Industrial Heavy & Chemicals

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Introduction

- *Chemicals consumed on large scale*

  eg- H_2SO_4 *,* HNO_3 *,* NH_3*,* Na_2CO_3 *, etc.*
- *Largely used to Manufacture: Fertilizers, explosive, dyestuff, plastics, lacquers (varnish), paints, pigments, paper & textile industry, petroleum industry, leather industry, metallurgical processes, etc.*
- *Industriliasation of country judged from consumption of heavy chemicals*
- ***plays imp. role in economical, commercial & industrial development of country.***

Manufacturing Processes to be discussed

Sr. No.	Manufacturing Process	Product Formed
1	Haber's Process	NH_3
2	Contact Process	H_2SO_4
3	Ostwald's Process Or Ammonia Oxidation Process	HNO_3
4	Solvay Process or Ammonia Soda Process	Na_2CO_3

Manufacture of Ammonia

- *Three different ways*

1) *From ammoniacal liquor in a coal gas industry*
2) *From compounds*
3) *From synthetic method.*

But Haber's Synthetic method is best one.

The Haber's Process

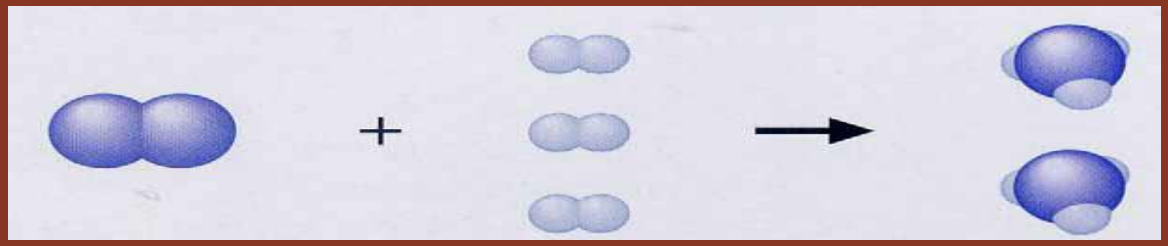
- Developed by Carl Bosch & Fritz Haber(1904-08)
- Haber got Noble prize 1978
- This reaction make ammonia from hydrogen and nitrogen.
- The nitrogen comes from the air (78% N).
- You don't need to worry about where the hydrogen comes from!

THE HABER PROCESS

The Haber process is a ***REVERSIBLE*** & ***EXOTHERMIC*** reaction

Catalytic combination associated with decrease in volume

$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} + 22800$ cal



Maximum yield obtained by **Le-Chatelier's principle** & optimum reaction conditions

"If a stress is applied to a system at eqm, the system will change to relieve that stress & re-establish eqm".

Physico-Chemical Principles

(Technical conditions)

1) **Temperature:** Reaction exothermic, decrease in tempt. favours formation of ammonia. But it decreases rate of reaction. So use catalyst.

   Optimum tempt.: 500-550 ^0C

2) **Catalyst:** Finely divided Fe + tracer Mo as promoter

   To form ammonia at low tempt, increases reaction rate.

3) **Pressure:** The pressure varies from one manufacturing plant to another, but is always high. The high pressure increases the percentage yield of ammonia at constant tempt.

   200-250 atmosphere.

3) **Concentration:** maximum yield when nitrogen and hydrogen is in (1:3) proportion.

4) **Rate of Flow:** for good conversion gases recirculated over catalyst. Conversion reaction depends upon time of contact

Haber's Process

It Involves

1)Preparation and purification of reactiong gases:

H_2 is obtained by mixing water gas(CO+ H_2), producer gas (CO+N_2) & steam

$$CO + H_2O + Fe_2O_3 \longrightarrow H_2 + CO_2 + 10{,}000 \text{ cal.}$$

CO_2 removed by dissolving in water and CO removed by NaOH

2) *Converter: consist of electrical heated catalyst* ***(500-550 ^0C)***

When exothermic reaction , temperature controlled by controlling speed of entering gases.

