

## Sulphuric acid $\rightarrow$ Reigel's Handbook

Ullmann's  
4

\* Largest volume chemical manufactured in the world.

\* Consumption cited as an indicator of its economy

\* World Production  $\sim$  230 million tons.

Africa 15%,  
Asia - 35%, North America - 24%,  
Western Europe - 10%, Russia & Eastern Europe - 18%.

Properties: 100%  $H_2SO_4$ , m.p. = 10.4°C  
b.p. = 299.6°C

Colorless, viscous liquid, colourless,

Oleum is formed by dissolving

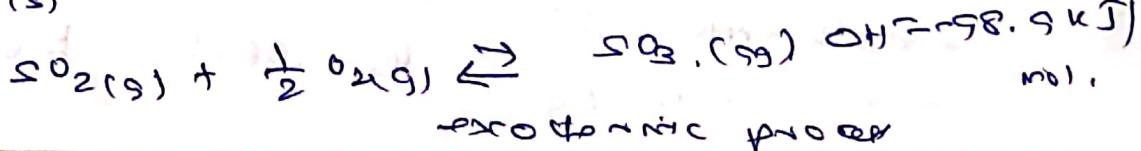
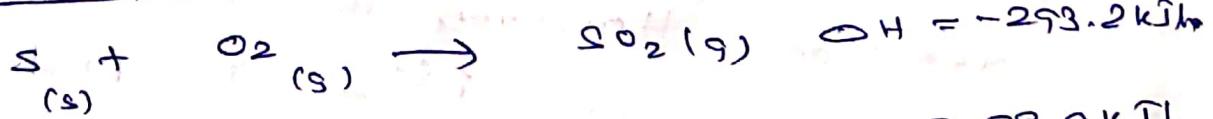
$SO_3$  in  $H_2SO_4$  (20% Sulfuric acid)

Applications: Fertilizers, dyes, plastics,  
(77%)

Pharmaceutical products, petroleum refining,

etc.

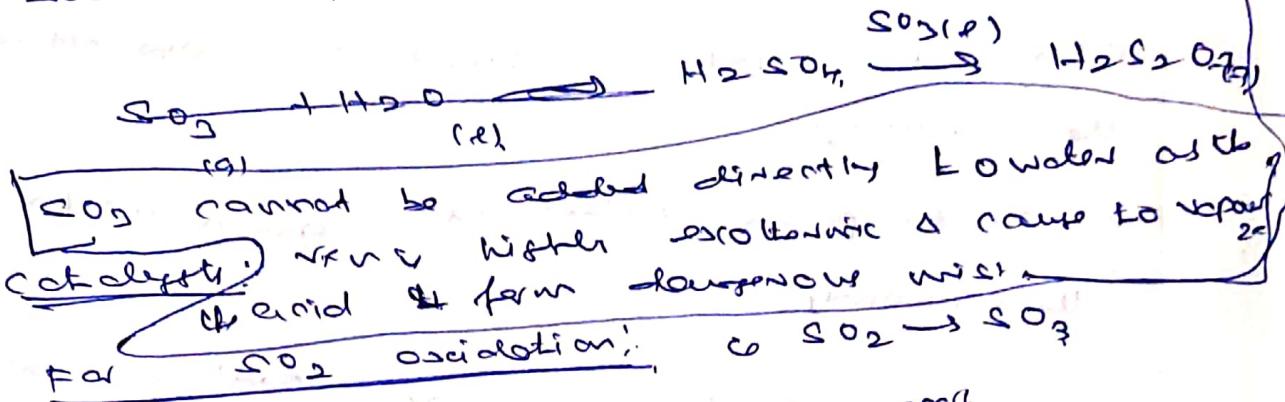
Combining:



Exothermic process

To avoid this,  $\text{SO}_2$  is dissolved in  $\text{H}_2\text{SO}_4$  then diluted with  $\text{H}_2\text{O}$

\* Raw Sulfur is unpaired from Scandinavia, Iran, Russia etc.



\*  $\text{H}_2\text{S}_2\text{O}_7$ ,  $\text{Na}_2\text{SO}_5$  or

Zeolite etc.

\* Alkali promoted.

Alkali promoted

\* operation temp  $410-440^\circ\text{C}$

\* In late 1960's, calcium-promoted

catalysts were introduced which are more active & reaction  $\leftarrow 360-400^\circ\text{C}$ .

### at evaporation:

\* At low temp, the yield would be very high, but the rate is very less.

\*  $\uparrow$  in  $T$  increase in the rate of reaction. However, the forward reaction is exothermic, so  $\uparrow$  in  $T$  pushes the equilibrium to the left to absorb the

the heat &  $\downarrow$  the yield.

\* High T can also damage the catalyst.

### Nitration:

\*  $T^{\text{opt}}$  in pressure pushes it to equilibrium  
to the right but low pressure equipment cost  
will be more,  $11-2$  (atmos) is preferred

Excess  $\text{O}_2$ : Also pushes it to equilibrium  
to the right field. However  
to stoichiometric  $\text{O}_2 : \text{NO}_2 \approx 1:2$ .  
1:1 ratio used.  
In the industry

Processes: ① Chamber process

② Contact process. (patented in 1881)

### Contact process:

① Production of  $\text{SO}_2$ :

### Sources of Sulfur:

① Elemental S from mines.

\* Supply of S is more than demand

② S from Claus process  $2\text{H}_2\text{S} + \frac{3}{2}\text{O}_2 \rightarrow \text{S} + 2\text{H}_2\text{O}$   
Produced by burning part of  $\text{H}_2\text{S}$ .

① From iron pyrite or PbS.

