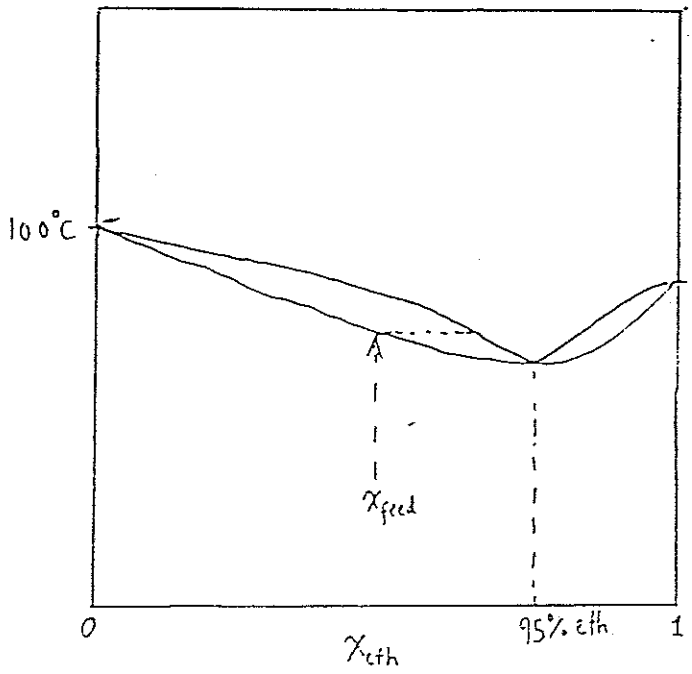
Since we're dealing with such low conc., regular separ. schemes are no good.
Use a high affinity dessicant.

(14) How to make N_2 and O_2 : Separation from air.

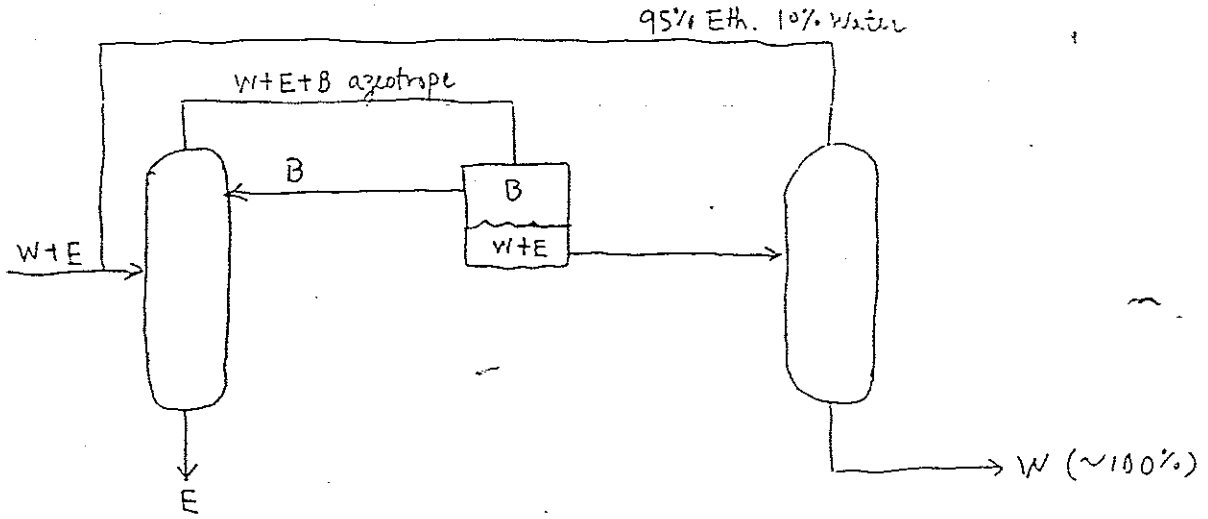
Linde process : distillation at high P



(24) Draw the xy curve for water-ethanol. How would you purify ethanol above 95%?



Note: This drawing is not correct

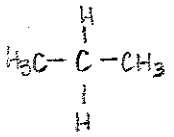


(21) Name some solid lubricants.

Graphite, wax, lard.

(12) How is H_2 made on a large scale basis?

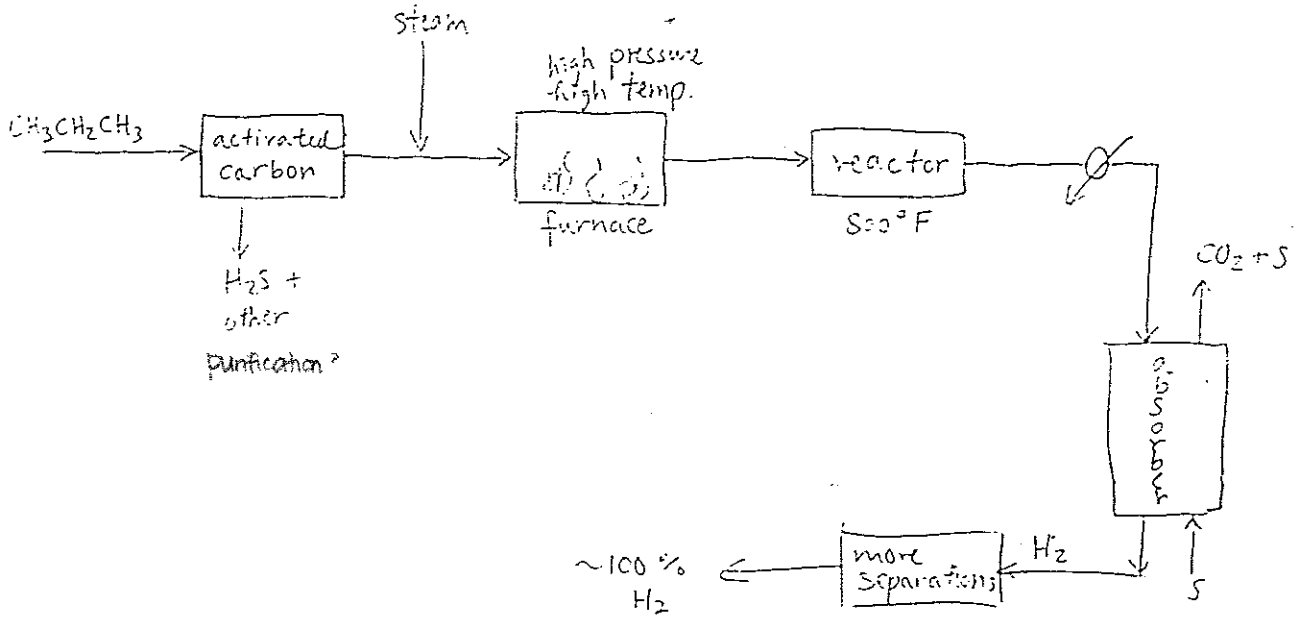
The most popular method to make H_2 is by steam reforming of light hydrocarbon gases.



propane

$$CH_3-CH_2-CH_3 + 3H_2O \longrightarrow 3CO + 7H_2$$

$$CO + H_2O \longrightarrow CO_2 + H_2 \qquad \text{water-gas shift rxn}$$



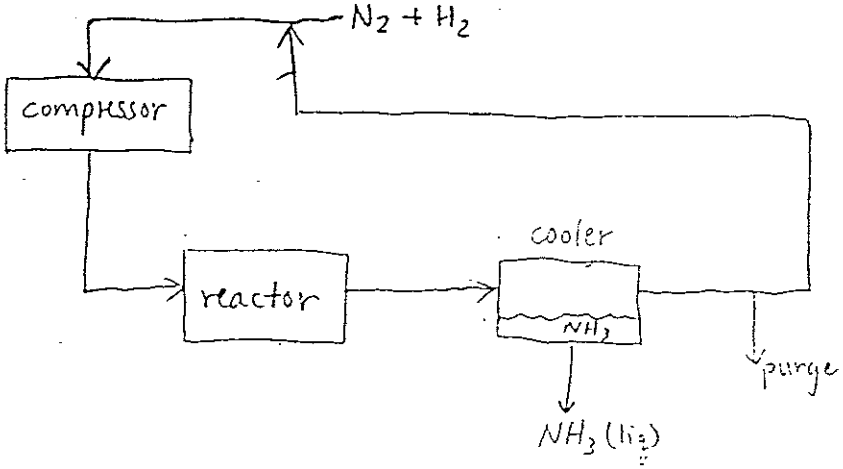
(26) Discribe the Haber process.

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

$400^\circ C < T < 500^\circ C$

$120 atm < P < 900 atm$

This is a very exothermic process because we are breaking and releasing the energy in the triple bond of N_2.



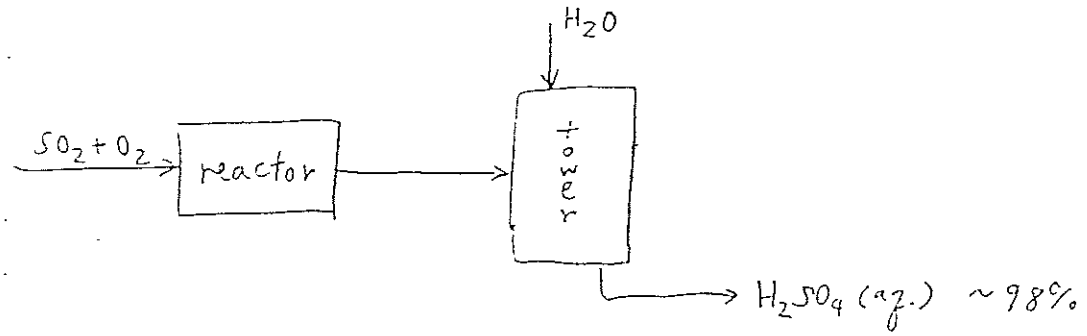
⑤. Commercially, how is $H_2SO_4(aq.)$ made?

