PRODUCTION OF AMMONIA

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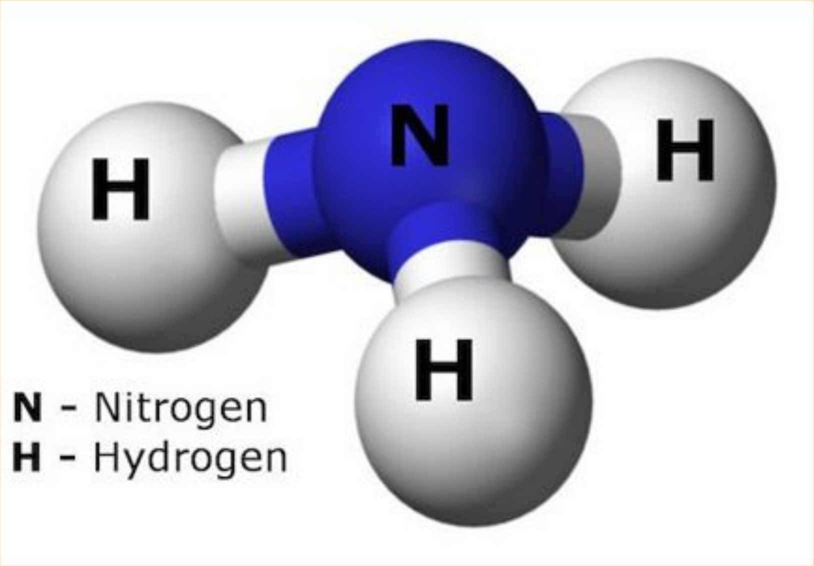
AMMONIA



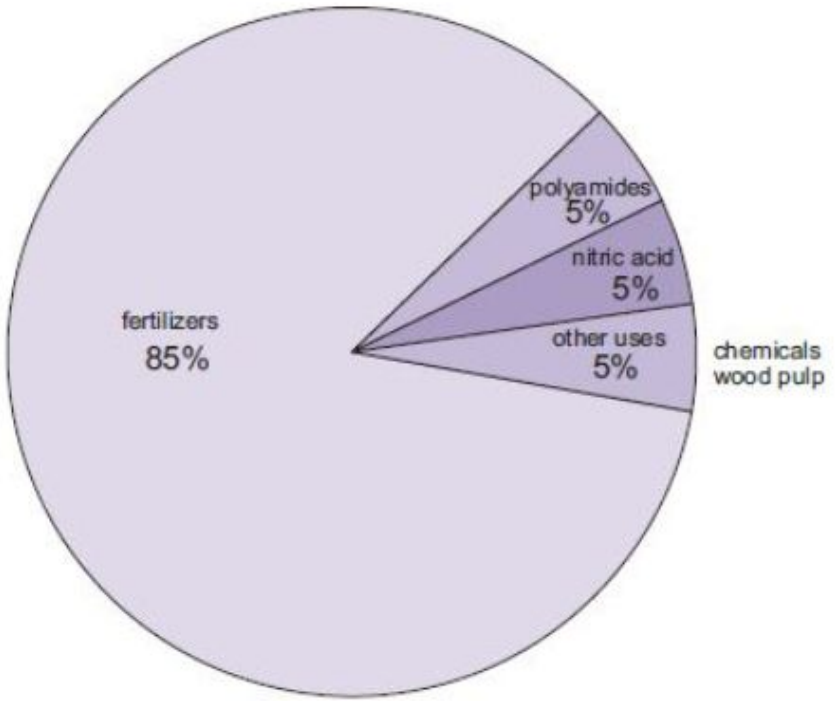
- Ammonia is a colorless, poisonous gas with a familiar noxious odor.
- Ammonia is one of the most highly produced inorganic chemicals.

Chemical/Physical properties of Ammonia

- At room temperature, ammonia is a colorless, highly irritating gas with a pungent, suffocating odor.
- In pure form, it is known as anhydrous ammonia and is hygroscopic (readily absorbs moisture).
- Alkaline properties and corrosive.
- Ammonia gas dissolves easily in water to form ammonium hydroxide, a caustic solution and weak base.
- Easily compressed and forms a clear liquid under pressure.
- Shipped as a compressed liquid in steel containers.
- Not highly flammable

Uses of Ammonia

- ❑ Ammonia in Industries
- ❑ For Manufacturing Various Compounds(nitric acid, Hydrogen cyanide, and a lot of other)
- ❑ Agriculture
- ❑ Household Products
- ❑ Metal Treating(furnace brazing, atomic hydrogen welding)