At consumption reduced

because of environmental neglect

flow sheet:

Oxidation of  $\text{SO}_2$

Done in multi stage - fixed bed

catalytic converters with interactor

boilers or heat exchangers to remove

heat of  $\text{NaNO}_3$  interaction

in single vertical 4 stages

\* typically 4 stages, 4<sup>th</sup> stage columns

\* catalyst dust formed during

operation separation in high sp. I

periodical catalyst demand

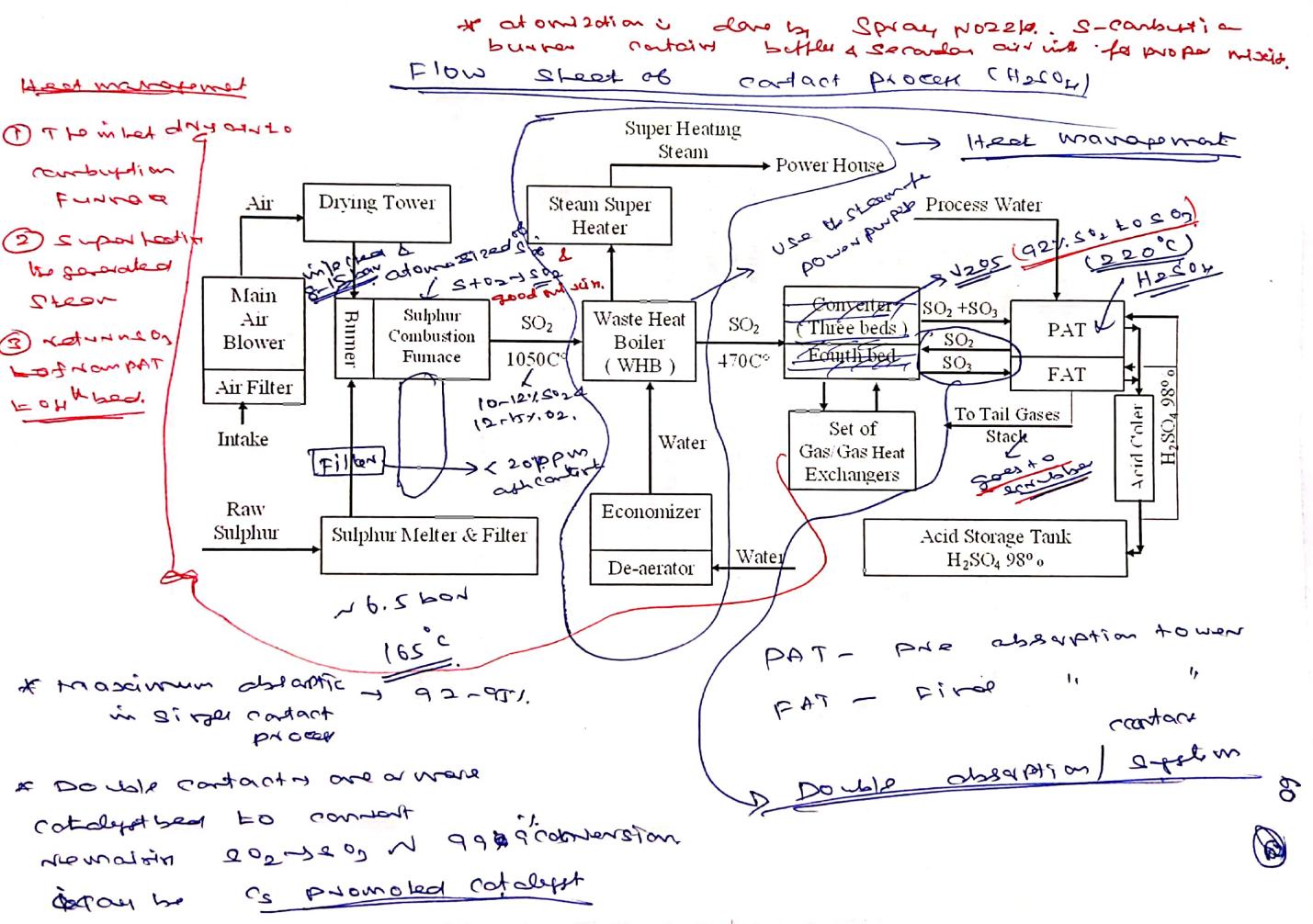
\* ring shaped catalyst large lower

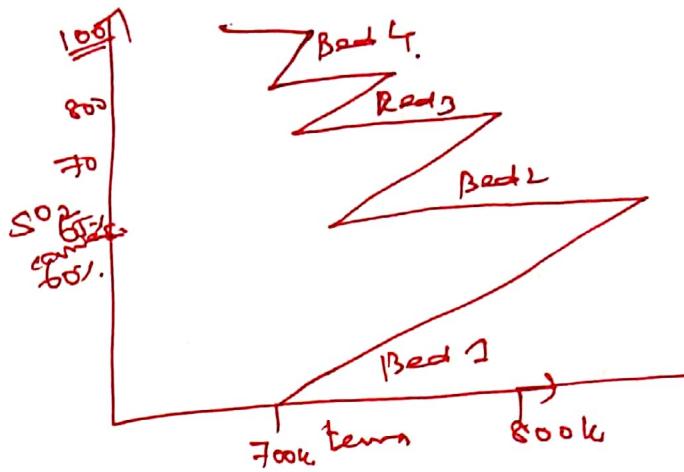
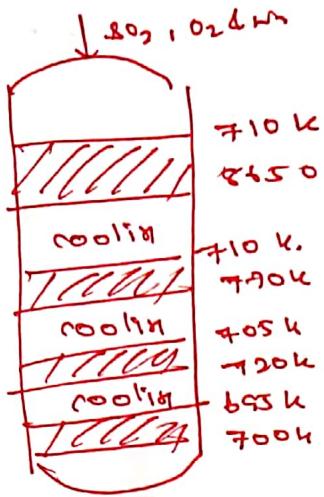
dust & presence droplets

Absorption of  $\text{SO}_3$ :

\* product gas u nobled to  $180-220^\circ\text{C}$

\* absorbed 98 w.t % of  $\text{H}_2\text{SO}_4$  v circulated





(+) Sulphur temp should be kept 410-425K.

Why?  
Harding & transpiration is easy because  
the viscosity is less. A

(8) Life of V - catalyst.

First bed - 3 years.

Second -  
Third & Fourth - 10-15 years.