3) *Removal of Ammonia: Resulting gases from converter contain 8% ammonia, cooled to -10 to -20 ^0C and condensed & obtained liq. Ammonia.*

Unreatced N_2 and H_2 compressed & passed back through circulatory system,

In each step 8% is obtained and nothing is lost

The Haber Process:

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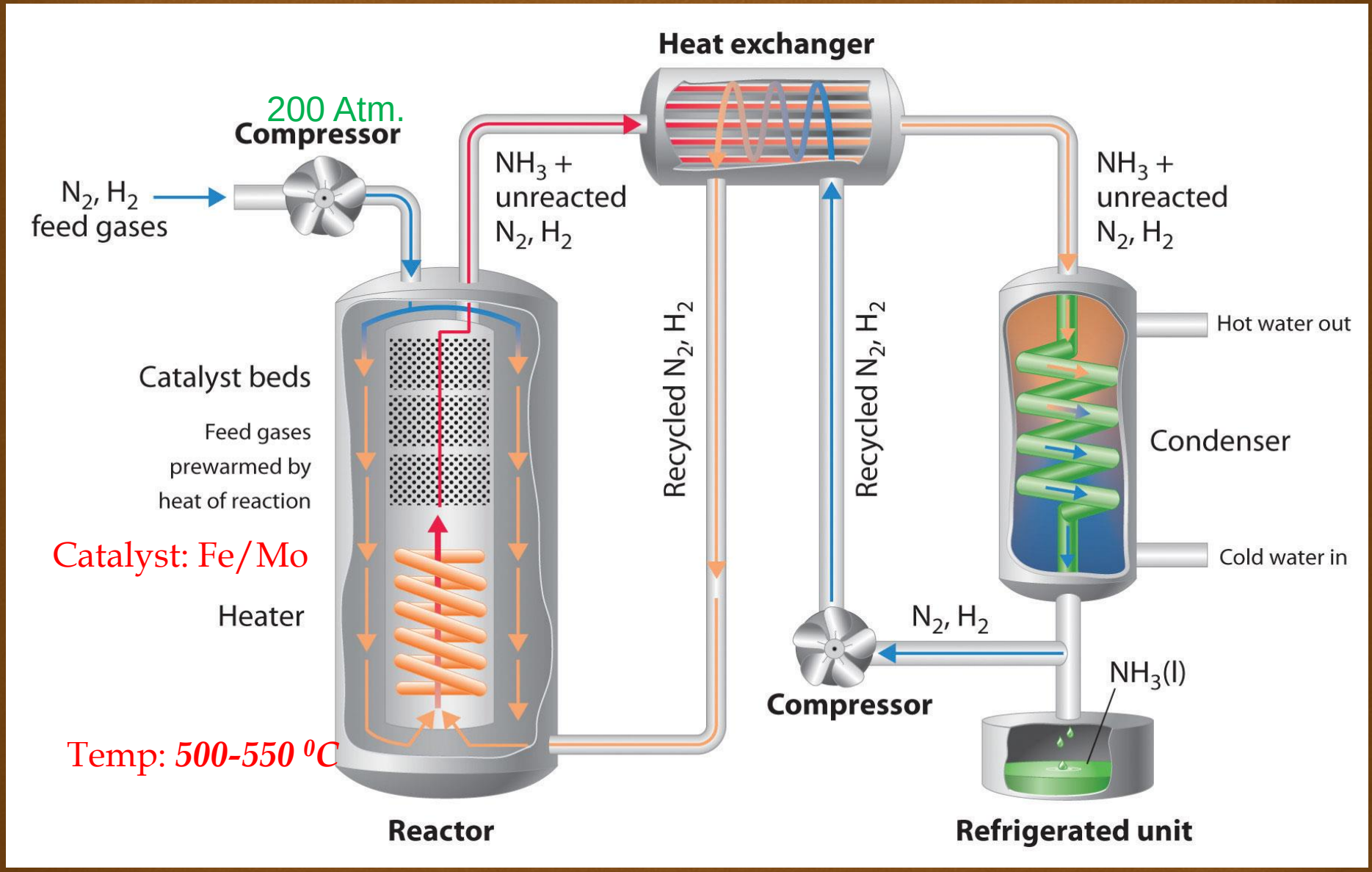


The Haber's Process

Key facts

1. N_2 *and* H_2 *are mixed in a 1:3 ratio*
2. *The reaction is reversible, So all the nitrogen and hydrogen will not convert to ammonia.*
3. *The ammonia forms as a gas but cools and liquefies in the condenser*
4. *The* N_2 *and* H_2 *which do not react are passed through the system again so they are not wasted.*

2. Contact Process: H_2SO_4

Imp heavy chemicals ,known as 'King of Chemicals'

- **Used in almost every industry**
- *Manufactured by two process*

  a). The Lead Chamber Process

  b). The Contact Process

- ***But now a days Contact Process is mostly preferred***

THE CONTACT PROCESS

Developed by Philips (1831)

Steps: 1) Sulphur dioxide by burning high grade sulphur or iron pyrites:

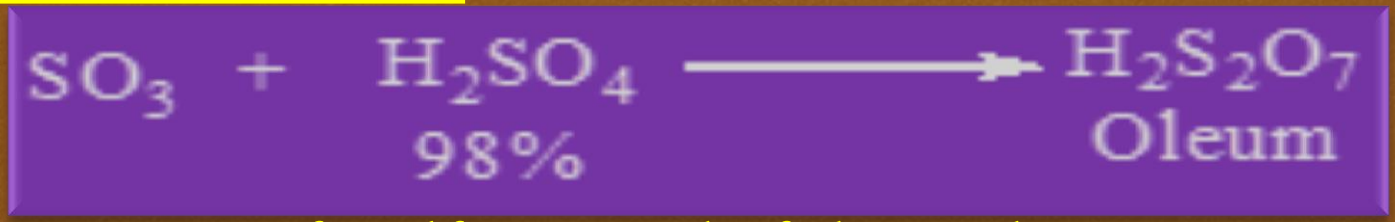
$$S + O_2 \xrightarrow{\text{Burning}} SO_2\uparrow + 70920\ \text{Cal}$$

OR

$$4FeS_2 + 11O_2 \longrightarrow Fe_2O_3 + 8\,SO_2 + 82340\ \text{Cal}$$

2). Oxidation of Sulphur dioxide by Air

3). Formation Oleum:



4).Preparation of Sulfuric acid of desired concentration:

Physico- Chemical Principles(Technical Condition)

Yield totally depends upon catalytic oxidation of SO_2 to SO_3

Reversible reaction, forword reaction is exothermic , associated with decrease in volume.

Better yield can be obtained by Le-Chatelier's Principle & by obtaining favorable conditions

1.Effect of Tempt.: Reversible reaction, forword reaction is exothermic , associated with decrease in volume,
equilibrium shifts towords right with decrease in tempt.
That is low tempt. Favours formation of SO_3.
But rate of reaction falls by decrease in tempt.
Tempt.= 434 ^0C , 99% conversion Optimum Tempt. Range: 425-450 ^{0}
Even at this tempt. Reaction rate is slow. Therefore Suitable catalyst is used.

2. *Effect of pressure:*
As per Le-Chatelier's principle high pressure required for better yield.
But high pressure is not suitable:
SO3 strongly adsorb on catalyst due to high pressure therefore conversion slows down
Corrosion also takesplace.
Optimum pressure: $1.515* 10^5$ to $1.717*10^5$ pa (1.5 to 1.7 Atm.)

3. Effect of Concentration:
High conc^n of reacting gases favours high yield
Molecular proportion : **2:3 (SO_2 : O_2)**

4. Effect of Catalyst: **Enhances rate of reaction**

Catalyst Used: Ferric oxide(Fe_2O_3), vanadium pentaoxide (V_2O_5), Platinum(best results but expensive)

V_2O_5 mostly preferred, efficient, cheap, dosen't get poisoned

Role of V_2O_5:

$$V_2O_5 + SO_2 \longrightarrow SO_3 + V_2O_4$$

$$V_2O_4 + 2\,SO_2 + O_2 \longrightarrow 2\,VOSO_4$$

$$2\,VOSO_4 \longrightarrow V_2O_5 + SO_3 + SO_2$$

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

5. Effect of Space Velocity:

no. of cubic feet gases pass over one cubic feet catalyst space per hour

Time of contact between catalyst and gas must be controlled.

Manufacturing of Sulfuric acid(Contact Process)

