AMMONIA SYNTHESIS

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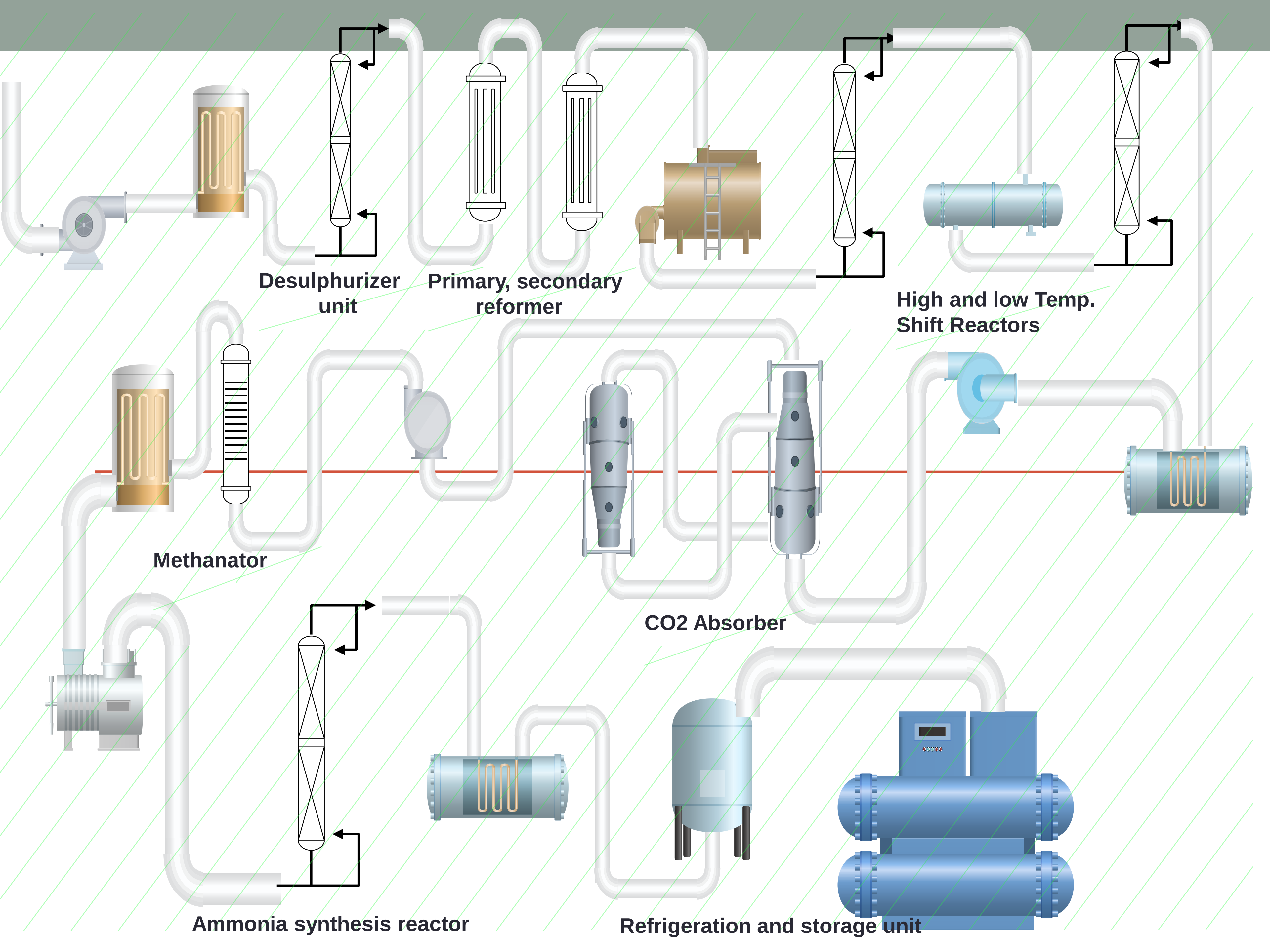
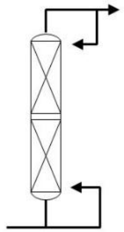
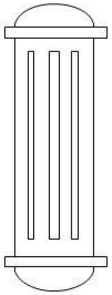
Flow sheet Overview