Degeneration due to breakdown of catalysts  
catalyst aging  
catalyst poisoning

### Questions

Why  $\uparrow$  in temperature & also  
not preferred?  $\rightarrow$  60 a

see next page  
 $SO_2 \rightarrow SO_3$

- (1) Catalytic conversion done. But  $\uparrow$  in the temperature decrease the yield of  $H_2SO_3$ . Why & How can it be circumvented?  
 \* Due to equilibrium shift towards left with cooling at evaporation stage.
- (2) Why  $SO_3$  removal is double contact process?

removal  $SO_3$  shift in equilibrium towards minimize  $\downarrow$   $SO_2$  concn  
right hand side

- (3) answer question the best of reaction  
yes, it is used to generate for

$SO_3$  is not directly dissolved

- (4) Why  $SO_3$  is not  $H_2SO_4$ ?  
 $H_2O + SO_3 \rightarrow H_2SO_4$ ?  
 It is exothermic reaction  
 heat of mist will be formed  
 break up.  $SO_3$  with dilution in  $H_2SO_4$   
 dilute with  $H_2O$   
 to form oleum the process is preferred)

- (5) Why double contact

- (6) How mist can be broken  
 Do not allow  $\rightarrow$  contact of bed of glass beads, or teflon fibers  
 smaller diameter or

(61) ~~Q~~  
Coulon

- \*  $\text{SO}_3$  is present in towers in current Eo & sprayed coolers conc  $\text{H}_2\text{SO}_4$  &  $\text{SO}_3$  is absorbed by the acid to give steam.
- \* Steam is diluted in  $\text{H}_2\text{O}$  to produce  $\text{H}_2\text{SO}_4$  which is reinsulated in contact with steam.
- \* Absorption efficiency  $\rightarrow 99.9\%$
- \* Mist  $\downarrow$  eliminate  $\rightarrow$  placed on the top of Eo breaks the mist  $(\text{SO}_2) \xrightarrow{\text{H}_2\text{O}_2} \text{H}_2\text{SO}_4$ .
- \* Tail gas  $\xrightarrow[\text{Acid storage tank}]{} \text{carbon steel}$ .

### Chlor-Alkali Industry

2008-09

- |                                       |               |                |
|---------------------------------------|---------------|----------------|
| Soda ash ( $\text{Na}_2\text{CO}_3$ ) | $\rightarrow$ | 1, 985, 045 MT |
| Caustic soda ( $\text{NaOH}$ )        | $\rightarrow$ | 2, 050, 030 MT |
| Chlorine ( $\text{Cl}_2$ )            | $\rightarrow$ | 1, 402, 847 MT |

Soda ash: Tatari stone salt  $\rightarrow$  not larger  
Mol. Wt. + 106, M.P. 85°C, br.P. + decomposition

method of production: ① naturally available  
deposit

② solvay or ammonia  $\xrightarrow{\text{soil}}$  de process

### uses:

- ① Glass manufacture
- ② Water softener,
- ③ Rustic soda, cleaned, soap,  
pulp & paper.

### solvay process:

- \* Raw material: Salt, coal and limestone
- \* Perfected by Ernest Solvay in 1865.
- \* Based on precipitation of  $\text{NaHCO}_3$   
When an ammoniacal solution of  
NaCl & carbonates with  $\text{CO}_2$
- \*  $\text{NaHCO}_3$  calcined to produce  
 $\text{Na}_2\text{CO}_3$ .

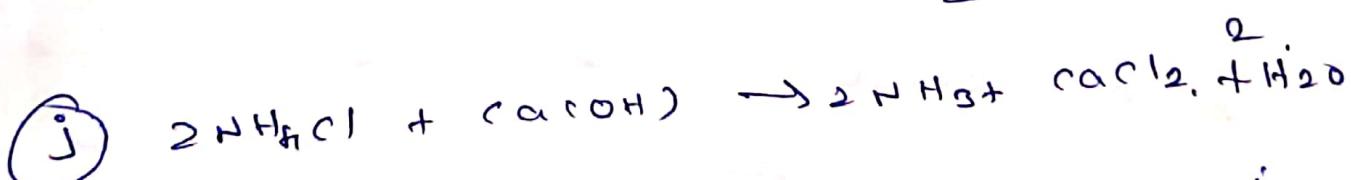
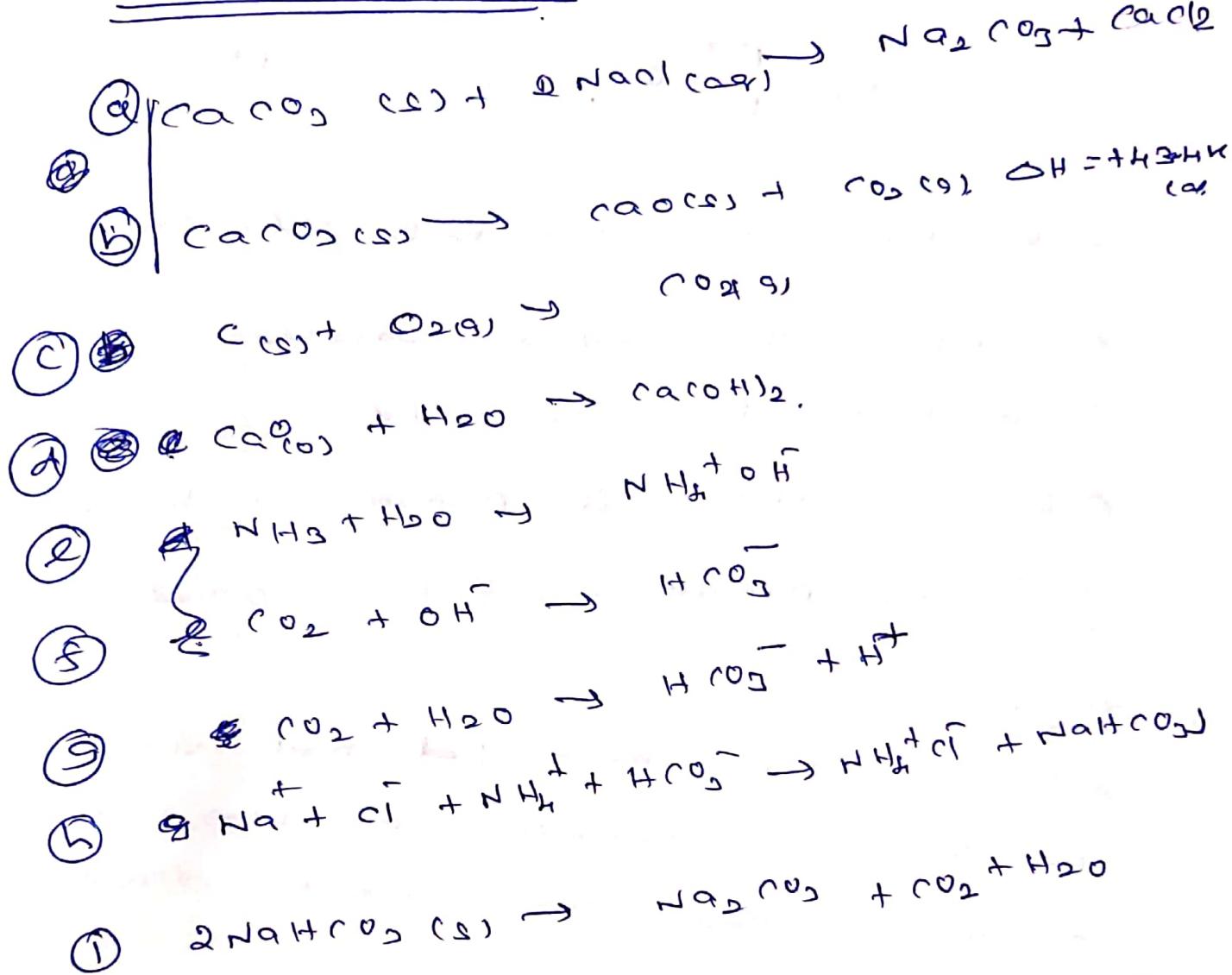
- ④ What is coming out of rotating filter  
 $\text{NaHCO}_3 + \text{NH}_4\text{Cl}$ .
- ⑤ How  $\text{NH}_4\text{Cl}$  is converted into  $\text{NH}_3$  & what  
 $2\text{NH}_4\text{Cl} + \text{CaO} \rightarrow 2\text{NH}_3 + \text{CaCO}_3 + \text{H}_2$   
 in combined  $\text{NH}_3$  still.
- ⑥ What is the role of lime kiln?
- ⑦ What are the challenges?  
 ⑧ Adsorption unit: Donor & acceptor group  
 $\text{NaHCO}_3$  attach. / It should be easily  
 washable. Scale should be removed  
 red incrustation will be affected  
 otherwise
- ⑨ Filtration unit: Define shows in case  
 filter & solid calc.  
 enhanced options
- ⑩  $\text{NH}_3$  recovery  
 cost is high  
 because