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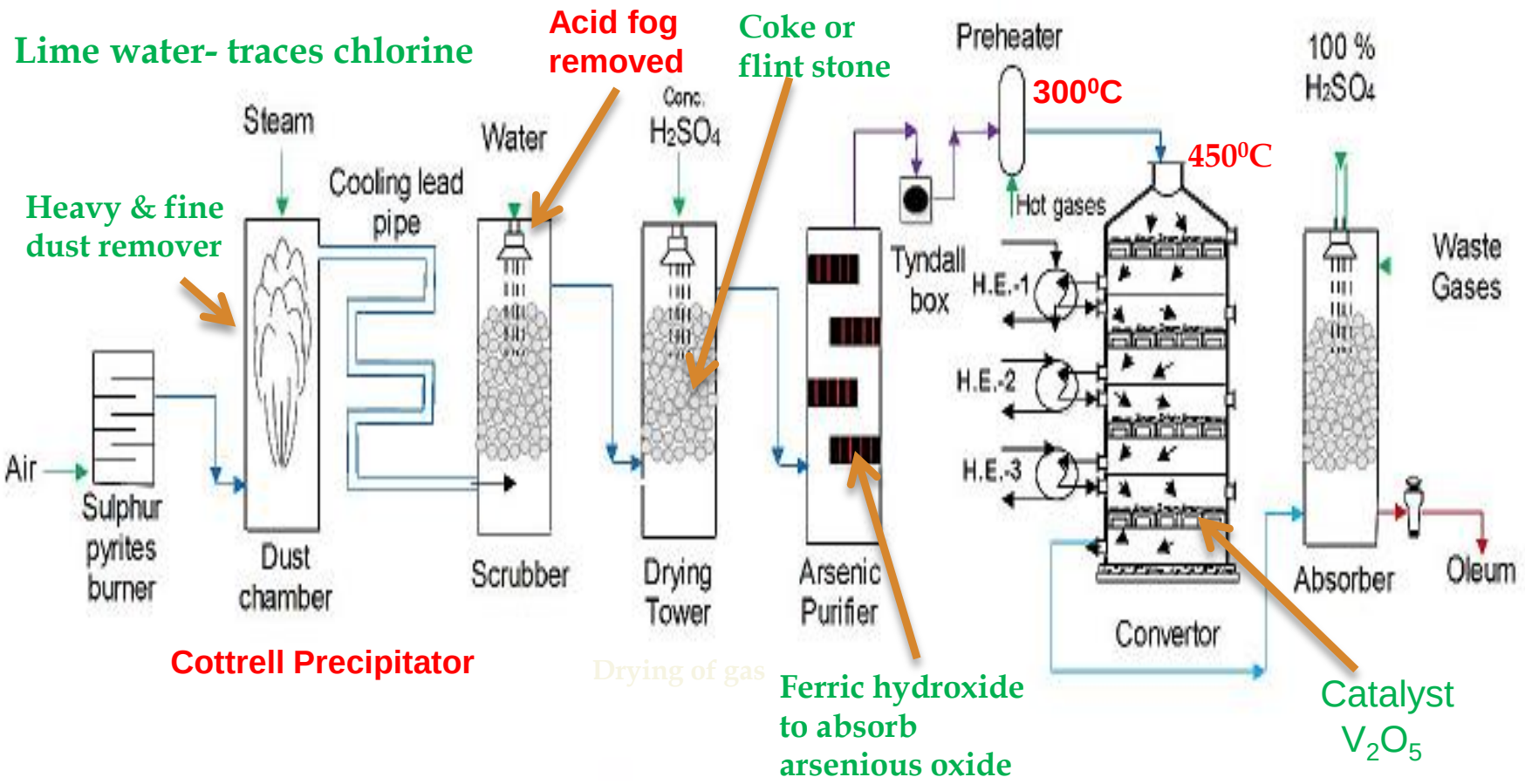

Figure: Manufacturing of Sulfuric acid by Contact process

Superiority of contact process

- *High improvement in engineering & catalyst performance*
- *Extremely pure, high strength acid*
- *Cheap, good economy*
- *Wide use.*

Ostwald Process of Nitric Acid:

Also known as Aqua fortis,

Two Processes:

1). Birkeland-Eyde's Arc process

2). Ostwald's Process : Modern process mostly preferred

2). Ostwald's Process : Steps

i)Production of nitric oxide:

ΔH= -216.6 kcal

ii) Conversion of nitric oxide to nitrogen dioxide:

ΔH=-27.1 kcal

Exothermic reaction with decrease in volume, So According to Le-Chatelier's principle reaction is favoured by low temperature (below 150^0C) & high pressure,

Reaction is slow, so sufficient contact time for oxidation is required. Smaller quantity of N_2O_3 & N_2O_4 also formed.

iii) Reaction between NO_2 and water:

$$4\,NO_2 + 2\,H_2O + O_2 \longrightarrow 4\,HNO_3 \quad \Delta H = 32.2 \text{ kcal}$$

Physico-chemical Principle(technical condition):

1)Effect of temperature: Exothermic

$$4\,NH_3 + 5\,O_2 \xrightarrow{Pt\text{-}Rh} 4\,NO + 6\,H_2O \quad \Delta H = -216.6 \text{ kcal--1 Very Fast}$$

(10%)

$$4\,NH_3 + 3\,O_2 \longrightarrow 2\,N_2 + 6\,H_2O \quad \Delta H = -302.7 \text{kcal ---2}$$

$$4\,NH_3 + 6\,NO \longrightarrow 5\,N_2 + 6\,H_2O \quad \Delta H = -431.9 \text{ kcal --3}$$

$$2\,NO + O_2 \longrightarrow 2\,N_2O_4 \quad \Delta H = -13.9 \text{ kcal ---4}$$