Make it from SO_2. SO_2 is made by burning $S(s)$ with air.

$$S \xrightarrow[\text{combustion}]{\text{air}} SO_2$$

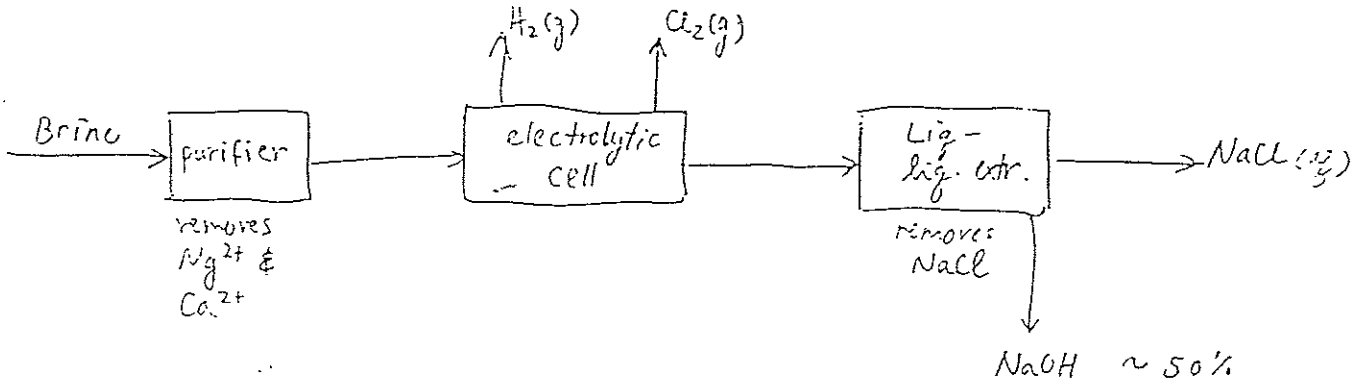
$$2\,SO_2 + O_2 \longrightarrow 2SO_3$$

$$SO_3 + H_2O \longrightarrow H_2SO_4(aq)$$



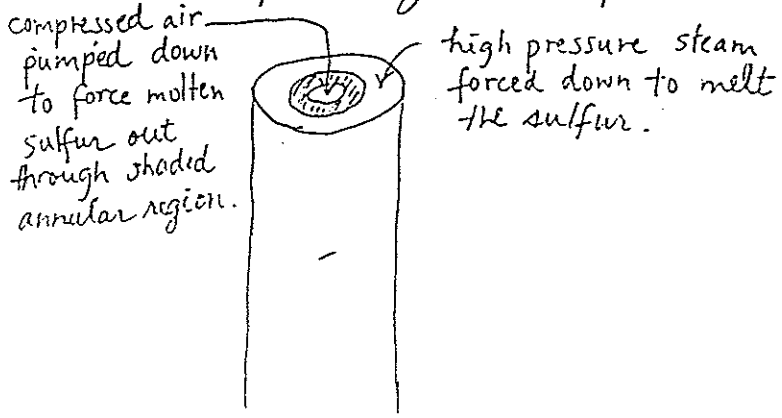
How is NaOH made? Electrolysis of salt.

$$NaCl + H_2O \longrightarrow NaOH + H_2 + Cl_2$$



How is sulfur obtained?

Sulfur deposits found deep in earth. Use Frasch process.

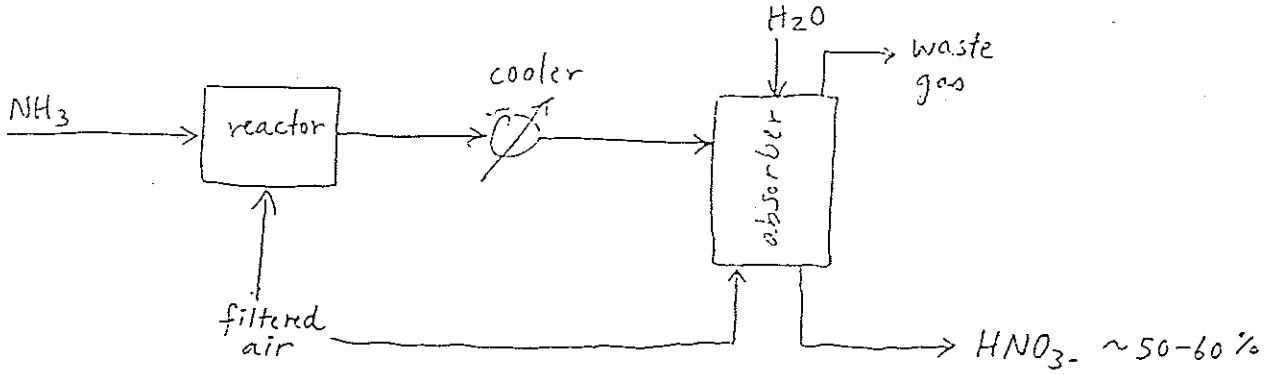


How to make HNO_3 commercially?

$$4\,NH_3 + 5O_2 \longrightarrow 4\,NO + 6\,H_2O$$

$$2\,NO + O_2 \longrightarrow 2\,NO_2$$

$$3\,NO_2 + H_2O \longrightarrow 2\,HNO_3 + NO$$



ethylene oxide | $H_2C\langle^{O}_{}\rangle CH_2$

General Info

- colorless gas or colorless mobile liquid
- mostly used for ethylene glycol, ethanolamines, and nonionic detergents

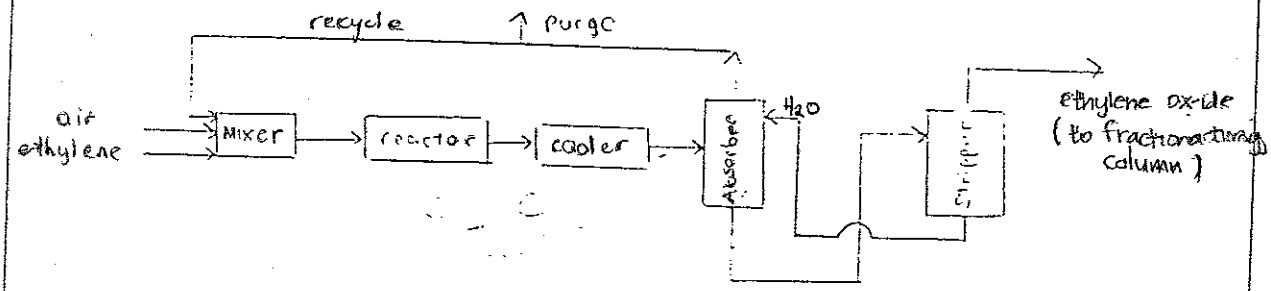
usage

ethylene glycol	60%
polyglycols	10%
miscellaneous	30%

process - catalytic oxidation of ethylene w/ air

$$CH_2 = CH_2 + \tfrac{1}{2} O_2 \xrightarrow{Ag} CH_2\text{—}CH_2 \text{ (epoxide O)} + (CO \rightarrow H_2O)$$

55-65% yield



- reactor: ethylene and air are mixed (1:8) and passed over a silver oxide carrier. T = 210° - 290°C; about 60% conversion.
- absorber: Effluent gases washed w/ H_2O under pressure
- stripper: ethylene oxide sent to a vacuum stripping column, which passes overhead to a column for final purification. Note: bottoms product (mostly H_2O) is used as an absorbant for the absorber.

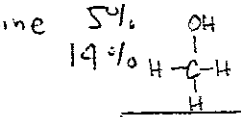
formaldehyde | H-C(=O)-H

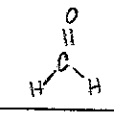
General Info

- colorless, pungent, highly irritating gas. May be liquefied / solidified by chilling.
- production driven by demand for phenol-, urea-, melamine formaldehyde resins

Usage

resins	60%
pentaerythritol	9%
ethylene glycol	12%
hexamethylenetetramine	5%
miscellaneous	14%



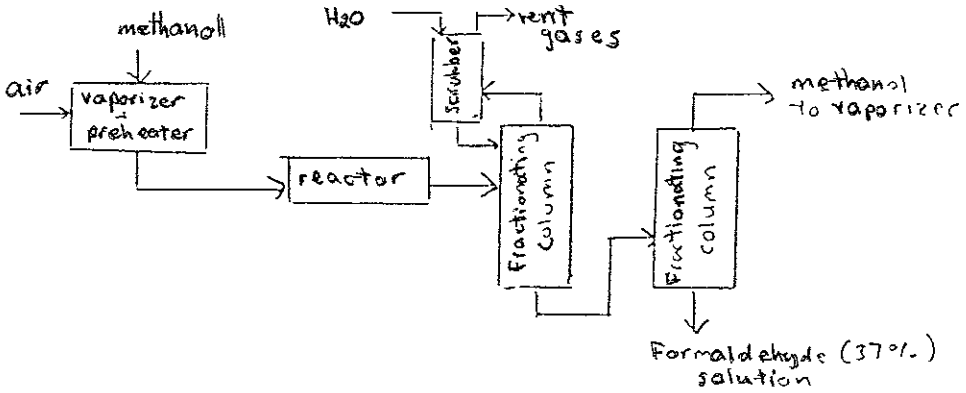


Process - from Methanol

$$CH_3OH + \tfrac{1}{2}O_2 \xrightarrow{cat.} CH_2O + H_2O$$

$$CH_3OH \longrightarrow CH_2O + H_2$$

85-90% yield



- Vaporizer/preheat : air and CH_3OH mixed (30-50% volume CH_3OH) and heated 100-300°C.
- reactor ; T = 450-600°C , reactor has metal (Ag or Cu) or metal oxide catalyst. Combined dehydrogenation and oxidation rxns ∴ catalyst type affects dominant rxn.
- column(s) : First column seperates methanol and formaldehyde. Scrubber removes 19-20% H_2 and 74-75% N_2, 4-5% CO_2.

  Effluent from first column sent to another column, which seperates 37% CH_2O w/ desired amount of CH_3OH stabilizer.

  Overhead methanol returned to vaporizer.

Hydrochloric Acid | $HCl_{(aq)}$

General Info

- It is a solution of HCl (colorless, pungent, poisonous gas) dissolved in water.
- Production of it is much less than sulfuric, phosphorous, and nitric acids.
- About 80% of the HCl produced is by-product acid; HCl production depends more on industrial usage of chlorine rather than consumer demand for the acid.

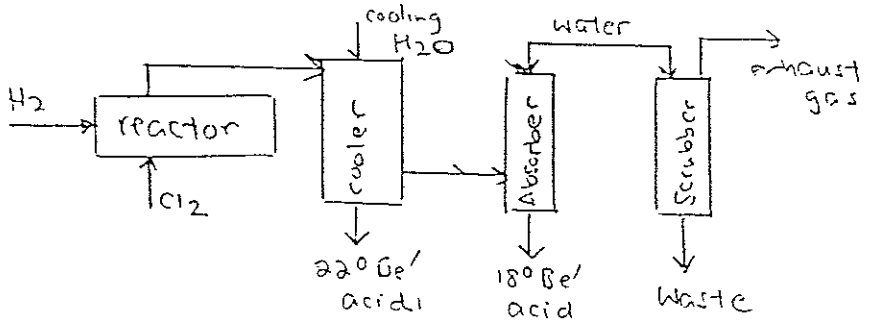
Usage

51%	Chemicals manufacture
21%	Metals industry
9%	Food / Glucose
7%	Oil-well acidizing
12%	Miscellaneous

Grades	% HCl	
18° Be	28	– yellow
20° Be	32	} colorless
22° Be	36	} colorless

Process – Using Cl_2 and H_2

$$H_{2(g)} + Cl_{2(g)} \longrightarrow 2\,HCl_{(g)}$$



- reactor: Cl_2 is burned w/ slight excess of H_2, making $HCl_{(g)}$. Temp. is around 260°C, 90–99% overall yield.
- Cooler: Burner gases pass through a Silica-S-bend cooler. Cooling is external using water, temp. about 38°C. A trap removes 22° Be' acid directly.
- Absorber: HCl gas contacted with water to make acid (18° Be') (stripper)
- Scrubber: Gases scrubbed with water and then vented.