Design Basis :

- Location
- Amount

Design Basis : Location

Table: State-wise Natural Gas Production Trends (MMSCM)						
State/Source	2014-15	2015-16	2016-17	2017-18	2018-19	2019-20 (upto Dec'19)
Onshore						
Andhra Pradesh	541	619	868	959.16	1081.31	688.84
Arunachal Pradesh	34	30	28	29.51	27.81	31.75
Assam	2958	3025	3128	3219.02	3289.06	2462.51
Gujarat	1527	1490	1580	1606.66	1402.22	1011.78
Rajasthan	1178	1338	1277	1441.93	1483.25	1343.80
Tamil Nadu	1192	1011	983	1207.22	1207.85	824.18
Tripura	1140	1332	1430	1440.37	1554.30	1173.64
CBM-WB, MP, Jharkhand	228	392	564	734.80	710.46	485.07

States include in regional market :

1. Gujrat
2. Rajasthan
3. Maharashtra
4. others

Location : Gujarat

Source: https://www.expertmarketresearch.com/reports/indian-ammonia-market

PROCESS DESIGN

1. Haber –Bosch Process
2. Electrochemical Processing
3. Thermochemical Synthesis

Haber - Bosch Process

The currently adopted ammonia production process, this is well known process. About 85% of total production of ammonia worldwide is produced by this process.

$$3\ H_2 + N_2 \rightarrow 2\ NH_3 \quad \Delta H°27\ °C = -46.35\ kJ/mol$$

- ❑ Ammonia synthesis is an exothermic reaction, and it occurs spontaneously at low temperatures .
- ❑ To effectively synthesize ammonia , the reaction should be performed at a relatively high temperature and pressure of 400–500 °C and 10–30 MPa, respectively, with the assistance of an iron-based catalyst.

Electrochemical Processing

- ➔ The reactions at both cathode and anode in proton conducting cells are shown below:

$$N_2 + 6H^+ + 6\ e^- \rightleftharpoons 2\ NH_3$$

$$3\ H_2 \rightleftharpoons 6\ H^+ + 6\ e^-$$

- ➔ The reactions at each cathode and anode are basically reversible.
- ➔ Four different types of electrolytes are currently available: (a) liquid electrolytes, (b) molten salt, (c) composite membranes and (d) solid state electrolytes

Thermochemical Cycle of Ammonia Production

In this Process The system consists of two circulated processes: reduction (nitrogen activation) and steam-hydrolysis (ammonia formation).

$$Al_2O_3 + 3C + N_2 \rightarrow 2\,AlN + 3\,CO \qquad \Delta H°25\ °C = 708.1\ kJ/mol$$
$$2AlN + 3\,H_2O \rightarrow Al_2O_3 + 2\,NH_3 \qquad \Delta H°25\ °C = -274.1\ kJ/mol$$

- ❑ Unlike the Haber–Bosch process, this thermochemical cycle can be carried out at atmospheric pressure and without a catalyst.
- ❑ The heat required for reduction is covered by heat generated by the combustion of fuel gases produced during ammonia production.

SELECTION OF PROCESS

Energy source	Process	Energy GJ/ton NH_3	CO_2 emissions t/ton NH_3
Natural Gas	Steam reforming	28	1.6
Water	Electrolysis	34	0
Naphta	Steam reforming	35	2.5
Heavy Fuel Oil	Partial oxidation	38	3.0
Coal	Partial oxidation	42	3.8

Energy Consumption and CO2 emissions for different feedstock

Feedstock	Amount of feedstock	HHV GJ/ton NH_3	Feedstock price NOK/ton NH_3
Natural Gas	353.18 kg/ton NH_3	-17.7	414.87
Electrolysis	7.69 MWh/ton NH_3		2360.83
Nitrogen enriched air	0.160 MWh/ton NH_3		49.12
Coal	528.89 kg/ton NH_3	-17.35	282.31

Amount of feedstock and heating value for different feedstock.