By:
Nikhil Kumar Chauhan


Desulphurizer unit
Primary, secondary reformer
High and low Temp. Shift Reactors
Methanator
CO2 Absorber
Ammonia synthesis reactor
Refrigeration and storage unit

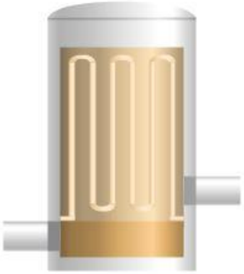


Fixed layer of small particles or objects arranged in a vessel to promote inti mate contact between gases, vapors,liquids, solids, or various combinations thereof; used in catalysis, ion exchange, sand filtration, distillation, absorpti on.

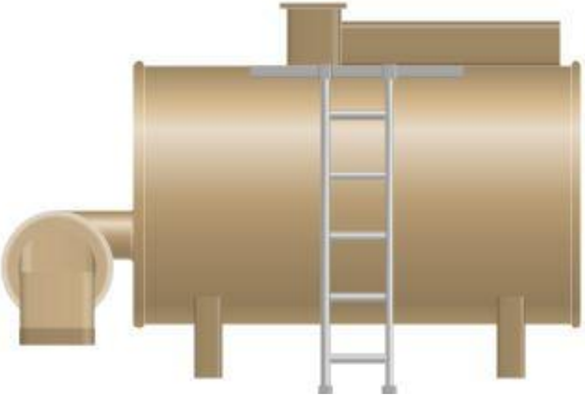


A **methane reformer** is a device based on steam reforming, autothermal reforming or partial oxidation and is a type of chemical synthesis which can produce pure hydrogen gas from methane using a catalyst

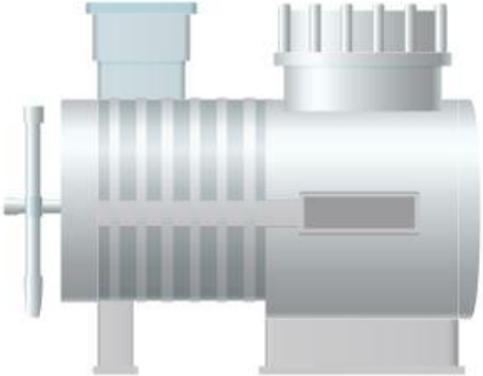
A **fluidized bed** is formed when a quantity of a solid particulate substance (usually present in a holding vessel) is placed under appropriate conditions to cause a solid/fluid mixture to behave as a fluid.



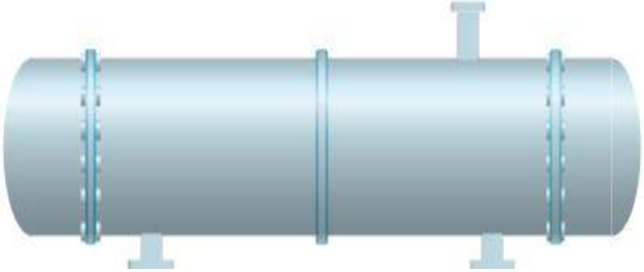
Equipment for the heating of chemical process streams (gases, li quids, or solids); usually refers to furnaces, in contrast to heat exchangers.



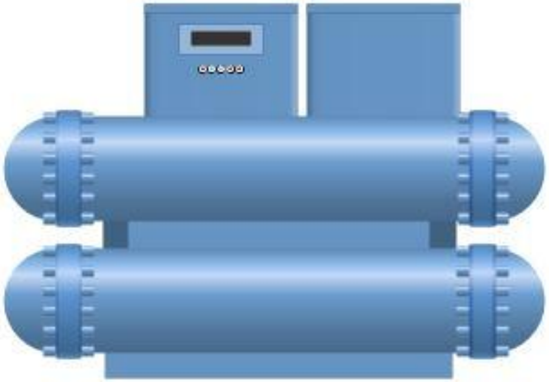
BOILER



COMPRESSOR



CONDENSER



REFRIGERATION UNIT

Process and Flow sheet Description

- By :