Alternative Processes

- Use Methane + air: $2Cl_2 + CH_4 + Air \longrightarrow 4HCl + CO_2$ — same sep. system
- Use Salt + H_2SO_4: $NaCl + H_2SO_4 \longrightarrow HCl + NaHSO_4$
  $NaCl + NaHSO_4 \longrightarrow HCl + Na_2SO_4$

  ⊖ Furnace required. (Temp around 840°C)
  ⊖ Coke Tower needed after cooler to remove H_2SO_4
  ⊖ Also only get 18° Be grade.

hydrofluoric acid	H_2F_2	

General Notes

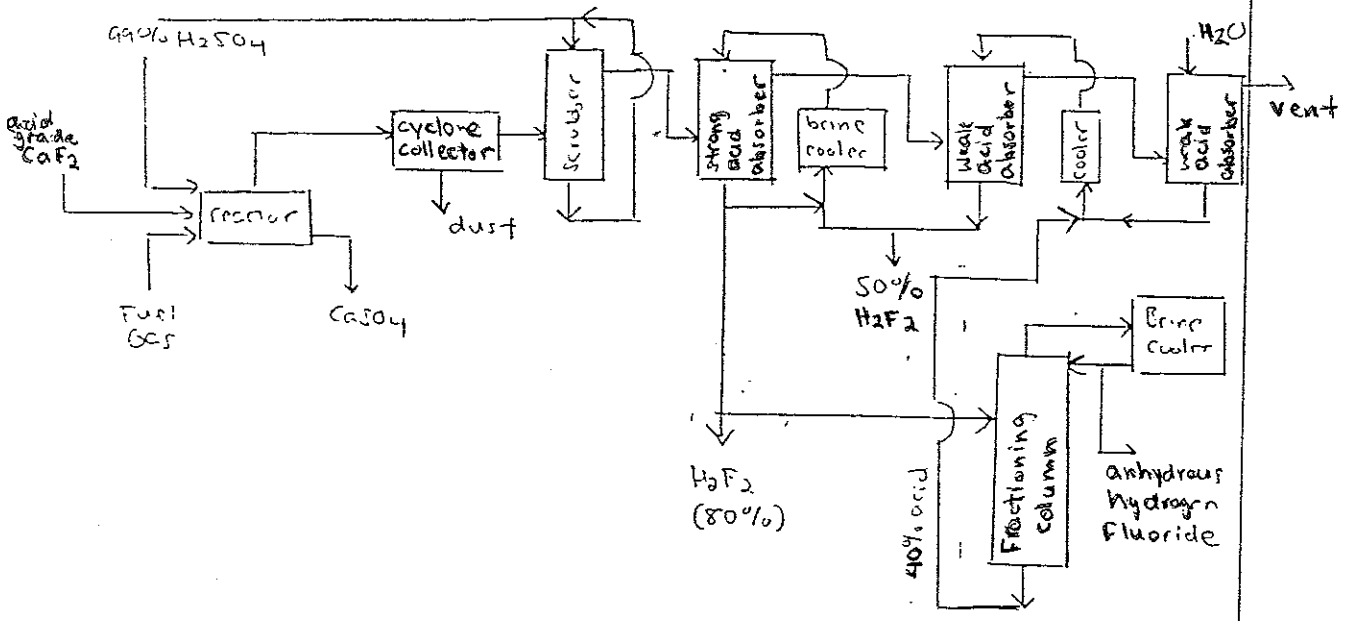
- anhydrous H_2F_2 is colorless, fuming, corrosive liquid. Serious burns w/ skin contact; vapors very irritating to eyes & mucous membranes.
- Industry driven by fluorinated plastics, aluminum fluoride industries. Formerly driven by CFC's industries and WW II as weapon.

Usage

Fluorocarbons	40%
Al industry	35%
Atomic Energy	10%
Alkylation	5%
Stainless Steel	3%
Miscellaneous	7%

$$CaF_2(s) + H_2SO_4(l) \rightarrow H_2F_2(g) + CaSO_4(s)$$

Process - H_2SO_4 + Fluorspar (CaF_2)



- **Reactor**: Powered, acid-grade CaF_2 is mixed with H_2SO_4 in a furnace (1 : 1.1-1.3). ($CaSO_4$ residue withdrawn & 70-75% H_2F_2 (g) withdrawn at 250 - 350 °F. $CaSO_4$ dust also removed.
- **Scrubber**: Entrained H_2SO_4 separated & recycled in scrubber. Gases cooled to about 150 °F.
- **Absorption System**: Basically removes H_2F_2. Effluent from last towers sent to preceding towers to concentrate acid to 50-52% in weak acid towers and 80% in strong acid towers. 80% H_2F_2 may be stored or used to make anhydrous acid.
- **Fractioning**: Feed is stripped at 240° F, anhydrous H_2F_2 leaves the top, and diluted acid is returned to absorption system.

hydrogen	H_2		

General Info

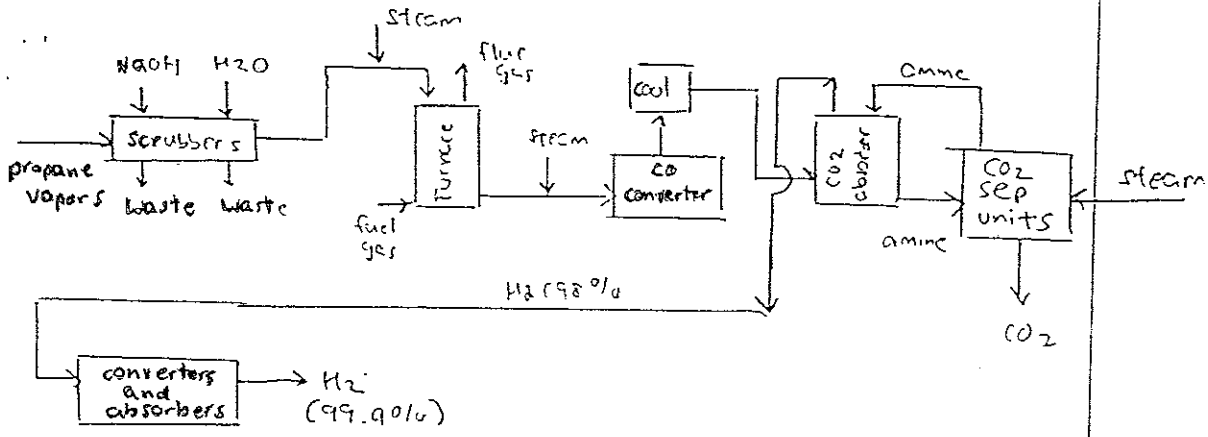
- colorless, highly flammable gas.
- is integral part of other chemical manufacturing operations.

Usage

ammonia	68%
Methanol	13%
refinery	6%
liquid	1%
other chemicals	5%
miscellaneous	7%

Process - from hydrocarbons & steam (Popular Process)

$$CH_3-CH_2-CH_3\ (g) + 3H_2O\ (g) \rightarrow 3CO\ (g) + 7H_2\ (g)$$
$$3CO(g) + 3H_2O\ (g) \rightarrow 3CO_2\ (g) + 3H_2\ (g)$$
$$CH_3-CH_2-CH_3\ (g) + 6H_2O\ (g) \rightarrow 3CO_2\ (g) + 10H_2\ (g)$$



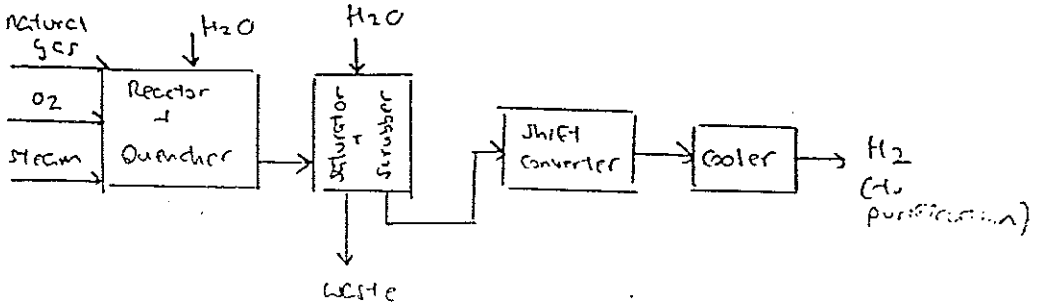
- Scrubbers: Propane heated to 700°F, removed of sulfur, and scrubbed separately with NaOH and H_2O.
- Furnace: Reforming furnace; steam & propane react. T = 1400° - 1800°F. P = 450 psi. Reformed gases later cooled to 700°F w/ steam.
- CO converter: Cat. = Iron oxide, T = 800°F, basically converts CO to CO_2 & H_2. Gases later cooled to 100°F.
- CO_2 absorber: Packed Tower; amine ($-NH_2$) is circulated to remove CO_2, and CO_2 is recovered from the amine by more downstream operations. Amine solution recycled back to absorber.
- Converters/Absorbers: Gases from absorber goes through 2 more stages to remove CO and CO_2.

Other Processes

From Hydrocarbons by Partial Oxidation

$$C_nH_{2n-2} + nO_2 \rightarrow x\,CO_2 + (n-x)\,CO + (n-1-y)\,H_2 + y\,H_2O$$

$$CO + H_2O \rightarrow CO_2 + H_2$$



- Reactants all preheated to 1200°F, sent to furnace @ 200-500 psi. Effluent gases quenched from 2600°F to 1000-1500°F. Mostly CO, H_2, H_2O, CO_2, CH_4 in effluent.
- In shift converter, CO and H_2O changed to CO_2 and more H_2. (water-gas shift)
- This method more expensive since O_2 required. Advantageous since many feed stocks are viable.

hydrogen cyanide	HCN	

General Notes

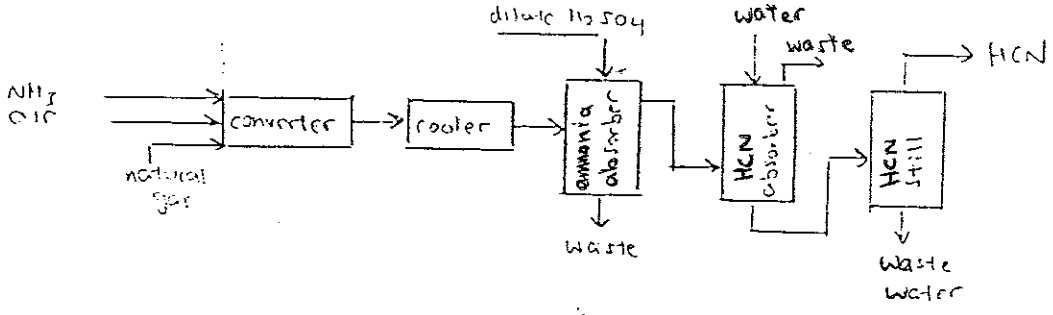
- Colorless, mobile liquid, bitter-almond odor & highly poisonous
- Production tied closely with making intermediates for synthetic fibers and plastics.

Usage

Acrylonitrile	50%
Methyl Methacrylate	18%
Adiponitrile	15%
Sodium Cyanide	7%
Miscellaneous	10%

Process - Using NH_3, air, and CH_4

$$2NH_3(g) + 3O_2(g) + 2CH_4(g) \xrightarrow{Pt} 2HCN(g) + 6H_2O(\ell)$$ 75% yield



- converter: reactant gases passed over Pt catalyst at high temperatures. (1900 - 2000 °F). P = 20 - 25 psi. Reaction is endothermic, so heat evolved by burning CH_4 less than that needed to make HCN. O_2 concentration kept below the amount needed to completely burn NH_3 and CH_4.
- NH_3 absorber: Acidified water used to separate NH_3.
- HCN absorber/still: Final purification & concentration of HCN.