Feedstock	Price	Feedstock price NOK/ton NH_3	Profit NOK/ton NH_3
Natural Gas	1.175 NOK/kg [14]	414.87	1906.27
Electrolysis + NEA	0.307 NOK/kWh[8]	2409.95	-88.55
Coal	0.534 NOK/kg[2]	282.31	2038.83

Calculated Prices and profits for different feedstock

- Based on energy consumption there is an advantage using methane which also has the lowest carbon emissions among the fossil feedstocks.
- electrolysis process is good for being the green alternative, but the huge requirement for electric power makes hydrogen from electrolysis non beneficial.
- The coal and heavier hydrocarbon feedstocks will be discarded due to high energy requirements and carbon emissions

Selected Process : Using Methane

IMPLEMENTATION OF DESIGN USING DWSIM

Design Method

Choose Components :

1. Methane
2. Water
3. Carbon monoxide
4. Carbon dioxide
5. Hydrogen
6. Nitrogen
7. Ammonia

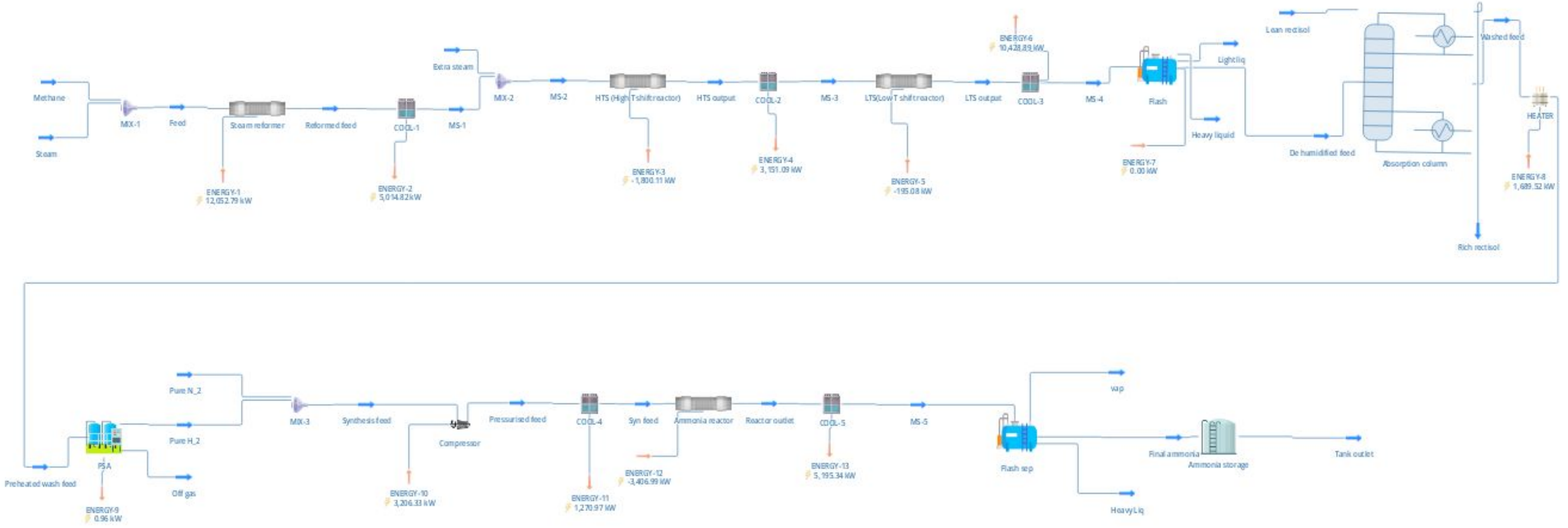
Choose Fluid Package:

- Peng - Robinson

Reaction sets :

1. Water gas shift reaction
2. Steam reforming reaction
3. Haber bosch process

Flow Diagram



Result

Object	Methane	N_2	H_2	Ammonia
Mass flow rate	3600 kg/h	7115.4 kg/h	1534.89 kg/h	3846.16 kg/h
Volumetric Flow rate	1714.34 m^3/h	403.722 m^3/h	1206.21 m^3/h	5.1769 m^3/h

COST ESTIMATION

The purchased equipment cost on a US Gulf Coast basis can be calculated by given equation:

$$C_e = a + bS^n$$

Where a and b are cost constants, S is the size parameter and n is the exponent for that type of equipment. The values for a, b and n are given in table 6.6 in Sinnot & Towler.

All the values were calculated on a US Gulf coast basis from January 2007. At this year the CE index (CEPCI) was 509.7.