  Shalini Ahuja

Process Description

For ammonia synthesis, hydrogen and nitrogen are required in 3:1 ratio. This syn gas required is generated by steam reforming of natural gas under pressure. The process of manufacturing ammonia

can be divided into four steps:

1. Desulphurization
2. Reformation
3. Gas purification &
4. Ammonia synthesis

Desulphurization

- Aims at removing Sulphur from feed gas as H_2S
- The raw gas compressed to 40 Kg/cm2 is preheated to 340^0 C. It is mixed with recycle gas from synthesis compressor and heated to 385^0 C after which it is passed through HDS reactor cum H_2S adsorber
- The gas leaving contains not more than 0.2ppm sulphur
- The top bed is of Ni Mox catalyst (NiO 2-3% wt, MoO3-9-12% by wt, Na max 0.1% by wt. & Cl max 30 ppm) which converts the sulphur in to H2S. And the bottom bed is of Zinc Oxide

- The following reactions take place:

On the first catalyst bed:

RSH (From raw gas) + H_2 (From recycle gas) = RH + H_2S

R_1SSR_2(From the raw gas) + $3H_2$ = R_1H + R_2H + $2H_2S$

COS (From raw gas) + $2H_2$ = CO + H_2S

C_4H_4 S + $4H_2$ = C_4H_{10} + H_2S

- Hydrogen sulphide is subsequently adsorbed on second catalyst bed.

  $ZnO + H_2S = ZnS + H_2O$

Reforming

- Required stoichiometric hydrogen-to-nitrogen ratio is achieved by introducing air into the process.
- This is done in by reforming which is split into two stages:

➢ Primary reforming

➢ Secondary reforming

- The desulphurized gas at is mixed with superheated steam at 360^0 C and the mixture is heated to 520^0 C in waste heat recovery section of primary reformer
- The steam to carbon ratio is maintained as 3.2 as per the design
- This is then passed to catalyst filled tubes of Primary Reformer

$$C_nH_m + 2H_2O + Heat \rightarrow C_{n-1}H_{m-2} + CO_2 + 3H_2$$

$$\text{OR } CH_4 + 2H_2O + Heat \rightarrow CO_2 + 4H_2$$

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

- The outgoing gas at 792^0C & 30.4 Kg/cm^2 pressure contains (Approx.):
- Gas composition on dry basis:

Component	H2	N2	CO	CO2	AR	CH4
Inlet	2.15	0.73	0.0	0.01	0.01	94.22
Outlet	68.83	0.23	9.59	10.15	0.00	11.20

- The process gas mixed with compressed air and reformed further to 0.3% methane across the catalyst bed of Secondary reformer, which finally yields a temperature of 910^0C

$O_2 + N_2 + 2\,CO \rightarrow 2\,CO_2 + N_2$ (Exothermic)

On Bed: $2\,CH_4 + 2\,H_2O \rightarrow 2\,CO + 6\,H_2$ (Endothermic)

$2\,CO_2 + 2\,H_2 \rightarrow 2\,CO + 2\,H_2O$ (Endothermic)

- Gas composition on dry basis after secondary reformer:

Component	H_2	N_2	CO	CO_2	Ar	CH_4
Inlet	68.83	0.23	9.59	10.15	0.00	11.20
Outlet	56.12	22.83	13.16	7.31	0.28	0.30

Gas Purification

- Unwanted gases are removed and hydrogen percentage is increased
- Shift conversion in two steps:

  $CO + H_2O \rightarrow CO_2 + H_2$ (Exothermic)

  HT Shift converter(430^0C)

  LT Shift converter(200^0C)
- CO is reduced to 0.17%
- CO_2 in gas is reduced from 18.92% to 0.10% by absorption in Benfield solution

  $K_2CO_3 + CO_2 + H_2O \rightarrow 2KHCO_3$

- Residual CO and CO_2 is converted back to methane in Methanator

$$CO + 3H_2 \rightarrow CH_4 + H_2O$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$