(65) a

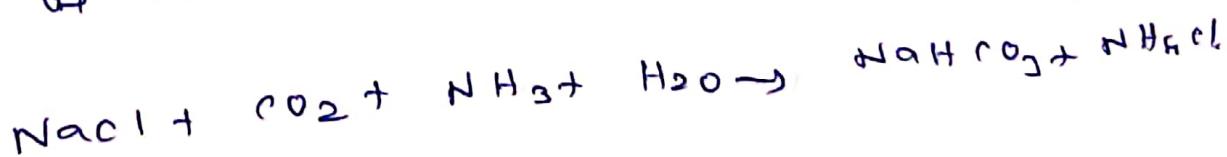
Questions

- ① Why do we need to purify the lime  
to remove calcium carbonate  
ppt along with  $\text{Na}_2\text{CO}_3$ .
- ② How do you purify lime.  
A solution of soda ash & caustic is added to ppt the  $\text{Ca}^{2+}$  as  $\text{CaCO}_3$  & rest of  $\text{NaOH}$   
Impurities are removed as floccules  
in a settler.
- ③ Why do we need to ~~add~~<sup>add</sup>  $\text{NH}_3$  followed by carbonation  
to lime fines  
otherwise,  $\text{Na}_2\text{CO}_3$  will not ppt.
- ④ How  $\text{CO}_2$  is generated  
 $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$   
need to cool the reaction mixture
- ⑤ Why do we often ammonia town.  
NH<sub>3</sub> in lime is a soluble  
reaction. Thus cooling & release  
of ammonia leads to removal of  
soluble part in & cooling soil of  
carbonation town.
- ⑥ How do we sand hot ammonia  
and convert it to  
 $\text{NH}_4\text{CO}_3$  and  
 $(\text{NH}_4)_2\text{CO}_3$  and  
lime reacts with  $\text{CO}_2$  to form  $\text{Na}_2\text{CO}_3$ .

One oil reaction



key to the products should occur in  
the order shown



$\text{NH}_3$  thrown  
down  
down

Bottom first, ~~down~~ bottom absorbed  
pH  
 $\text{CO}_2$ ,  $\text{NaHCO}_3$  ppts out.  
 $\text{NH}_3$  then

\* Reaction must occur in the order shown

\* First  $\text{NH}_3$  must be absorbed in  
brine first then  $\text{CO}_2$  added.

Otherwise  $\text{NaHCO}_3$  is prepared and brine  
added, no precipitation of  $\text{NaHCO}_3$  occurred.

### Process:

\* Prior to brine feed, well brine  
purified to remove  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions  
otherwise there can precipitate during  
carbonation

\* A solution of soda ash and  
caustic is added to precipitate the  
 $\text{Ca}^{2+}$  as  $\text{CaCO}_3$  and  $\text{Mg}^{2+}$  as  $\text{Mg(OH)}_2$ .  
Impurities are removed as flocculates  
in a settler

- \* Purified  $\text{NH}_3$  drives up pumped  $\text{CO}_2$ - $\text{H}_2\text{O}$
- \*  $\text{NH}_3$  absorbed (sparked) water at dissolved  $\text{NH}_3$  with liberation of heat (reaction e). Some  $\text{CO}_2$  also dissolved in the tower.
- \*  ~~$\text{NH}_3$~~  Ammoniated partially carbonated  $38^\circ\text{C}$ . (Typical)
  - Brine is cooled to shows that  $\text{NH}_3: 90\%$ ,  $\text{CO}_2 = 40\%$ ,  $\text{NaOH} = 26.9\%$ )
  - This is pumped to the carbonator tower that runs on cooling duty.
  - It must all be maintained to a point
  - This is carbonated just short of crystallization
- \* Carbonating towers: 22-23 m high, 1.8-2.5 m diameter
- \* Tower gradually becomes fouled as bicarbonate cakes on the cooling surface,

- \* Liquor from calcining tower A passed through a series of 4 to 5 remaining towers in a production line.
- \* towers generally as make part of cycle for 3 days & cleaning portion of 12 h.
- \* In the washing portion of tower, raw limestone kiln gases and injected rich  $\text{CO}_2$  gas from the bicarbonated calcium are decomposed and pumped to the bottom of the tower.
- \* In the make towers reaction first takes place.
- \* Solids from rotary filter calcined at  $200^\circ\text{C}$ .
- \* Daily production rate  $\sim 200 \text{ ton/day}$  of ~~lime~~ finished soda.