To approximate the price in 2022 , all purchased equipment cost had to be multiplied by the ratio of cost in year 2016 and cost in year 2007 as given in equation

$$I_{2022,2007} = 806.9/509.7$$

$$= 1.583$$

Compressor

Cost for one compressor is given by

$$C_e = 490000 + 16800(W)^{0.6}$$

Where W is sizing factor , duty [kW] of the compressor,

from simulation W = 3206.52 kW

$$C_e = 490000 + 16800(3206.52)^{0.6} = \text{Rs. } 2622699.43$$

Material cost factor of stainless steel 304 is 1.3 and multiply it with CE index ratio $I_{2022,2007}$

$$C_e = 26622699.43 * 1.3 * 1.583$$

$$= \text{Rs. } 5397253.159$$

Reactors

For estimating the cost of the reactors,

$$C_e = 53000 + 28000(V)^{0.8}$$

where V is the reactor volume. It can be calculated by

$$V = \hat{V} \tau / \varphi$$

where $\hat{V}$ is the volume flow into the reactor, τ the residence time and the void fraction, φ.

We can get value of $\hat{V}$ and τ from simulation model , φ was assumed to be 0.45 for every case.

1. **HTS(High T shift Reactor) :**

$V = 44.44\ m^3$, $C_e = 53000 + 28000(44.44)^{0.8}$

$= \$\ 635609.11$

2. **LTS(Low T shift Reactor) :**

$V = 33.34\ m^3$, $C_e = 53000 + 28000(33.34)^{0.8}$

$= \$\ 515946.18$

3. **Ammonia Reactor :**

$V = 66.67\ m^3$, $C_e = 53000 + 28000(66.67)^{0.8}$

$= \$\ 858939.41$

Total reactor cost = (cost of HTS + cost of LTS + Ammonia reactor) * material factor * $I_{2022,2007}$

$= \$\ 337919813.9$ = Rs. 27597894305.22

4. Reformer :

The high alloy reformer tubes are expensive and account for a large part of the reformer costs, the volume of the reformer tubes was estimated for the sizing parameter.

$$V = 41.03\ m^3$$

$$C_e = 53000 + 28000(41.03)^{0.8}$$

$$= \$\ 599561.76$$

Material we are using is inconel , material factor of inconel is 1.7.

$$C_e = \$\ 599561.76 * \text{material factor} * I_{2022,2007}$$

$$= \$\ 599561.76 * 1.7 * 1.583$$

$$= \$\ 1613480.652 = \text{Rs. } 131772884.17$$

Heat Exchanger

We have 5 coolers and 1 heater as heat exchanger.

For estimating the cost of the exchangers,

$$C_e = 24000 + 46A^{1'2}$$

where A is the heat transfer Area. It can be calculated by

$$Q = UA\Delta T_{AM}$$

Where Q [W] is the duty of the cooler/heater and U [W/m²K] is the coefficient of the heat transfer.

U is assumed to be 400 W/m²K, which is a typical value for industrial heat exchangers at these conditions.

1. **Cooler 1 :**

   $A = 12.14\ m^2$, $C_e = 24000 + 46(12.14)^{1'2}$

   $= \$\ 24920.06$

2. **Cooler 2 :**

   $A = 13.3\ m^2$ $C_e = 24000 + 46(13.3)^{1'2}$

   $= \$\ 25026.55$

3. **Cooler 3 :**

   $A = 63.87\ m^2$, $C_e = 24000 + 46(63.87)^{1'2}$

   $= \$\ 30747.053$

4. **Cooler 4 :**

   $A = 4.11\ m^2$, $C_e = 24000 + 46(4.11)^{1'2}$

   $= \$\ 24250.82$

5. Cooler 5 :

$A = 29.15\ m^2$, $C_e = 24000 + 46(29.15)^{1'2}$

$= \$\ 26632.23$

6. Heater :

$A = 12.31\ m^2$ $C_e = 24000 + 46(12.31)^{1'2}$

$= \$\ 24935.55$

Total Cost = (cost of cooler 1+cooler 2 +cooler 3 + cooler 4 + cooler 5 + heater) * 1.3 *$I_{2022,2007}$

= 156512.26 * 1.3 * 1.583

= \$ 322086.58 = Rs. 26304794.88

Separators

We have 3 Separator, Flash, Flash sep and PSA

For estimating the cost of the separator,

$$C_e = 15000 + 68^* (m_{shell}^{0'85})$$

where m_{shell} is the shell mass of the separators. It can be calculated by

$$m_{shell} = \pi D_v h \, t_w \rho$$

where tw is the wall thickness(> 2.5mm) ,ρ is the density of the metal which is 8030 kg/m3 for stainless steel 304.