Methanol	CH_3OH	

General Info

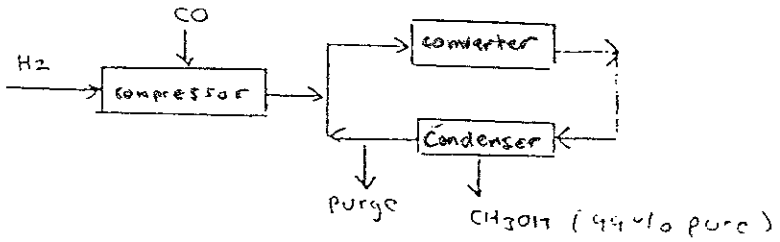
- clear, colorless, flammable, volatile, very mobile liquid
- Chief outlet is for formaldehyde, also demand for methacrylates.
- Commonly integrated w/ NH_3 plants (uses similar equipment)

Usage

formaldehyde	40%
other chemicals	30%
solvent	10%
exports & miscellaneous	20%

Process - from CO and H_2

$$CO(g) + 2H_2(g) \rightarrow CH_3OH(g)$$
60% yield w/o recycle



- compressor: CO and H_2 mixed (1:2), compressed to 3000 to 5000 psi and heated in heat exchangers.
- converter: Uses a metallic oxide (Zn, Mn, Al, Cr) oxide. T = 300 °C by removing the exothermic heat of reaction. (proper heat interchange + space velocity)
- condenser: Gases cooled to 0°-20°C, condensing CH_3OH under full operating pressure. Gases recycled back to converter.

Purge stream prevents inerts buildup.

Nitric Acid | HNO_3

General Data

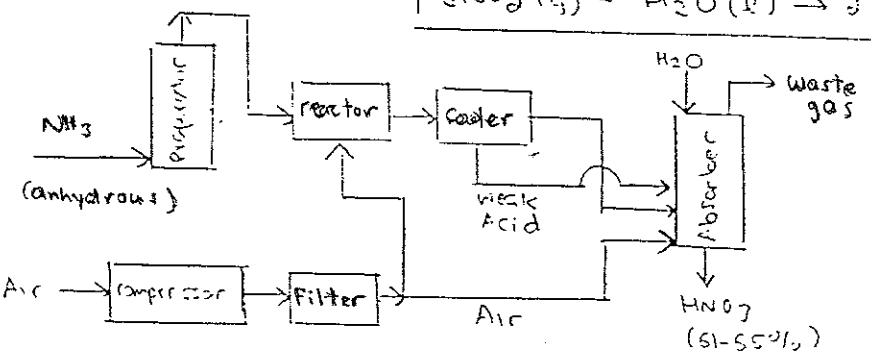
- Pure HNO_3 is a colorless, highly corrosive liquid with powerful oxidizing properties.
- Tied very closely to fertilizers and explosives.
- New potential uses: oxidant for missiles/rockets and as acidulant for superphosphate manufacture.

Usage

Fertilizer	75%
Explosives	15%
Miscellaneous	10%

Process - Using NH_3

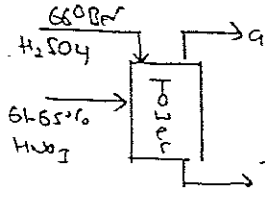
$$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$$
$$2NO(g) + O_2(g) \leftrightarrow 2NO_2(g)$$
$$3NO_2(g) + H_2O(l) \rightarrow 2HNO_3(l) + NO(g)$$



- Feed: Compressed (100 psi), filtered, and preheated (300°C) air is mixed with anhydrous $NH_3(g)$ and fed to reactor. (90% air by volume)
- reactor: Reactor has **Pt-Rh** (2-10% Rh) wire-gauze catalyst. Temp = 750°C, P = 100 psi. Catalysts packed in sheets of fine gauze. **Hot** NO-air mixture is sent to water cooler.
- Cooler: Cooling of NO-air mixture. More air is **added** to oxidize NO to NO_2.
- Absorber: Most of the rxn. occurs here (Keq favored at low T). Tower continuously **cooled** w/ H_2O externally. Some H_2O is added to (1) hydrate NO_2 to HNO_3, and (2) to scrub the gases. 61-65% HNO_3 obtained from bottom of tower.

Other Notes

- Why high pressures? => acid strength +15%, rxn rate x50, tower volume for oxid. & absorb. reduced overall cost => reduced by 50%.
- To concentrate HNO_3:



Use Si-Fe tower or Stoneware Tower

Phosphoric Acid	H_3PO_4		

General Notes

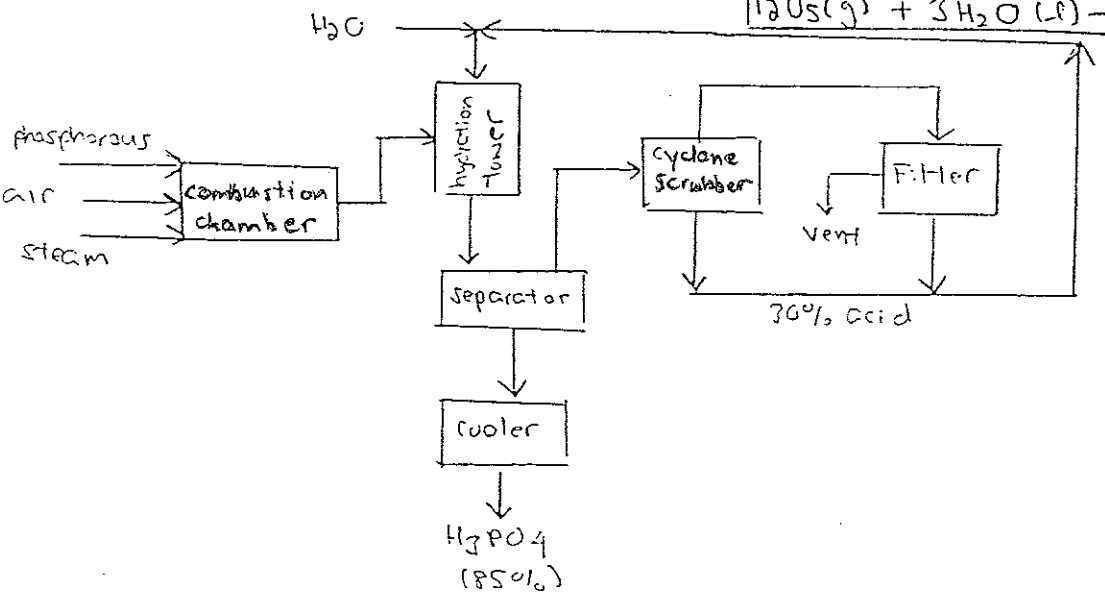
- Clear, colorless, sparkling, mobile liquid.
- Tremendous growth - high demands for triple-superphosphates and synthetic detergents. low manufacturing costs.
- Grades: technical (50, 75, 85%)
  food (75, 80%)

Usage

Fertilizer	65%
Soap/Detergents	20%
Miscellaneous	15%

Process: Oxidation + Hydration of P.

$$2P(s) + \frac{5}{2}O_2(g) \rightarrow P_2O_5(g)$$
$$P_2O_5(g) + 3H_2O(l) \rightarrow 2H_3PO_4(l)$$



- Combustion: Molten P mixed w/ air and steam, $T \approx 3600°F$ to make P_2O_5 gas.
- Hydration: Hot gases sprayed w/ dilute H_3PO_4. P_2O_5 is hydrated to H_3PO_4 (75-85% pure).
- Separator: Acid mist leaving hydration tower is recovered.
  eg: use cyclone scrubber + filter, or packed towers.

Other Processes

- Note all of them are widely used.

- use electric furnace on phosphate rock. } More complicated separations
- use blast furnace " "
- use H_2SO_4 " "

Phenol |  |

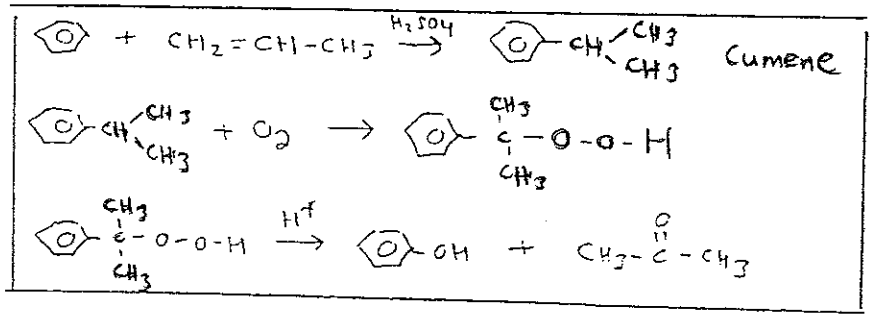
General Notes

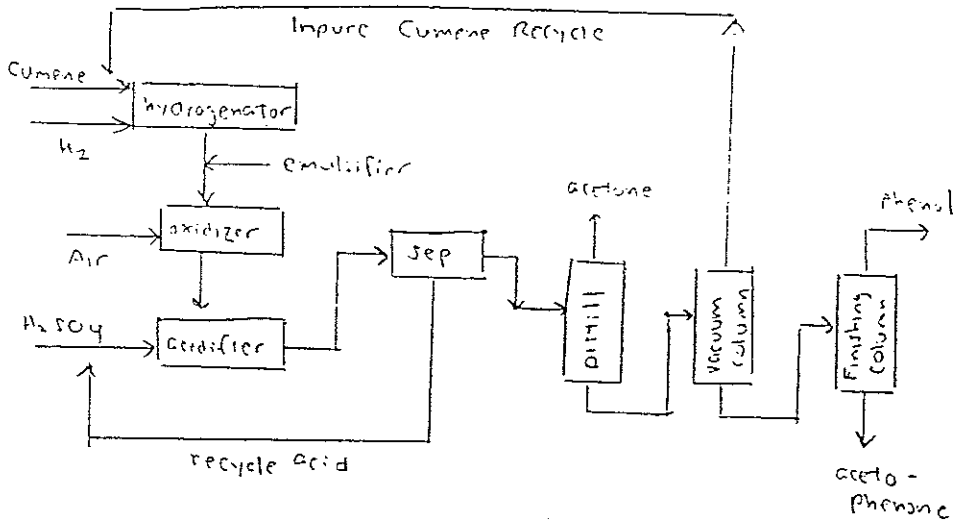
- White, crystalline solid. Turns red/pink from impurities, light, or air.
- production driven by demand for specialty chemicals & new phenol derived plastics.

Usage

phenolic resins	50%
caprolactam	10%
alkylphenol	10%
bisphenol-A	7%
Misc. & export	23%

Process - Cumene Peroxidation





- hydrogenator: Converts impurities in cumene recycle to more cumene. (α-methylstyrene)
- oxidizer: Both cumene streams mixed w/ air, held @ 130°C until 35-50% of cumene is converted to hydroperoxide. (Purpose of emulsifier is to supply proper pH & ideal reaction conditions)
- acidifier: Mixture from oxidizer (50% cumene) mixed w/ 10% H_2SO_4. T = 45-65°C, mild pressure. Acid cleaves the cumene hydroperoxide into phenol and acetone.

- distill: Acetone removed overhead, bottoms sent to vacuum column to remove cumene. Vacuum column bottoms sent to last column, where Phenol and acetophenone is separated.