Ammonia Synthesis Section

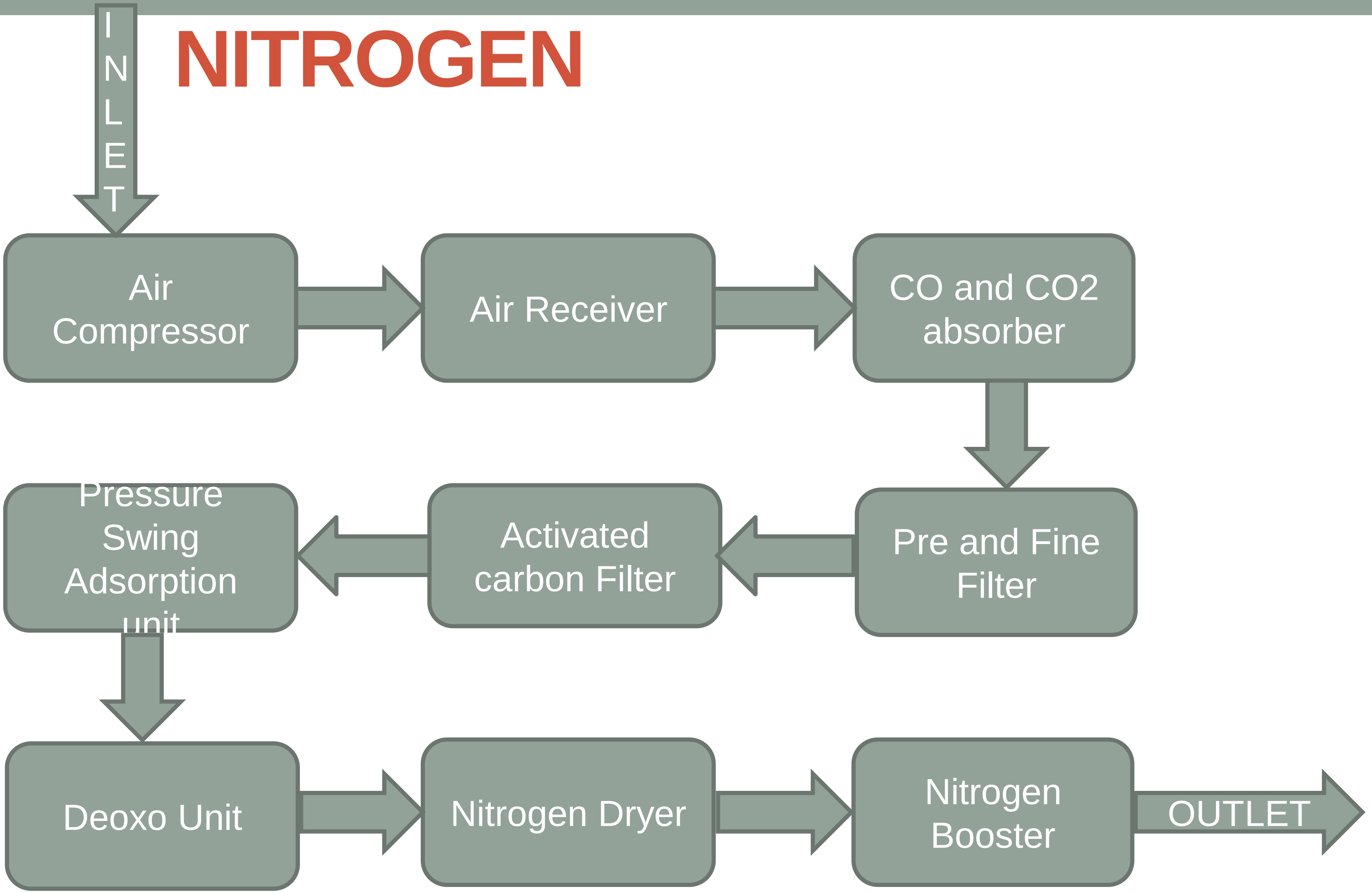
- Synthesis gas is passed over a catalyst bed. The catalyst used is iron catalyst with oxides (primarily of K, Ca and Al) as Promoters.
- The normal operating pressure is about 207 kg/cm^{2}g and reaction temperature in the catalyst bed is 380 - 520°C
- Heat is liberated by the reaction (about 750 Kcal/kg produced ammonia).
- Only about 21% of Synthesis gas at Converter inlet is converted into ammonia and rest gas is therefore recycled back to Converter.