And D_v, minimum vessel diameter = $\sqrt{[4 (V\hat{} / u\pi)]}$

here u , settling velocity = $0.007\sqrt{[(\rho L - \rho V)/ \rho V]}$

h , total height of separator = $h_L + D_v/2 + D_v + 0.4$

here $h_L = V_L / (D_v^2 * \pi) * 4$

$V_L = V\hat{}(10*60)$ [assume hold on time 10 min]

1. **Flash :**

$m_{shell} = 3.14*2.65*58.411*0.0027*8030 = 10543.13$

$C_e = 15000 + 68* (10543.13^{0'85})$

= $ 127430.61

2. Flash sep :

$$m_{shell} = 3.14 * 1.023 * 15.605 * 0.0027 * 8030 = 953.26$$

$$C_e = 15000 + 68 * (953.26^{0'85})$$

$$= \$\ 31439$$

3. PSA :

$$m_{shell} = 3.14 * 4.581 * 20 * 0.0027 * 8030 = 6239.13$$

$$C_e = 15000 + 68 * (6239.13^{0'85})$$

$$= \$\ 88893.82$$

Total C_e = (cost of Flash + cost of flash sep + cost of PSA) * 1.3 * $I_{2022,2007}$

$$= 247763.53 * 1.3 * 1.583 = \$\ 509872.57 = \text{Rs. } 41641267.30$$

Absorber

Assuming 0.5 m between the stages, gave a height of the absorbers to be 9.5 m. The diameter was assumed to be 1.5 m . Total no. of stages 15.

For estimating the cost of the sieve trays,

$$C_e = 110 + 380\, D^{9/5}$$

where D is diameter .

For estimating the rest of cost Absorber,

$$Ce = 15000 + 68\, (m^{0.85})$$

For sieve trays ,

$$C_e = 110 + 380\,(1.5)^{9/5} = 229.018$$

For rest of the absorber,

V_{total} = 24.02, m = 24.02 * 8030 = 112620.558

$$C_e = 15000 + 68\,(112620.558\text{^}0.85)$$

$$= 1352777.651$$

Total cost = (cost of trays + rest of the costs) * 1.3 * $I_{2022,2007}$

= $ 2784352.424

= Rs. 227397923.25

Total Fixed cost

Total fixed capital cost = C_{FC} = $(C_{SS} + C_{NI})(1 + OS)(1 + D\&E + X)$

C_{SS} for all the equipment in material 304 stainless steel

$$F = [(1 + f_p)f_m + (f_{er} + f_{el} + f_i + f_c + f_s + f_l)] = 3.2$$

$$C_{SS} = \sum C_{e,i,SS}\, F \quad = 2371774859$$

C_{NI} costs of the reformer,

$$F = [(1 + f_p) + (f_{er} + f_{el} + f_i + f_c + f_s + f_l)/f_m] = 2.6$$

$$C_{NI} = \sum C_{e,i,NI}\, F \quad = 24306393.91$$

Total fixed capital cost , C_{FC} = (2371774859+24306393.91)(1+0.3) + (1 + 0.3 + 0.1)

= Rs. 3114905630

Steam

We have 2 streams of steam named steam and extra steam.

Cost of steam coal in gujarat = Rs.10886.22/ton

For Extra steam , mass flow = 16.53 ton/h

Cost = 16.53 * 10886.22 = Rs. 179949.22

For Steam , mass flow = 3.97 ton/h

Cost = 3.97 * 10886.22 = Rs. 43196.52

Total cost = Rs. 223145.738/h

Compressor work

Compressor duty , W = 3206.33 kW

Cost of electricity in Gujarat = Rs. 4.57 /kW

Total cost of electricity = 4.57 * 3206.33

= Rs. 14652.928

Methane

Mass flow , m = 3600 kg/h

Cost of methane in Gujarat = Rs. 180.7858/kg

Total cost of Methane = 3600 * 180.7858

= Rs. 650828.86

Total variable cost

Total variable cost = Cost of methane + cost of steam + cost of compressor work

= Rs. 888627.5261

Above cost for one hour of work, calculate for one year,

If plant is operating for 15 hours/ day and total of 330 days/ year

Total variable cost per Annum = 888627.5261 * 15* 330

= Rs. 4398706254

Ammonia

Mass flow = 3846.16 kg/h

Cost of ammonia in Gujarat = Rs.23/kg

Total cost = 3846.16 * 23

= Rs. 88461.68

Total cost per annum = 88461.68 * 15 * 330

= Rs. 437885316

Conclusion

- Ammonia is a very good industrial chemical which is widely use all over the world.
- Most economic method for producing ammonia is by using Methane as feedstock with haber-bosch process.
- Amount of ammonia produced 3846.16 kg/h .
- Total fixed capital cost for ammonia plant is Rs. 3114905630.
- Total variable cost for ammonia plant per annum is Rs. 4398706254.


THANK YOU