(64)

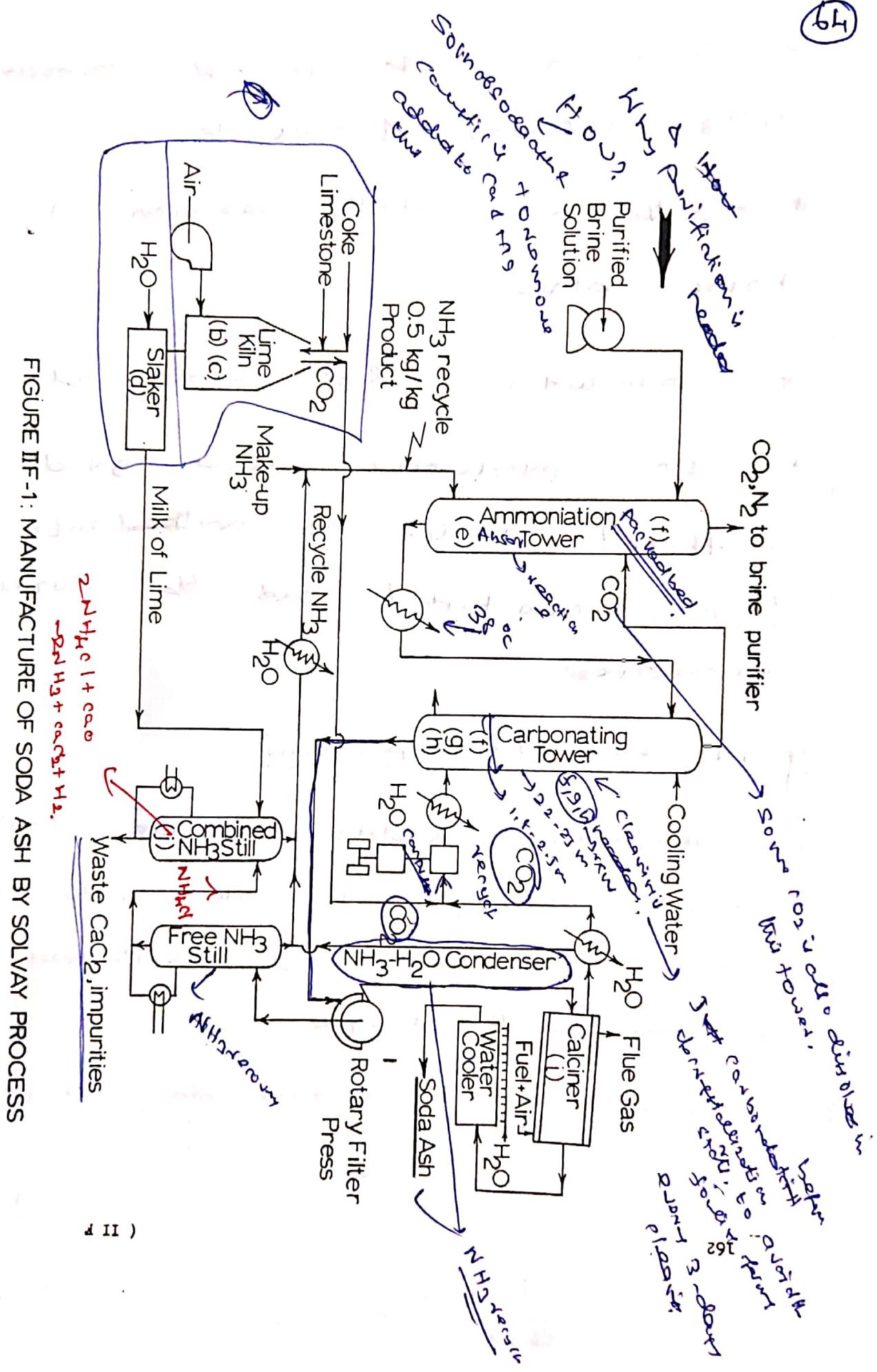
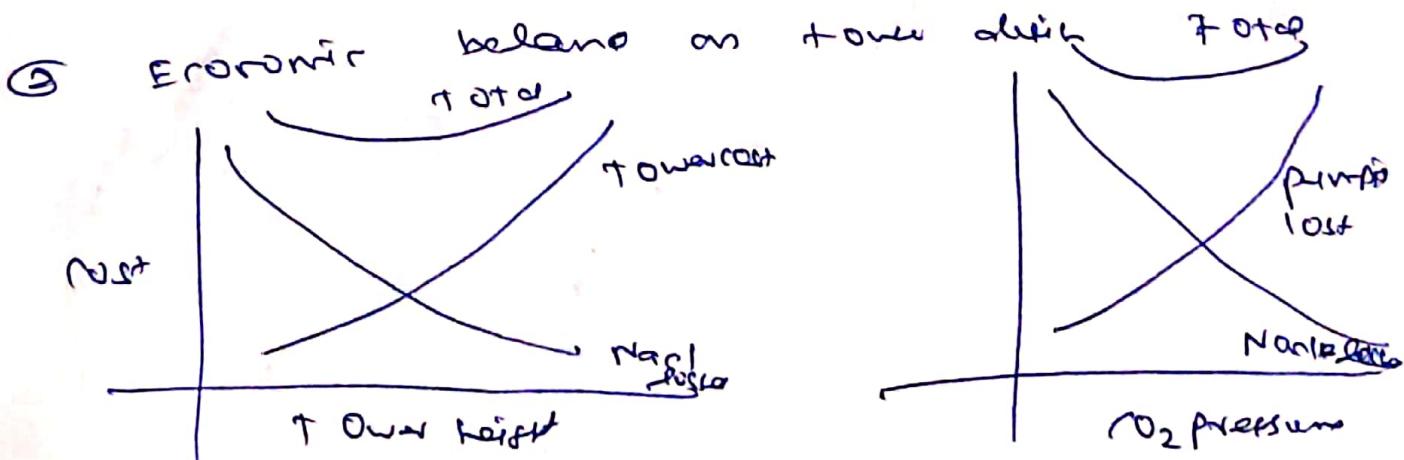


FIGURE II-F-1: MANUFACTURE OF SODA ASH BY SOLVAY PROCESS

- \* Rest of the process concerns  $\text{NH}_3$  recovery & recycle.
- \* In the lime still, reaction takes place.
- \* Product is light soda ash
- \* For production dense soda water is withdrawn into sufficient water to form more hydrate and the ammonia recycled.