Ammonia	NH_3	

General Notes

- Anhydrous NH_3 is colorless gas w/ pungent odor.
- NH_3 use tied to agriculture, also to demands for urea, aniline, and organic amines.

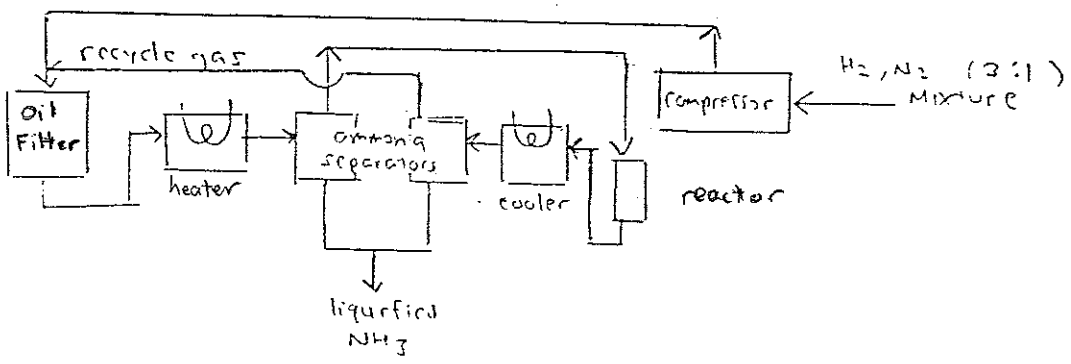
Usage

Fertilizer	78%
Industrial / Military	22%

Process - Haber Process

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(l)$$

85% yield



- Important => refer to processes for obtaining N_2 and H_2! In the above flow diagram, H_2 was made from an upstream natural gas reforming plant, hence the need for an **oil filter.** (removes dust, etc.)

- reactor: H_2-N_2 mixture compressed to 300 atm and joined by recycle stream to constitute reactor feed. T = <175°C from internal heat exchangers. Promoted iron oxide catalyst used.

- cooler: Reactor effluent cooled (-10°C to -20°C), causing some NH_3 to liquefy.

- separators: Some of the cooled NH_3 is **purged** to prevent diluent (Ar) accumulation. Purge gas = fuel. Remaining gas is recycled and re-compressed.

Vinyl-chloride	$CH_2=CH-Cl$	

General Info

- colorless, mobile liquid or flammable gas w/ pleasant, ethereal odor.
- only general end-use is for plastics; surpassed only by PE.
- It's the design project of 1994 University of Washington's Senior ChE class! Contact Daniel Chinn for specific questions.

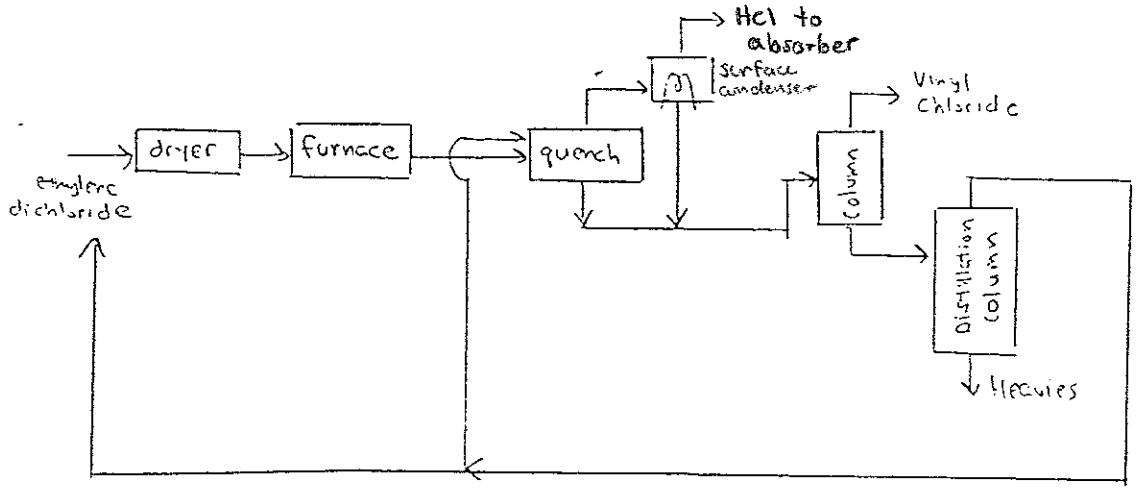
Uses (PVC)

flooring	14.5%	wires/cables	13.1%	records	5.5%
sheet	14.5%	extrusions	10.0%	slush	2.8%
adhesives	13.3%	film	5.7%	miscell.	20%

Process - pyrolysis of EDC

$$\begin{matrix} CH_2-CH_2 \\ | \quad | \\ Cl \quad Cl \end{matrix} \xrightarrow{\Delta} CH_2=CH-Cl + HCl$$

~95% yield



- Furnace: Dried EDC(g) heated in a furnace, 50 psig, 900-950°F, 50% conversion, 95-96% yield. Contact catalyst (charcoal) is packed in tubes.
- Quench: Hot furnace effluent cooled w/ EDC(l) recycle stream. Uncondensed gases sent to surface condenser, where condensables are sent to the columns and noncondensables scrubbed w/ H_2O to recover HCl.
- Separations: Combined liquid streams enter pressurized tower to yield vinyl chloride. Bottoms are sent to a still to separate heavy by-products and overhead EDC(l) for recycle.

Note: EDC is made from C_2H_4 and Cl_2 in a very exothermic rxn.

Sulfuric Acid	H_2SO_4	

General Data

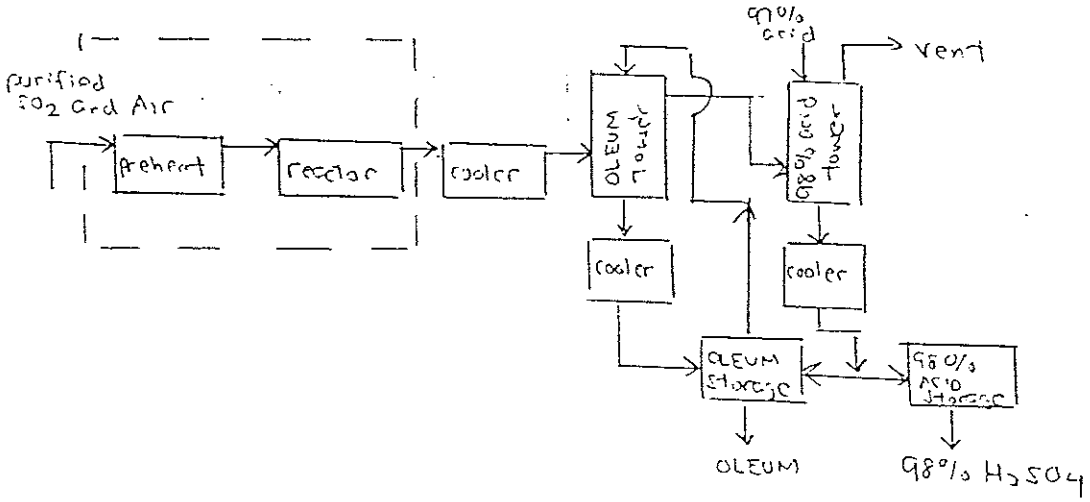
- Pure H_2SO_4 is a colorless, odorless, heavy, oily liquid.
- Widely used, H_2SO_4 industry is very static. Decrease in one use of H_2SO_4 is balanced by increase in another.
- can dissolve lots of SO_3, making "oleum!" when mixed with water, more H_2SO_4 is made.

Usage

Phosphate Fertilizers	30%	nonferrous metals	3.5%
Pigments	9%	aluminum sulfate	2.5%
Ammonium sulfate	6%	Other chemicals	9%
Iron/steel pickling	5%	Miscellaneous	33%

Process – contact process

$$2\,SO_2(g) + O_2(g) \leftrightarrow 2\,SO_3(g)$$
$$SO_3(g) + H_2O(l) \longrightarrow H_2SO_4(l)$$



- reactor: Pure, dry gas (7-10% SO_2, 11-14% O_2) heated and fed to a reactor. Temps around 500°C – 600°C for fast kinetics and later lowered to 400°C – 450°C for suitable keq. Catalyst is Pt or V_2O_5. Designs vary w/ each plant.

- oleum Tower: Gases cooled to 100°C and fed to internally cooled oleum tower. Tower is packed with quartz. Some SO_3 is absorbed onto the oleum. Gases then enter acid tower.

- 98% acid tower: Gases scrubbed with 97% H_2SO_4 in a cooled tower to make 98% acid. Acid purities below 97% cannot be used for scrubbing due to mist formation & SO_3 losses.

Sources of SO_2

- Burn sulfur (99.5% – 99.9% pure) w/ air
- From Iron pyrites (42 – 45% S)
- From Smelters
- Burn H_2S w/ special furnace

Urea	$H_2N-\overset{O}{\overset{\|}{C}}-NH_2$	

General Info

- White, somewhat hygroscopic crystals or powder, looks like sugar
- Production driven by demand for urea-formaldehyde resins. (fire retardents)

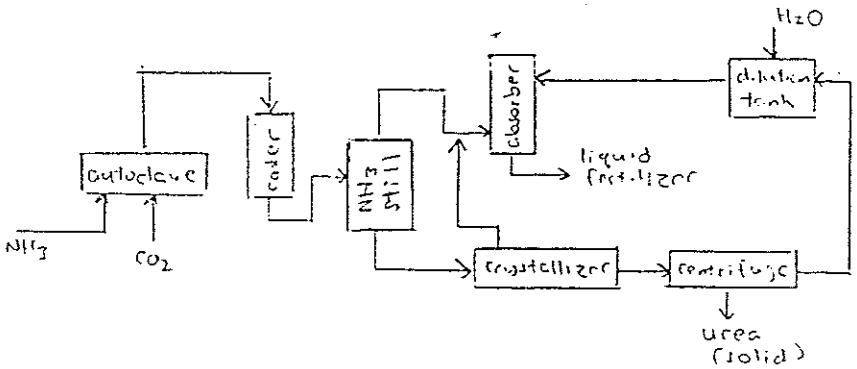
usage

solid fertilizer	47%
liquid fertilizer	34%
animal feed	12%
other, plastics	7%

Process - from NH_3 and CO_2

$$2NH_3(\ell) + CO_2(\ell) \rightarrow NH_2-\overset{O}{\overset{\|}{C}}-O-NH_4 \rightarrow H_2O + NH_2CONH_2$$

80% yield



- autoclave: NH_3 and CO_2 fed 3:1 compressed to liquids and charged separately in steam-heated, silver lined autoclave. T = 190°C, P = 1500 - 3000 psi. Reactants forms intermediate, and subsequently urea and H_2O.

- cooler: Reactor mixture cooled to 150°C.

- NH_3 still: T = 60°C, 60-65% unreacted NH_3 and CO_2 distilled and absorbed.

- crystallizer: Residue from NH_3 still cooled to 15°C. 70% remaining NH_3 removed by vacuum and sent to absorber.

- Centrifuge: Slurry from crystallizer centrifuged to separate crystalline urea. Material not centrifuged mixed with water and used as absorbent for NH_3 recovery system.

acetic acid	$CH_3\overset{O}{\overset{\|}{C}}-OH$	

General Notes

- colorless liquid w/ pungent odor, sharp acid taste.
- Vinegar for food industry made by fermentation.
- Industry driven by demand on cellulose acetate & solvents.