Tempt.= 750-900 ^{0}C, 95% coversion NH_3 to NO

2) Effect of Pressure: In Reaction increase in volume is observed, so no need of pressure, just use of slightly above atmospheric pressure to maintain flow, contact, rate of reaction , catalytic effect and combustion temperature

$$\underset{(10\%)}{4\,NH_3} + 5\,O_2 \xrightarrow{\text{Pt-Rh}} 4\,NO + 6\,H_2O$$

$$4\ \text{Vol.} + 5\ \text{Vol} \longrightarrow 4\ \text{Vol.} + 6\ \text{Vol.}$$

3) Effect of Concentration: Proportion of NH_3 & Air is 10% & 90%
If O_2 used instead of Air then 1: 1.25 , But practically O_2 is used little excess

4) Effect of Catalyst: Alloy of 10% Pt-Rh is used, O_2 is adsorbed on catalyst, According to Bodenstein(1934) reaction are as

$$NH_3 + (O) \longrightarrow NH_2OH$$

$$NH_2OH + O_2 \longrightarrow HNO_2 + H_2O$$

$$4\,HNO_2 \longrightarrow 2\,H_2O + O_2 + 4\,NO$$

5) Rate of flow of gases: Appropriate flow to get more yield.

ABSORPTION OF NO_2 INTO WATER

- *Nitric oxides on oxidation gives different oxides of nitrogen.*
- *Mixture of oxides react with water*
- *Reactions controlled by cooling gases,*
- *Produced NO again oxidized to NO_2 and absorbed by water to convert nitric acid.*
- *Obtained nitric acid is dilute, it is concentrated by distillation (68.4%) at 122 ^{0}C.*

Manufacturing of Nitric Acid

- *Catalyst: Alloy Pt-Rh*
- *NH_3+ Air =11:89;*
- *Oxidation Chambers :Iron lined with acid proof stone*

Manufacturing Process

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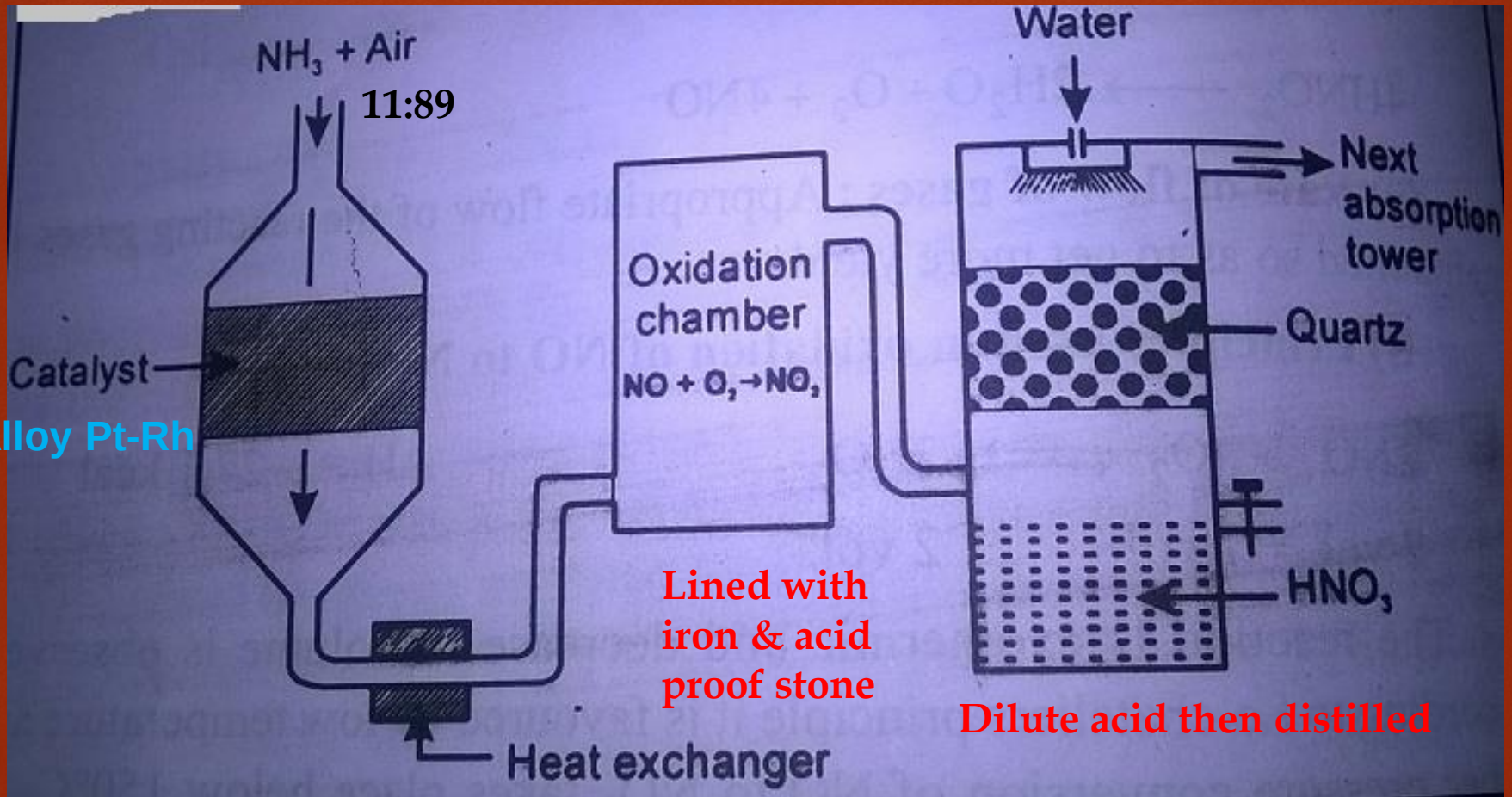