### Major engineering problems:

- ① Development of suitable calcining equipment  
 → moist  $\text{NaHCO}_3$  will cake on the side of kiln, reducing heat transfer. must be equipped with scraper



③ NH<sub>3</sub> recovery:

NH<sub>3</sub> was expensive after Na<sub>2</sub>P<sub>3</sub>O<sub>6</sub> environment. now

④ Waste disposal → large amount of  
CaCO<sub>3</sub> must be disposed off.

Fuel and Industrial gases

\* Used for fuel and for synthesis of  
important inorganic and organic chemicals  
compounds

\* Sources - Coal, natural gas, petroleum

Types of gas:

①

## Steam cracking of hydrocarbons

- ① Used to produce light olefins (C<sub>2</sub>, C<sub>3</sub>, C<sub>4</sub>, 10%) & BTX from hydrocarbons.
- × Provides raw material for petrochemical industry
  - × Naphtha or LPG hydrocarbon feed is diluted with steam & heated in furnace without the presence of oxygen.

### Feed Stock

Ethane - propane mixture

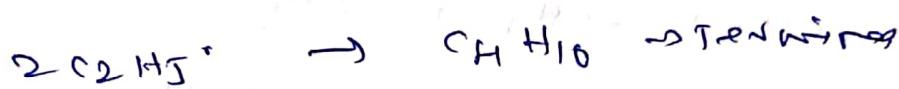
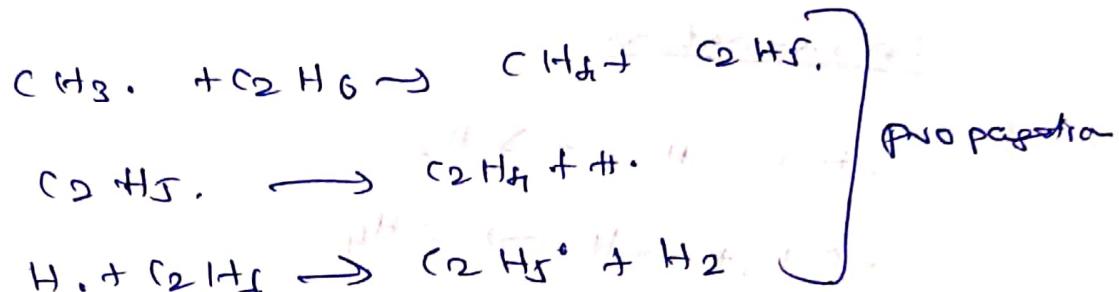
or naphtha

### Indian Scenario

I PCL vadodara	naphtha	130,000 TPA ethylene
RIL - Harsina		75,000
<del>I PCL -</del>		63,000
HPCL, Andhra		40,000
Haldia petrochemical		55,000
I OCL Panipat		80,000 TPA ethylene
Productions	ethylene	2008-09 - 2.64 x 10 <sup>6</sup> <u>T PA</u>

(66)

Chomistry Free radical mechanism, hundreds  
of simultaneous reactions

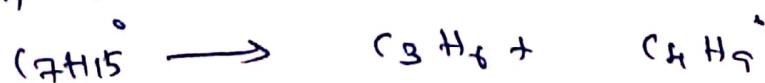
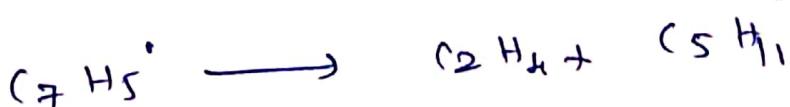
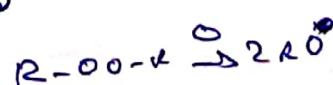


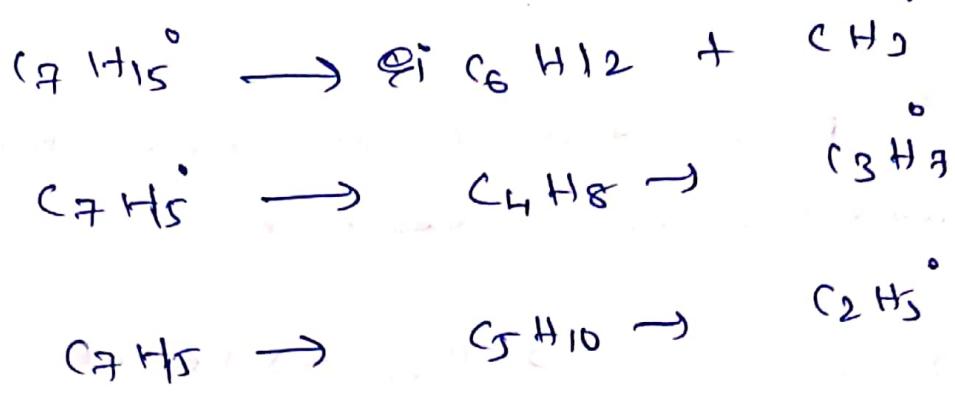
than the parent  
products larger also be formed  
molecule can



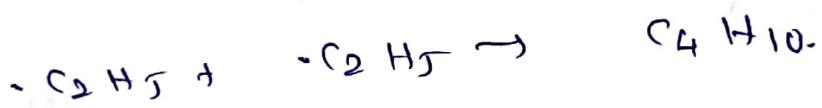
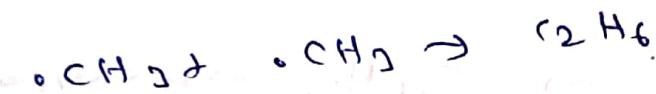
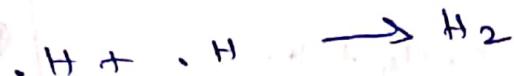
$\beta$ -Scission'

Free radical one formed upon splitting  
the carbon-carbon bond.