Usage

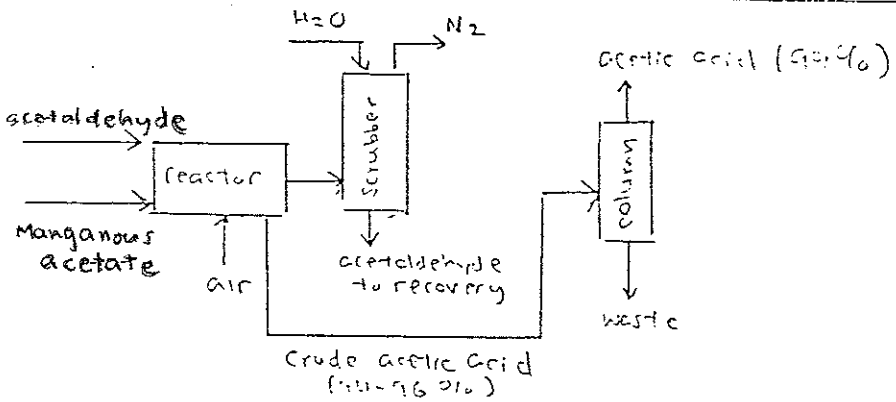
cellulose acetate	47 %
vinyl acetate	25 %
other esters	16 %
miscellaneous	12 %

Grades

glacial = 99.5 %
dilute = 36 – 37 %
technical = 80 %

Process - from acetaldehyde

$$CH_3-\overset{O}{\overset{\|}{C}}-H\,(l) + \tfrac{1}{2}O_2\,(g) \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-OH\,(l)$$



- **Reactor:** Air at 70–75 psi bubbled through 99–99.8 % solution of acetaldehyde and 0.1–0.5 % $Mn(CH_3COO)_2$. Manganous acetate needed to decompose explosive intermediate. Temp ~ 55° – 65°C. Reactors may be batch or CSTR's.

- **Scrubber:** Gases from the reactor are scrubbed w/ H_2O. N_2 is vented and the liquid is sent to recovery system.

- **Column:** Liquid phase from reactor is rectified to yield glacial acetic acid.

Alternate Processes

- Use mix of ethanol and acetaldehyde w/ catalytic air oxidation. Acetaldehyde is recycled, ethanol added as makeup. (∴ vapor phase alcohol oxidation to acetic acid)

- Use above process, but in a liquid acetic acid phase w/ Cobalt or Chromium catalyst.

- Catalytic oxidation of butane (lots of organic by-products)

benzene

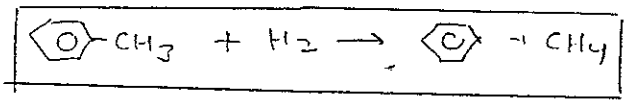
General Notes

- clear, colorless, flammable liquid. Smells NICE.
- Could be obtained from fractional distillation of light oil from gas and tar. Problem => need extensive seperations and benzene isn't always reagent grade.
- New processes include hydrodealkylation of petroleum / toluene.
- Production driven by demand for styrene, phenol, nylon, synthetic detergents.

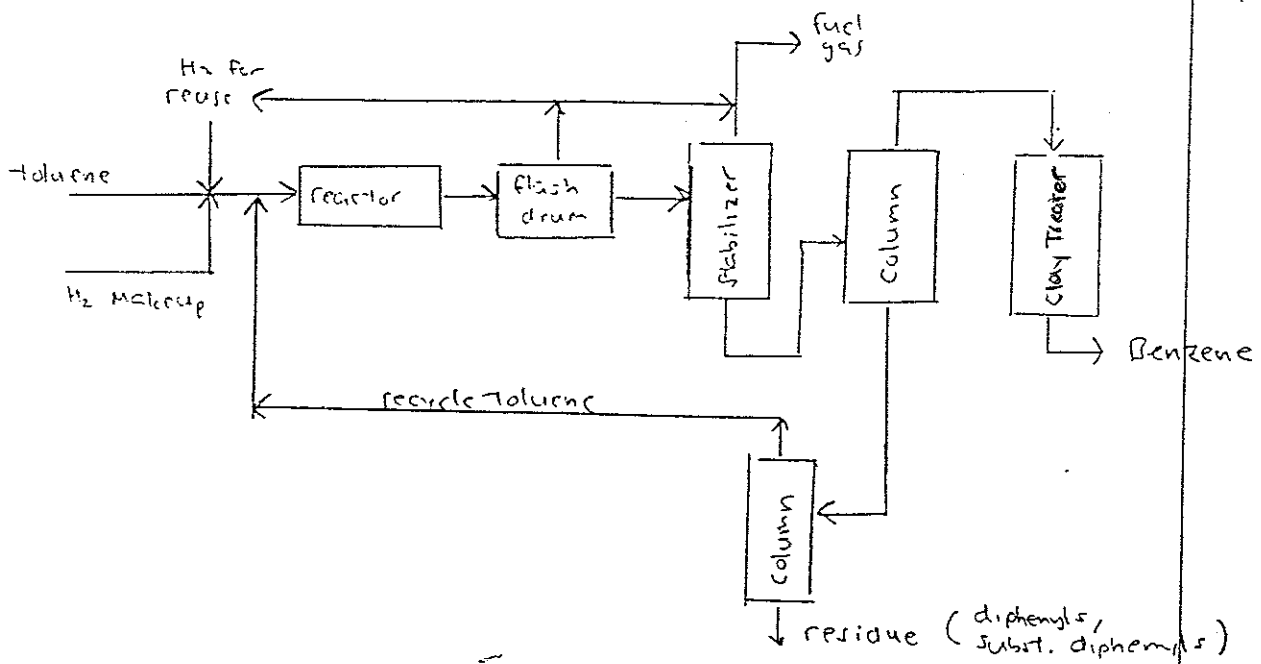
Usage

styrene	39%	cyclohexane	6%	chlorobenzenes	3%
phenol	18%	maleic anhydride	3%	aniline	3%
nylon	13%	DDT	3%	misc. & export	13%

Process - Hydrodealkylation of Toluene



96% selectivity



- Toluene & H_2 mixed, preheated to 1000 - 1200° F.
- Reactor P = 500-1200 psi, depending if rxn is thermal or catalytic.
- Flash drum reduces P, H_2 removed, fuel gas removed in stabilizer.
- Fractional distillation seperates out benzene. Benzene is treated w/ clay for stabilization.

Chlorine	Cl_2	

General Info

- Heavy, toxic green-yellow gas w/ pungent, irritating odor. Can be compressed to yellow liquid.
- Both Cl_2 and NaOH are as widely distributed industrially as H_2SO_4.
- Important to synthetic-organic-chemical industry.

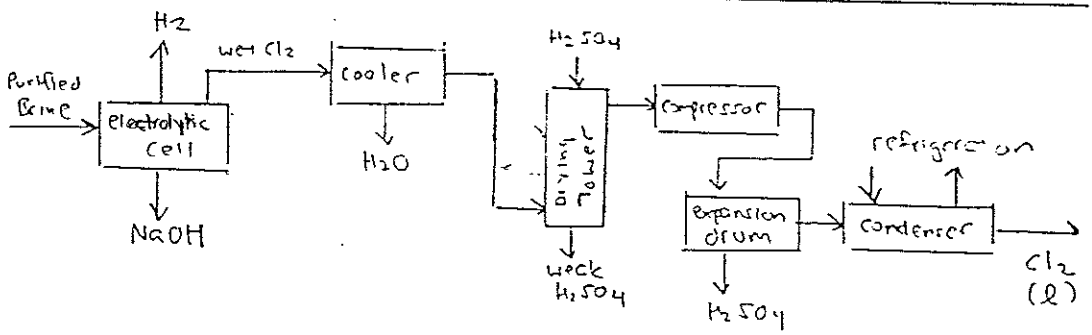
Usage

organic chemicals	65%	water and sewage	4%
Pulp / Paper	17%	Miscellaneous	5%
Inorganic chemicals	9%		

Technical Grade = 99.9%

Process – Salt Electrolysis

$$2NaCl(aq) + 2H_2O \xrightarrow{\text{direct current}} Cl_2(g) + H_2(g) + NaOH(aq)$$



- electrolytic cell – Hot $Cl_2(g)$ and H_2O vapor made at anode, H_2 at cathode.
- cooler – Gas temp reduced to 12-14°C, causing H_2O to condense.
- drying tower – Leftover H_2O removed by scrubbing with 66° Be' H_2SO_4. (Note dry Cl_2 may be contacted by metal).
- condenser – Dry Cl_2 is then compressed and liquefied (-30 to -45°C) using NH_3, CO_2, or Freon.

Note: the compressors create a partial vacuum that withdraws Cl_2 from the electrolytic cell.

ethanol	CH_3-CH_2-OH	

General Notes

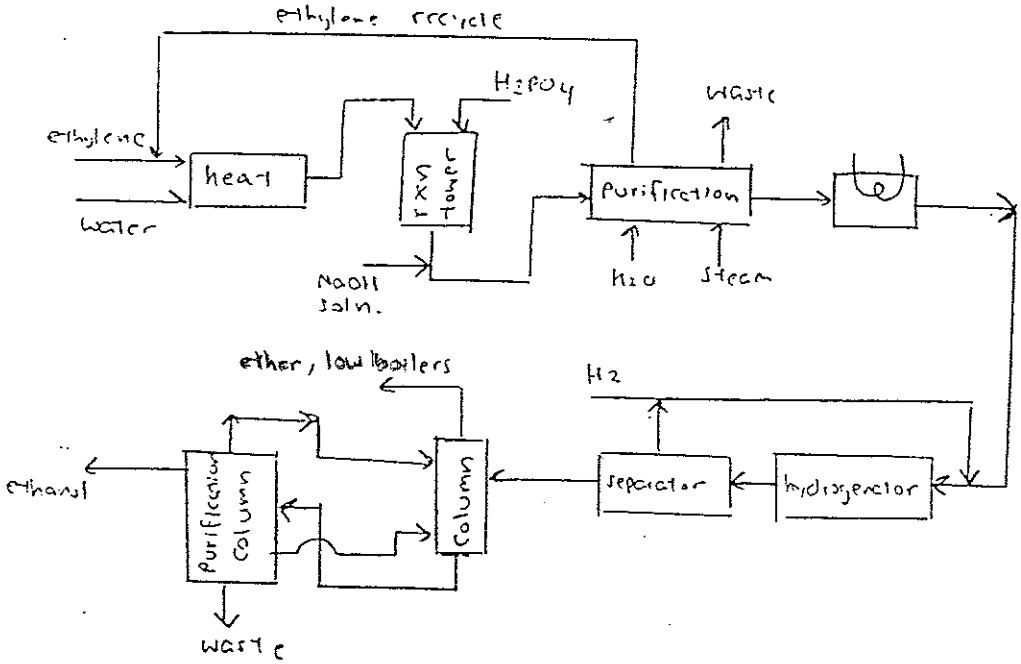
- Colorless, fluid liquid of characteristic odor.
- Although it could be made by fermentation, 91% of US industrial ethanol came from synthetic processes in 1963. Ethylene cheaper than molasses back then . . .