Fig. 1.3 : Manufacture of HNO_3 by Ostwald's process.

Manufacture of Sodium carbonate

Solvay Process

- Na_2CO_3 is used in glass, paper, textile, soap, chemical industries.
- Also Called as washing soda.
- In 1865 Ernst Solvay successfully produced Na_2CO_3 hence Known as Solvay Process

Physico-chemical Principles:

- Catalyst : Ammonia
- Conditions: Low Tempt. ,
- microcrystalline sodium bicarbonate formed, so difficulty in filtration may arise.
- To overcome these difficulty conditions vary little bit as

1) 4.9 mol/litre of NaCl & 4.5 mol/litre NH_3 instead of equimolar.
2) 2) Relatively high Tempt(60-65°C)in beginning is applied to form good crystal, then gradual cooling and filtration.

Reactions of Formation of Na_2CO_3

a) $CaCO_3 \longrightarrow CaO + CO_2 \uparrow$ — ΔH = + 43.4 kcals

b) $C + O_2 \longrightarrow CO_2 \uparrow$ — ΔH = - 96.5 kcals

c) $CaO + H_2O \longrightarrow Ca(OH)_2$ — ΔH = - 15.9 kcals

d) $NH_3 + H_2O \longrightarrow NH_4OH$ — ΔH = - 8.4 kcals

e) $2NH_4OH + CO_2 \longrightarrow (NH_4)CO_3 + H_2O$ — ΔH = -22.1 kcals

f) $(NH_4)CO_3 + CO_2 + H_2O \longrightarrow 2\,NH_4HCO_3$

g) $NaCl + NH_4HCO_3 \longrightarrow NH_4Cl + NaHCO_3$

h) $2\,NaHCO_3 \longrightarrow Na_2CO_3 + CO_2 + H_2O$ — ΔH = + 30.7 kcals

i) $2\,NH_4Cl + Ca(OH)_2 \longrightarrow 2\,NH_3 + CaCl_2 + 2\,H_2O$ — ΔH = + 10.7 kcals

Overall reaction for entire process

$$CaCO_3 + 2NaCl \longrightarrow Na_2CO_3 + CaCl_2$$

Role of NH_3 & CO_2 is important, determines yield of product.

The reactions d, e, f can be written as,

$$2\,NH_3 + CO_2 + 2H_2O \rightleftharpoons 2\,NH_4HCO_3$$

Manufacture of Sodium carbonate

Steps

- *1.Saturation Tank: Brine (NaCl) solution is Saturated by NH_3 (Brine top-down & NH_3 bottom -top) ,*
- *Brine Should be free from impurities (calcium, magnesium and iron compounds)*
- *Na_2CO_3 & NaOH added to remove impurity.*
- *exothermic reaction, water cooling system is fitted in saturator.*

2. Carbonation of Ammoniacal Brine:

- *Carbonation tower 75 feet,*
- ***Ammoniacal brine is trickling down,***
- *Ammoniacal brine reacts with upcoming* CO_2.
- ***Cooling coils fitted at 20 feet*** *to control temp, as reactions are* ***exothermic*** *in nature & to* ***precipitate*** $NaHCO_3$ *formed in process by cooling.*
- *During pptation, tempt at Bottom & Top of tower: 20-25˚C*
- *Tempt. at middle:* $45\text{-}55°C$ *(maintained by cooling coil)*
- *The tower gradually becomes flooded as sodium bicarbonate cakes formed.*
- ***After precipitation solid*** $NaHCO_3$ ***is dissolved in formed*** $(NH_4)_2CO_3$
- $(NH_4)_2CO_3$ *also reacts with* CO_2 *to form* NH_4HCO_3 *exothermally.*

- *Again NH_4HCO_3 further reacts with NaCl to form $NaHCO_3$.*

Milky liquid collected in vessel & allowed to cool, then $NaHCO_3$ crystallized by cooling, filtered & pressed. Then $NaHCO_3$ calcined to get Na_2CO_3.