### Termination



Processes in the one five steps  
involved in the processes

① Steam cracker: Pyrolysis is happening  
in this section. Which is the heart of  
the plant. Removing sections and to  
separate the products

\* Steam is injected into the HC  
feed. The typical ratio is 0.3 kg/m  
for ethane. 0.5-0.8 for propane.

# Ethylene Production

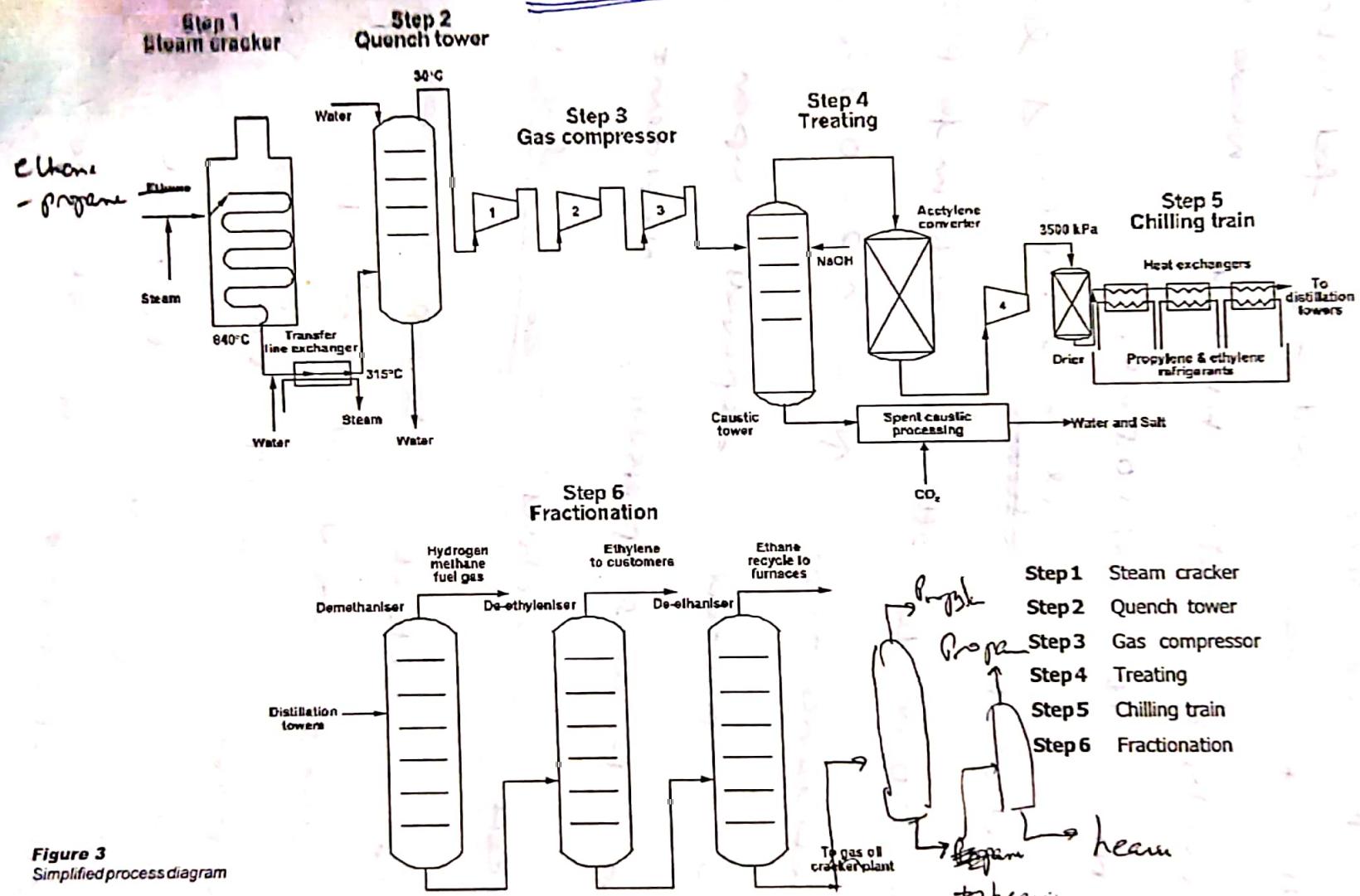


Figure 3  
Simplified process diagram

- \* Feed stocks are generally preheated to avoid external heat loss. Preheat Temp:  $550 - 700^{\circ}\text{C}$ .
  - \* HC + steam mixture is fed into the reactor.
  - \* Pyrolysis coil which is made up of ceramic at  $\sim 105^{\circ}\text{C}$ . coil  $\sim 2\text{-}4$  inch. in length.
  - \* id of the reactor tube is  $\sim 90$  mm for ethane. N for propane is  $60$  mm.  $N = 0.2 - 0.65$ .
  - \* Residence time depends upon Temp, process variables, and partial pressure.
  - \* The outlet temp of cracked ethane is  $\sim 85^{\circ}\text{C}$  for propane and  $\sim 97.0 - 800^{\circ}\text{C}$  for naphtha.
  - \* Conversion is typically  $60\%$ . Uncracked ethane/propane is recycled.
- process variables: See later page.

## (b) Quenching process for the transtition

(68)

- \* Reactor cracked products are rapidly generated in the transition line exchangers.
- \* The temp is dropped from  $400^{\circ}\text{C}$  to  $\sim 350 - 400^{\circ}\text{C}$  for naphtha pyrolysis & EO about  $\sim 300^{\circ}\text{C}$  for ethane pyrolysis.
- \* Why quenching is needed?  
In order to avoid stop the further cracking reaction & preventing coke formation in the heat exchangers.

## Quenching Tower:

The product from sent to a quench tower & get cooled to  $30^{\circ}\text{C}$  by direct contact with water.

### ③ Gas compression:

- \* The products has to be liquified for distillation.
  - \* For this gas needs to be compressed.
  - \* Compressor (First & 2nd) by unit centrifugal
  - ~~2nd~~ <sup>1st stage</sup> ~~interstage~~ with compressors
  - Cooling is used
- ### ④ Acid gas removal:
- \*  $H_2S$  &  $CO_2$  is formed during cracking process.
  - \* This has to be removed at between 1 to 2 stages in compressor because the location is preferred.
  - \* This gas volume is considerably reduced at the end of 2nd stage, while acidic components are still present in the gas phase.