Usage

Acetaldehyde	40%
Other chemical use	23%
Solvents & misc.	37%

Process – Catalytic Hydration of Ethylene

$$CH_2 = CH_2 + H_2O \xrightarrow{H_3PO_4} CH_3CH_2OH$$



- Feed: Olefin (97% C_2H_4, w/ CH_4, C_2H_6, C_2H_2, other olefins) mixed with water (1 : 0.6), compressed to 1000 psig and heated to 570°F in a furnace.
- rxn tower: Mixture passed over catalyst impregnated w/ H_3PO_4. Conversion only 4.2% per pass. Effluent partially condensed by HXG.
- Purification: NaOH used to neutralize H_3PO_4 vapors.
  H_2O used to scrub gases and separate alcohol.
  Gases recycled and purged.
  Steam is added to stripping column; concentrated ethanol overhead, water as bottoms.

- hydrogenator : H_2 is added to convert acetaldehyde (from hydration of acetylene) into ethanol. Ni catalyst used.
- separator : excess H_2 removed by condensation in a product heat exchanger and separation in product accumulator.
- columns : Conventional concentration & purification of ethanol.

Polyethylene	PE	

General Notes

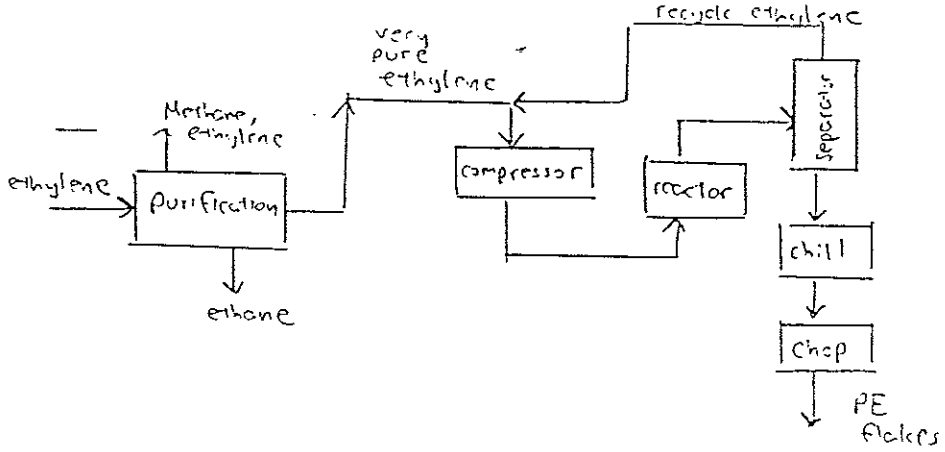
- Sold as 1/8" flakes, pellets, & powders. Specified as to use, viscosity, density, softening point.
- White, translucent solid. In thin sections, almost transparent.

Usage

film / sheet	33%
injection / blow molding	25%
coatings	10%
electrical	8%
miscellaneous	12%
export	12%

Process – High Pressure Polymerization (makes LDPE)

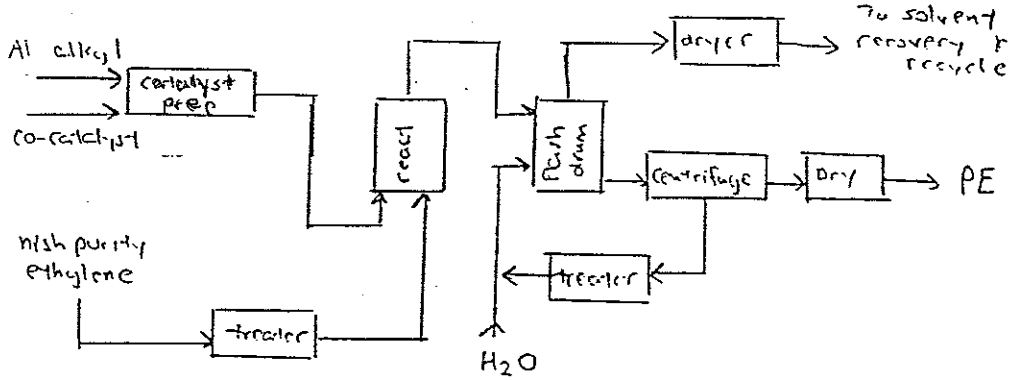
$$n\,CH_2=CH_2 \rightarrow \left(CH_2-CH_2\right)_n \quad \text{95\% yield}$$



- Purification: Fractionated of CH_4, C_2H_6. Compressed to 1500 atm, pumped to reactor. 600 ppm O_2 added to ethylene.
- reactor: PFR, peroxide catalyst. T ~ 375°F, very exothermic reaction. ≈ 25% conversion. Product is viscous, molasses like liquid.
- separator: O_2-free ethylene recycled back, strup chilled and later chopped into flakes.

Process – Low Pressure Polymerization (makes HDPE)

Rxn is the same!



- highly active catalysts used to make higher density PE. Mixed w/ dilute hydrocarbon soln. due to high flammability.
- ethylene mixed in, feed to reactor. T= 140–170°F, P= 100 psig.
- Effluent flashed (P= 3–5 psig, T= 150–160°F), separating polymer and solvent. H_2O cooled to destroy residual catalyst and to make PE slurry.
- Solvent is dried & recycled, slurry dried and centrifuged. Water goes back to the flash drum.

Sodium hydroxide	NaOH (caustic soda)

General Notes

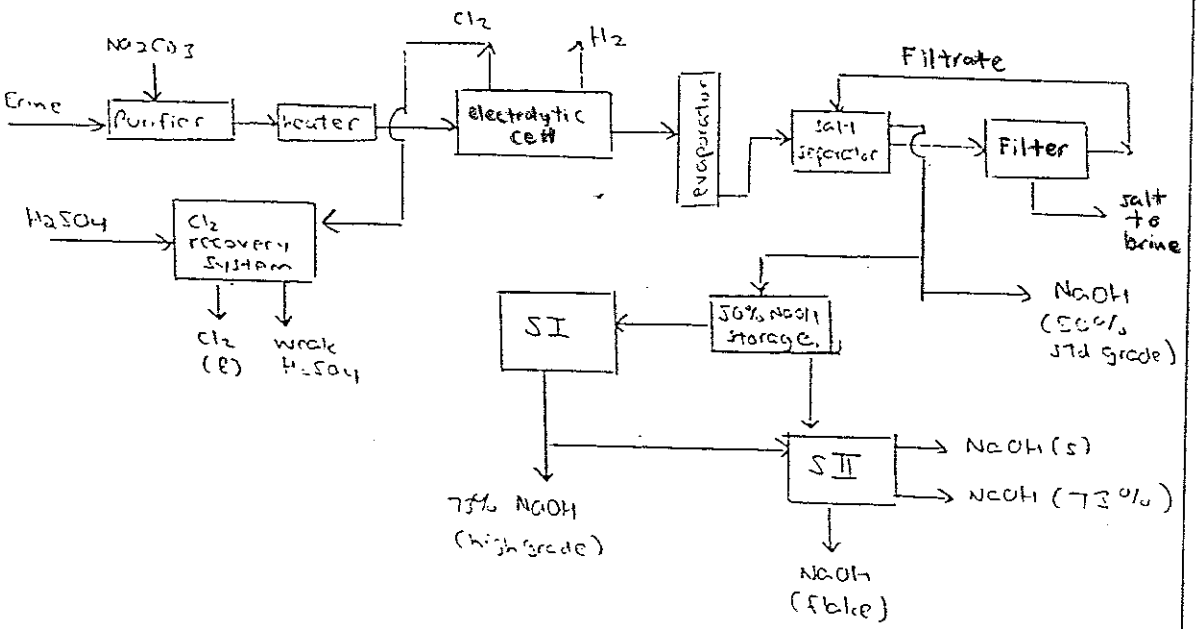
- White, deliquescent pieces, lumps, or sticks.
- Mostly made electrolytically due to Cl_2 demand.

Usage

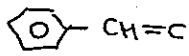
Chemicals	42%	Aluminum	6%	Soap/Detergents	4%
Rayon	12%	Petroleum	5%	Cellophane	3%
Pulp/Paper	10%	Textiles	5%	Miscellaneous	13%

Process – electrolysis of salt

$$2NaCl(s) + 2H_2O(l) \xrightarrow{\text{direct current}} 2NaOH(aq) + H_2(g) + Cl_2(g)$$



- Purification: salt from **natural sources** dissolved in water, heated, and **treated** w/ Na_2CO_3 to remove Ca^{2+} and Mg^{2+} compounds.
- electrolytic cells: H_2 **formed at cathode**, Cl_2 **at anode**, 10-12% NaOH solution left from salt brine decomposition.
- salt separator system: Colloidal iron is filtered
  Nacl and sodium chlorate removed w/ NH_3 in liquid-liquid diffusion tower. } $NaOH(aq)$ impurities
  Resulting 50% NaOH is sold or concentrated.
- "SI" sep system: Consists of an NH_3-purifying tower and single effect evaporator (75-100psi) to make 73% NaOH solutions.
- "SII" sep system: consists of fusion pots (500°C - 600°C) to boil off all H_2O. Molten caustic can be ~~treated~~ w/ S to precipitate Fe, and sold as solid caustic or sent to a flaker to make flaked caustic.

Styrene		

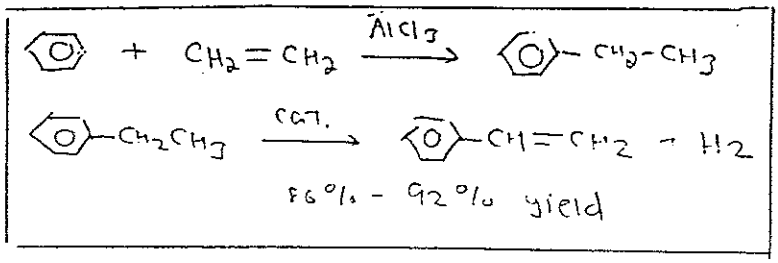
General Info

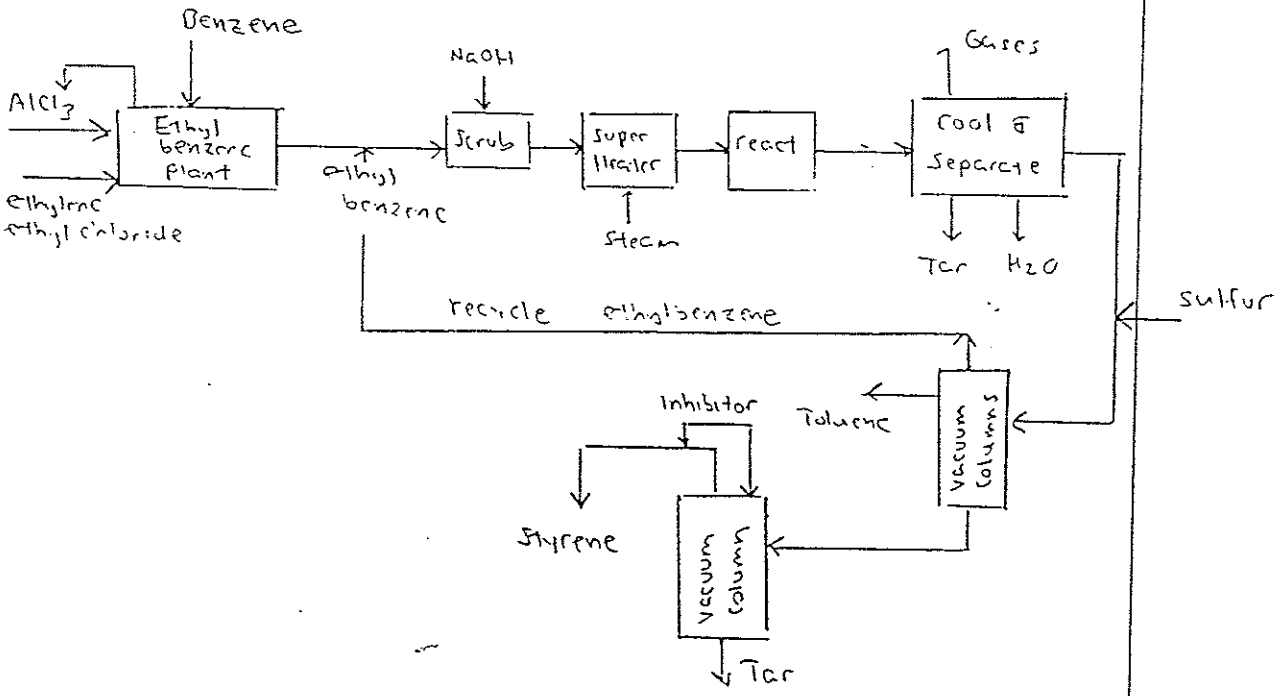
- Colorless to yellow, highly refractive oily liquid w/ characteristic aromatic odor.
- Growth of styrene dates from WW II to synthetic rubber demands. Currently, polystyrene is large outlet for styrene.