Alternative Way for Nitrogen Production

- By:

  Nikhil Kumar Chauhan

NITROGEN


INLET
Air Compressor
Air Receiver
CO and CO2 absorber
Pre and Fine Filter
Activated carbon Filter
Pressure Swing Adsorption unit
Deoxo Unit
Nitrogen Dryer
Nitrogen Booster
OUTLET

Process Utilities, Data and Environmental concerns

- By:

  Parag Jain

Raw Materials

- Associated Gas (Composition by vol. % : CH_4 – 97.01, C_2H_6 – 2.44, C_3H_8 - 0.46, C_4H_{10} – 0.11, CO_2 – 0.01, N_2 - 0.01)
- Water
- Air
- Various catalysts include NiMo, CDR 66A, ZnO etc. Catalyst manufacturers in Indian include Polygel, Johnson Matthey, Transpek-Silox (largest ZnO manufacturer in India)

Economic Factors

- Natural Gas which is one of the major raw materials costs around 4.2 USD/MMBTU (rates fluctuate on daily basis).
- Water which is another main component is either in the form of ground water or municipal water supply.
- Air which is taken from the atmosphere is to be compressed at high pressure which is a costly affair.
- Most of the catalyst cannot be regenerated and have to be replaced after specific time interval. Catalyst cost is one of the major costing among all the economic factors.

Pollution and Environmental Issues

- Ammonia leakage.
- Usage of chemicals like Sodium Pentachlorophenate for cooling water treatment.
- CO_2 discharge through chimneys
- Disposal of synthetic catalysts after usage.

WATER CONSUMPTION

OCTOBER-2014 to MARCH-2015

MONTH	INDUSTRIAL (M3)	DOMESTIC (M3)	TOTAL (M3)
OCTOBER	1504211	211989	1716200
NOVEMBER	1470141	199959	1670100
DECEMBER	1448917	202083	1651000
JANUARY	1413167	201733	1614900
FEBRUARY	1241717	181883	1423600
MARCH	1484917	204883	1689800
TOTAL	**8563070**	**1202530**	**9765600**

AMBIENT AIR DATA

OCTOBER-2014 to MARCH-2015

MONTH	SO_2	NH3	NO_X	PM -10 (N-E/E)	PM -2.5 (N)	Methyl H.C.	Non Methyl H.C.	CO	RPM
OCT -14	10.32	36.2	38.2	40.7	22.4	0.24	0.35	0.55	44.2
NOV -14	11.2	42.5	36.3	39.5	24.2	0.26	0.38	0.52	47.1
DEC -14	12.2	48.2	37.3	45.7	27.4	0.21	0.41	0.49	51.0
JAN -15	11.3	52.2	41.2	48.7	29.4	0.20	0.31	0.60	47.2
FEB-15	10.5	55.8	42.6	53.4	31.5	0.18	0.32	0.57	46.3
MAR-15	9.33	58.82	48.06	68.93	38.65	0.22	0.34	0.45	45.5
N.A.A.Q. Standards	80	400	80	100	60	---	---	---	---