Filtrate contain NaCl, NH4Cl, 10 % NaHCO3 and NH4HCO3 treated with lime to generate NH_3 & CO_2 in Ammonia recovery tower.

The hot Na_2CO_3 from calciner is cooled & packed in bags.

Manufacturing of Sodium Carbonate:

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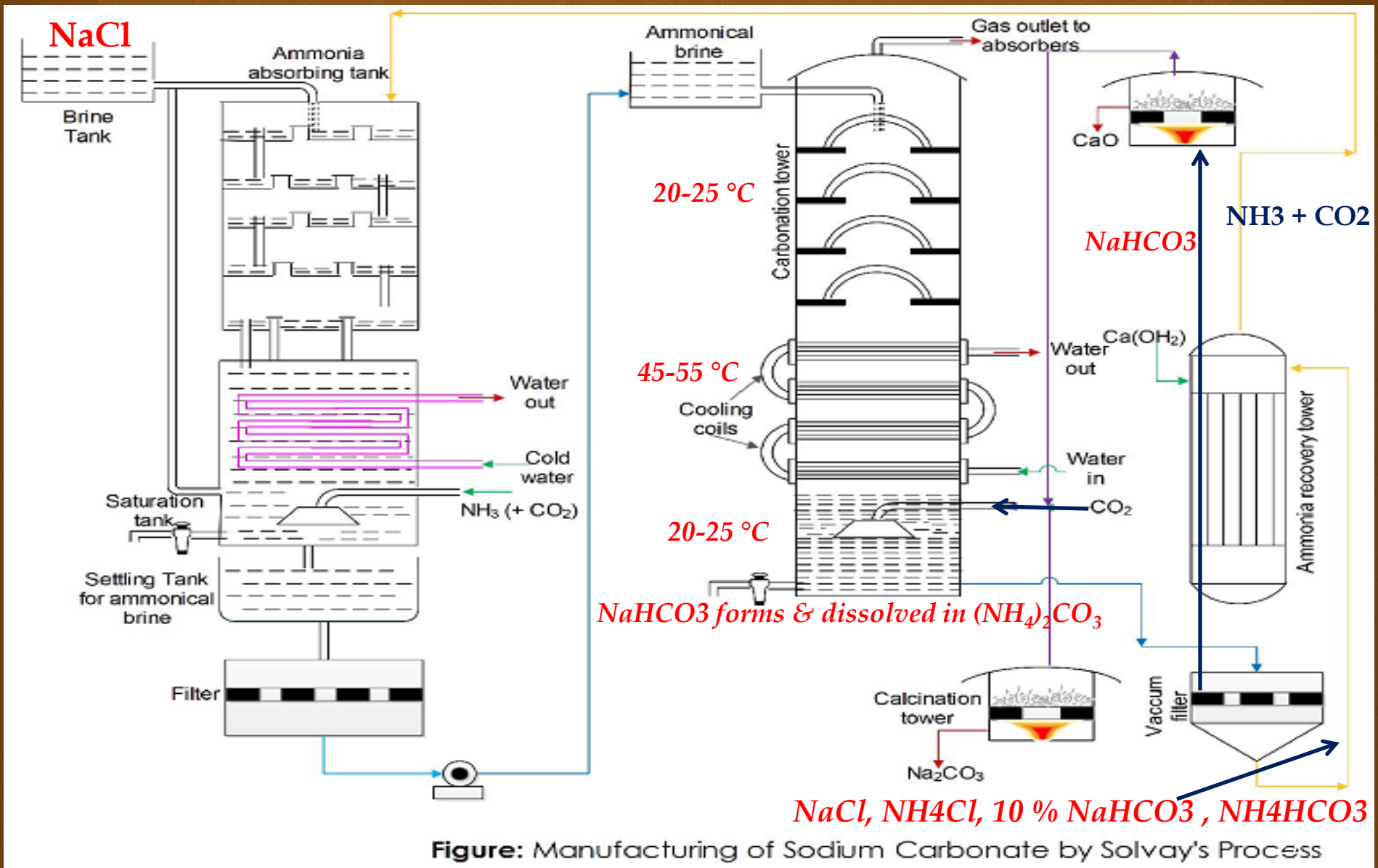
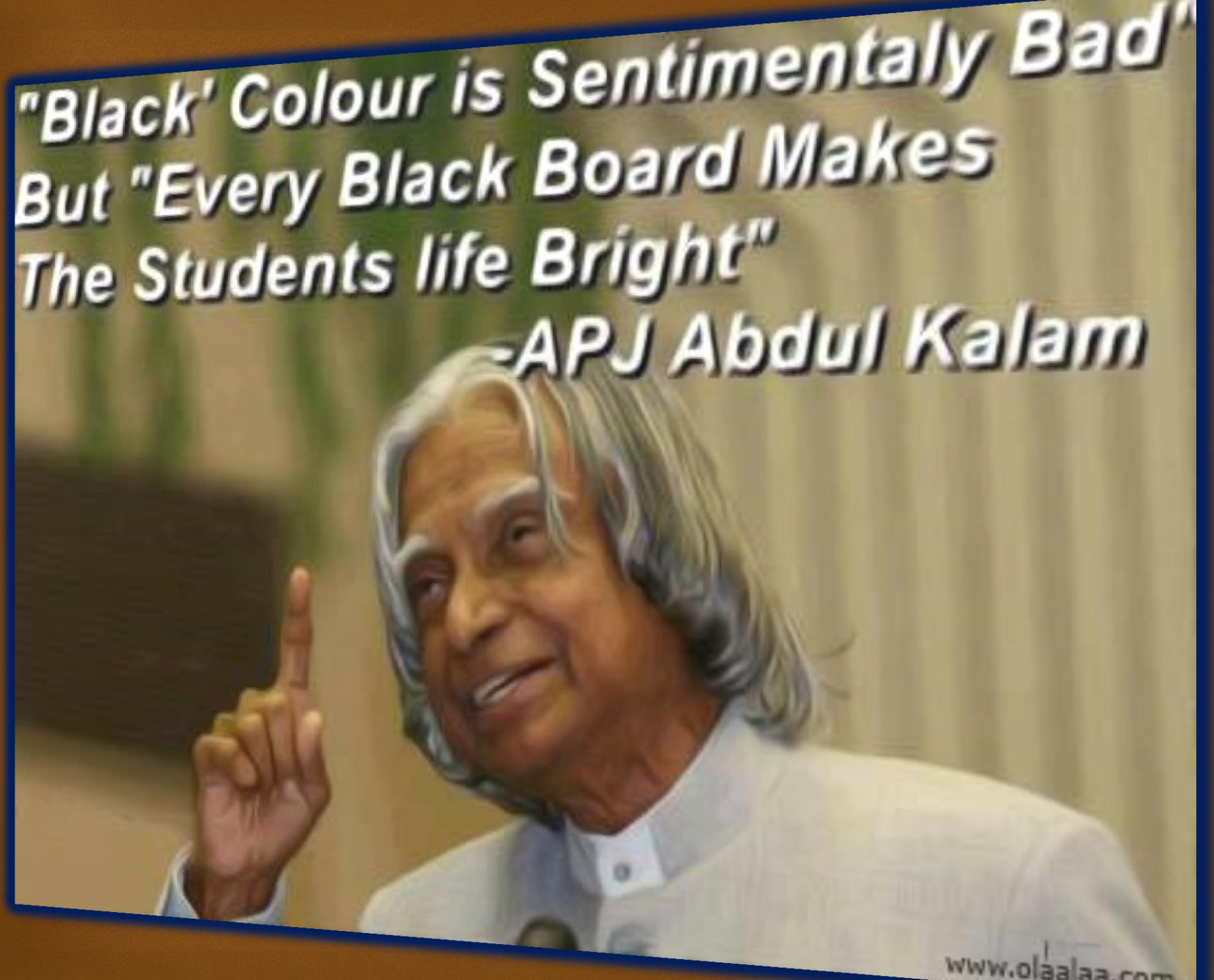


Figure: Manufacturing of Sodium Carbonate by Solvay's Process

Conclusion

Sr. No.	Manufacturing Process	Product Formed	Starting Materials Used	Reaction Conditions		
				Catalyst	Tempt . ^{0} C	Pressure(Atm.)
1	Haber's Process	NH_3	$N_2 + H_2$	Fe/Mo	500-550	200-250
2	Contact Process	H_2SO_4	S or Fes & O_2	V_2O_5, or Pt	425-450	1.5-1.7
3	Ostwald's Process Or Ammonia Oxidation Process	HNO_3	NH_3 & O_2, H_2o	Alloy Pt-Rh (10%)	750-900	Slight more than Atmosphere
4	Solvay Process or Ammonia Soda Process	Na_2CO_3	CO_2, NaCl, H_2O	NH_3	60-65, 40-45, 20-25	Atmospheric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But "Every Black Board Makes
The Students life Bright"
-APJ Abdul Kalam
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Questions ???


Thank you