Usage

polystyrene	50%	Polyester	4%
S-B rubber	25%	Styrene Copolymers	2%
Latex	7%	Misc & Export	12%

Process: From Ethylbenzene





- Ethylbenzene plant: dry benzene & ethylene alkylated @ 1 atm w/ a promoted catalyst. Rxn = exothermic, cooling water needed to maintain T = 95°C. Effluent cooled to 40°C, about 80% catalyst separated & recovered, and recycled. (using settlers).

Effluent then washed w/ NaOH, ethylbenzene removed after extensive separation process.

- Superheater: ethylbenzene mixed with superheated steam, 710°C and fed to reactor.
- reactor: has fixed dehydrogenation catalyst (Zn, Fe, MgO) (eg) on activated C. T = 630°C, 35-40% conversion / pass.
- cool & separate: Effluent cooled to 105°C w/ spray cooler, tars condense. Second condenser liquefies steam, styrene, toluene, benzene; vent gases sent to recovery. Hydrocarbons removed by decanting.
- vacuum columns: Effluent mixed w/ sulfur to inhibit polymerization. benzene, toluene distilled @ 157 mm Hg, 57°C; benzene recovered. Styrene & ethylbenzene distilled @ 35 mm Hg and 90°C, ethylbenzene recycled. Another column removes tar and sulfur from styrene. Inhibitor added at top.

sulfur	S	

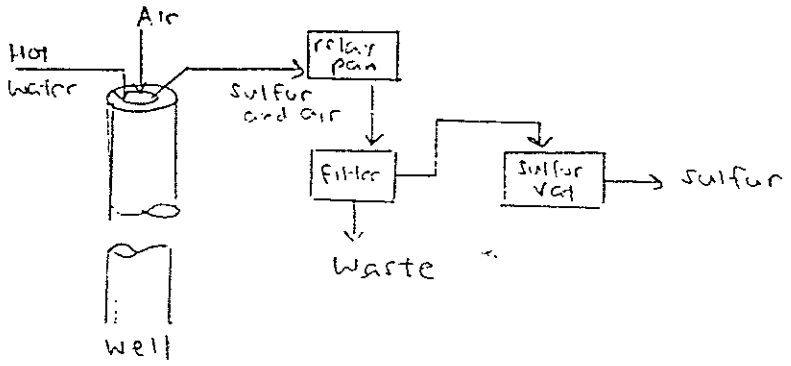
General Info

- Pale yellow, odorless, brittle solid w/ 2 crystalline forms.
- High quality deposits along Gulf coast of USA.
- 70% S used in USA comes from Frasch process.

Usage

sulfuric acid	66%
export	22%
other	12%

Process - From Underground Deposits by Frasch Process



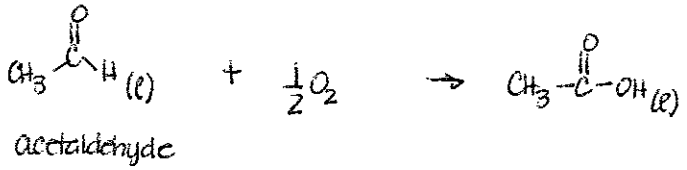
MINING

- Well: A well is drilled into sulfur-bearing deposit. Three strings of concentric pipe, perforated near the bottom is inserted.
- superheated water (325°F, 250 psi) pumped into well to melt sulfur.
- Compressed air forced down innermost pipe, so molten sulfur forced to the surface via annular space.

SEPARATIONS

- relay pan: Pans are fitted w/ steam coils in which air escapes.
- filter: Removes contaminants
- Vats: Made of solid sulfur (500,000 tons); molten sulfur is solidified and accumulated here.
- Finally, dynamite used to blast part of the block for shipping. (sulfur sold as lumps)

Acetic Acid

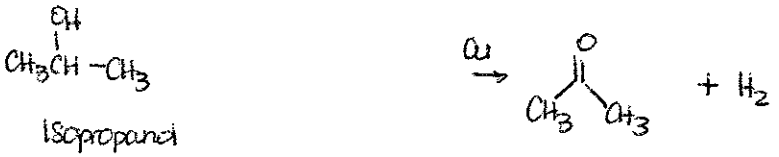


acetaldehyde

Formaldehyde

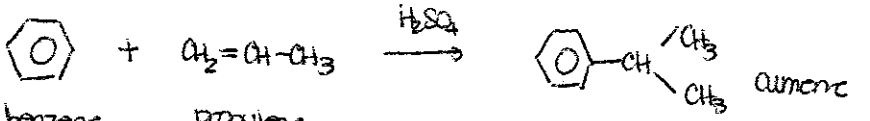
methanol

Acetone

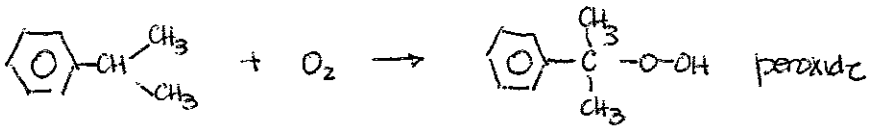


Isopropanol

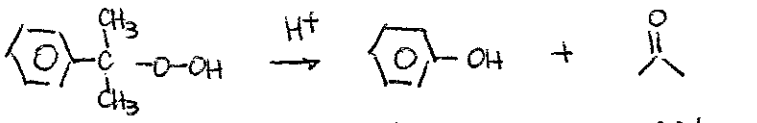
Phenol



benzene propylene cumene

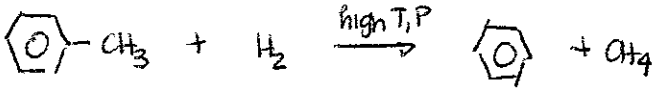


peroxide



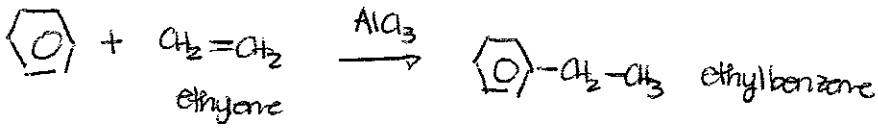
phenol acetone

Benzene

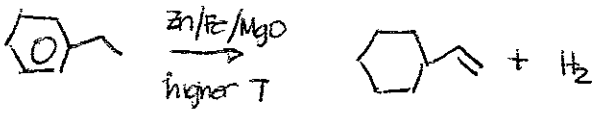


Toluene

Styrene



ethylbenzene



Styrene

Methanol

$$CO_{(g)} + 2H_{2(g)} \xrightarrow{\text{metal oxide}} CH_3OH_{(g)}$$

Ethanol

$$CH_2=CH_2 + H_2O \xrightarrow[\text{mod. high T}]{H_3PO_4} CH_3CH_2OH$$

ethylene

P

HCl

$$H_{2(g)} + Cl_{2(g)} \longrightarrow 2HCl_{(g)}$$

Nitric Acid

$$4NH_{3(g)} + 5O_{2(g)} \longrightarrow 4NO_{(g)} + 6H_2O_{(g)}$$ Pt-Rh catalyst

$$2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)}$$

$$3NO_2 + H_2O_{(l)} \longrightarrow 2HNO_{3(l)} + NO$$

Phosphoric Acid

$$2P_{(s)} + \frac{5}{2}O_2 \xrightarrow{\text{high T}} P_2O_{5(g)}$$

$$P_2O_{5(g)} + 3H_2O_{(l)} \longrightarrow 2H_3PO_{4(l)}$$

Sulfuric Acid

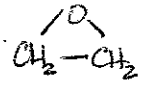
$$S_{(s)} + O_2 \longrightarrow SO_2$$

$$2SO_2 + O_2 \xrightarrow{Pt/V_2O_5} 2SO_3$$

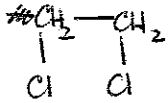
$$SO_3 + H_2O_{(l)} \longrightarrow H_2SO_{4(l)}$$

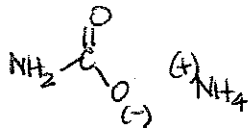
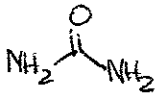
Hydrafluoric Acid $CaF_{2(s)} + H_2SO_{4(\ell)} \longrightarrow H_2F_{2(g)} + CaSO_{4(s)}$

Hydrogen Cyanide $2NH_3 + 2CH_4 + 3O_2 \xrightarrow[\text{high T, low P}]{Pt} 2HCN_{(g)} + 6H_2O$

Ethylene Oxide $CH_2{=}CH_2 + \frac{1}{2}O_2 \xrightarrow{Ag}$  $+ CO + H_2O$

Polyethylene $\left(CH{=}CH\right)_n \xrightarrow[cat.]{\text{Peroxide}} \left(CH_2{-}CH_2\right)_n$

Vinyl Chloride ~~Styrene~~  $\xrightarrow[\text{high T, mod.}]{\text{charcoal}} CH_2{=}CH{-}Cl + HCl$

Urea $2NH_{3(\ell)} + CO_{2(\ell)} \longrightarrow$  $\longrightarrow H_2O +$ 

Sulfur — Frasch Process

Ammonia $N_2 + 3H_2 \xrightarrow[\text{mod. high T}]{\text{high P}} 2NH_3$ Haber Process

H_2

Hydrogen

$C_3H_8 + 3H_2O \xrightarrow{\text{high P, T}} 3CO + 7H_2$ gas rxn

$3CO + 3H_2O \xrightarrow{FeO_2} 3CO_2 + 3H_2$ "

Chlorine

Sodium Hydroxide

$2NaCl + H_2O_{(l)} \xrightarrow{\text{current}} 2NaOH + Cl_2 + H_2$