* VALUES FOR RPM , SO2, NH3, NOX, SPM & ALDEHYDE ARE IN µ gm / m^3

* VALUES FOR CO & HYDROCARBON ARE IN PPM

LIQUID EFFLUENT DISCHARGE TO SEA AFTER TREATMENT

OCTOBER– 2014 TO MARCH - 2015

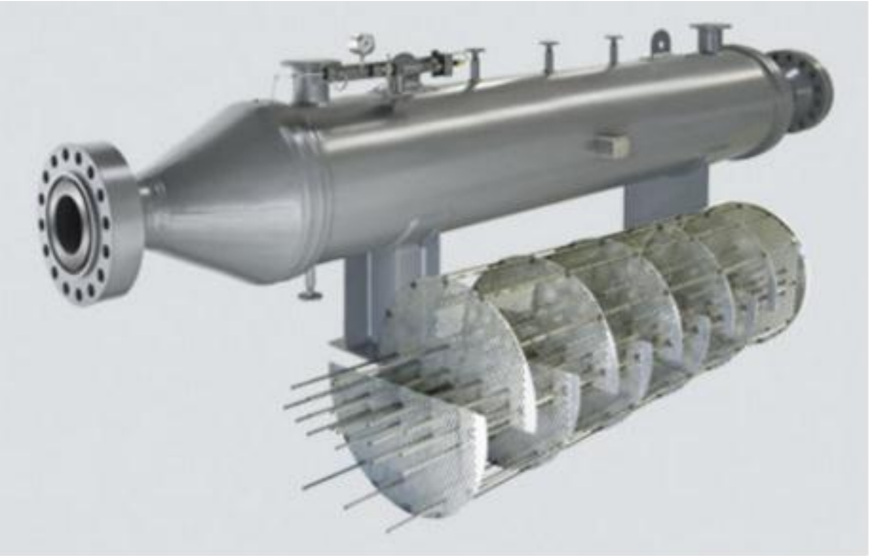
PARAMETERS / MONTH	OCT	NOV	DEC	JAN	FEB	March	MPCB LIMIT
pH	7.8	7.5	7.7	7.8	7.6	7.9	5.5 - 9.0
CYANIDE	N.T.	N.T.	N.T.	N.T.	N.T.	N.T.	0.2
FREE AMMONIA	N.T.	N.T.	N.T.	N.T.	N.T.	N.T.	
AMMONI N ITROGEN	31.4	27.8	29.8	27.6	31.3	34.4	50
T.K.N.	42.7	33.4	38.2	45.2	46.2	45.6	100
NITRATE NITROGEN	2.8	2.6	3.0	3.2	3.1	2.8	10
TOTAL SUS. SOLIDS	51.4	47.2	46.7	49.3	47.6	54.1	100
OIL AND GREASE	3.1	2.4	3.2	2.8	2.6	2.4	Lessthan 10
DISSOLVED OXYGEN	6.0	6.1	5.9	5.7	6.0	5.9	>5
C.O.D.	82.3	76.2	72.4	64.2	68.4	76.3	250
B.O.D.	32.8	31.4	28.8	28.2	29.6	33.4	100

Process Equipments and Future scope for Ammonia

- By:

  Abhishek Prasad

Natural Gas Preheater



Natural gas preheater

Manufacturers: Kelvion India Pvt. Ltd.
Bronswerk Marine Inc.
Wattco Co. Ltd.

HDS Reactor

Manufacturers: SKFT Pvt. Ltd
CMP Arles Pvt. Ltd.
ISGEC Heavy Engineering Ltd.

Steam Reformer

Manufacturers: Linde India Ltd.
Kapsom Mech. Co. Ltd.
Haldor Topsoe India Pvt. Ltd.

Methanator

Manufacturers: Tema India Ltd.
Haldor Topsoe India Pvt. Ltd.

CO Shift Reactor

Manufacturers: Linde India Ltd

. Haldor Topsoe India Pvt. Ltd.

Absorption Column

Manufacturers: Thermax India Ltd.

L&T Heavy Engineering

Mersen

Boiler

Manufacturers: Forbes Marshall
Thermax India Ltd.
Cheema Boilers

Condensor

Manufacturers: Thermax India Ltd.
Alpha Technovac LLP

Compressor

Piping

Future of Ammonia Synthesis

- Coupling of ammonia and urea synthesis reactions increases overall efficiency and prevent emission of greenhouse gases. Also running two reactions within close proximity would conserve reactor space, require less labour and energy.

- Another innovative approach aims to replace the WGS (Water Gas Shift) membranes with a Pd-Ag centrifugal membrane. This would decrease overall membrane costs and also increase yield.

Future of Ammonia Synthesis

- Also, low pressure reaction of ammonia synthesis can be considered for additional 10% single-pass conversion.

- The effects of water dependence on ammonia synthesis can be researched when compared to the effects of natural gas dependence if scaled for global production.

Conclusion

- Ammonia is one of the key compound used in the manufacturing of fertilizers and around 85% of ammonia is used for the same.
- Apart from the conventional use of ammonia, there are minor and emerging uses such as **refrigerant (R717)**, stimulant, in textile industry, fuel, etc.

Thank You!