(69)

\* Removed in a Caustic tower

using dilute NaOH (8-12%)



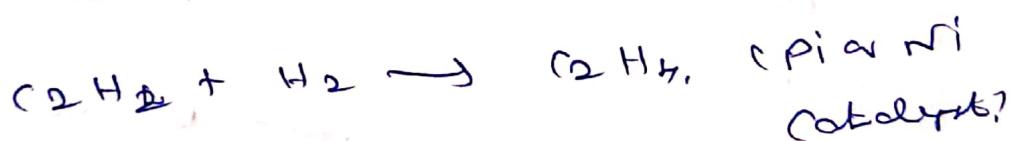
spent caustic is discharged  
after treatment.

\* Hoses leading to scrubber  
contain  $< 1 \text{ ppm}$  acid gases.

(5)

~~Acid Acetylene removal~~

Removal of Acetylene by hydroperoxide  
 $\text{EO C}_2\text{H}_4$ .



Undesirable rxn  $\text{C}_2\text{H}_2 + \text{H}_2 \rightarrow \text{C}_2\text{H}_6$

(6)

Drying has streams has to be  
dried because all to gas stream  
will be cooled to  $\approx 100^\circ\text{C}$ .  
So, any traces of water will be  
crystallize as ice & block the  
pipes.

Drying done by passing through  
molecular sieve.

### ④ Distillation columns

To get u cooled to  
then  
there are liguidities and i  
sent to the distillation column.

\* For naphtha to separation &  
complex.

### Coke formation

- \* Due to the high temp, coke  
deposits on the walls of the pyrolysis  
coils.
- \* Though the amount of coke  
is only ~ 0.01% of the  
deposits accumulate  
feed, in the core of naphtha  
ether.
- \* It's more in comparison

\* coke formation depends upon the material of carbonization of treated pitch and operating conditions of the reactor.

\* Formed by two mechanisms

① metal surface of the reactor catalyzed the growth of the filamentary type of coke containing metal particles.

② coke is formed by polymerization or condensation, agglomeration in the gas phase.

\* coke formation depends on catalyst, partial pressure, with hydrocarbon

temp & conversion.

\* How can we avoid?

① metal surface can be passivated by sulfidation.

④ Industrial participation in

pre-sulfide the reaction and 1 or  
add trace amounts of S compound  
with the feed during the run.

\* How it affects the process?

\* area of the pressure drop

A tube skin temp can increase  
with run time.

\* What is to be done to remove  
deposits over the limit?

① To plant

start down.

Typical run time is 45-60 days  
for naphtha.

70-80 days for ethane propane

How can it be reduced by  
making charge in the coil? ① Larger coil diameter at the  
outlet section

→ Reduced  $\rightarrow$  hydrocarbon partial pressure

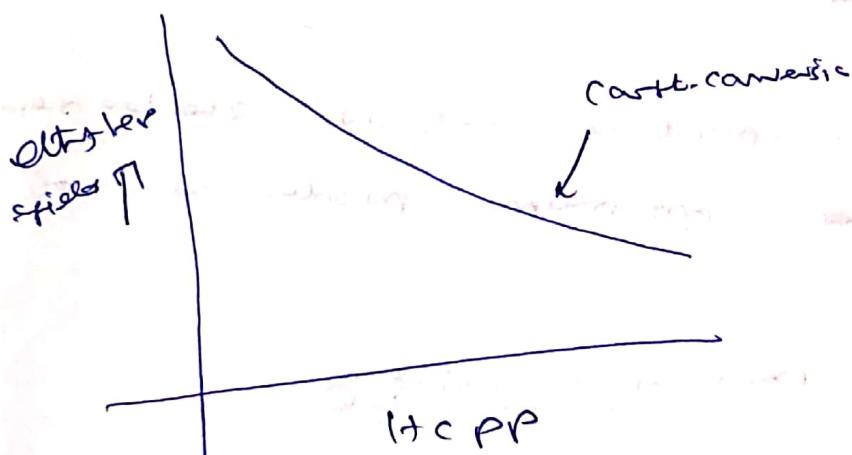
(7)

~~Process~~  $\rightarrow$  decrease in the coil diameter than in reactor coil length many short smaller diameter tubes Long tubes decreased rate  $\downarrow$

\* reactor coil

process variables:

① HC partial pressure:



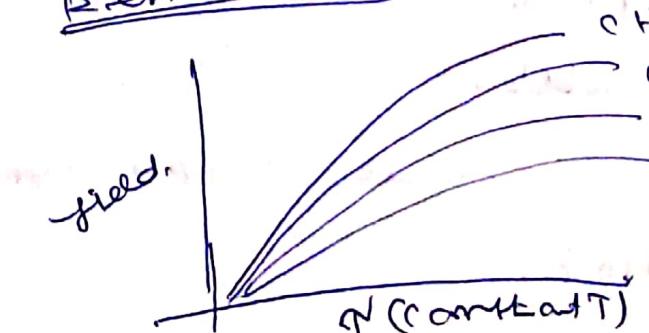
Low HC partial pressure  
→ long reactor  
for same conversion

Steam is used instead to reduce the

HC partial pressure

more regeneration more coke formation  
oligomerization  
At high N

② Residence time:



C2H4 starts to crack after residence time ~ 300 ms

Start residence time were active function

1 s

(3)

### Conversion:

LPG (propane)

Higher conversion  $\rightarrow$  more coke

formation & side products.

(4)

### Temp.:

- \*  $NH_3$  at  $0^\circ C$  Hc chains ~~not cracked~~
- \* in the center of molecules
- \* PSC in temp crack at the end of low minutes
- molecules PSC in the platinum former.
- \* Higher temperature require shorter residence times for optimum production of ethylene.

(5)

### Types of Pyrolysis coils:

- \* coil dia usually 3 inch to 4 inch dia
- \* coil outlet pressure usually 2 atm ( $0.2 \text{ MPa}$ )
- \* very few companies have the expertise (Kellco, Stone & Webster)
- \* maximum tube wall temp's typically around  $1050-1100^\circ C$ .