

# Ammonia Production using Steam Reforming Process (Plant Design Capacity: 250TPD)

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**Abstract**— Separation of the hydrogen needed for the ammonia synthesis reaction, from its source is difficult. Hydrogen production method is the main source of distinction between the various ammonia production routes. Most of the improvements in the technology regarding the ammonia synthesis were concerned with the hydrogen production step. Hydrogen can be produced by steam reforming, partial oxidation, gasification. The bulk of the world ammonia production is based on the steam reforming. The major hydrogen sources are natural gas, naphtha and coal. In this project different methods available for hydrogen separation from its source are analysed and the best possible way to produce synthesis gas which will form ammonia from natural gas is found out. The mass balance calculation for the 250 tons per day of ammonia production is presented in this work.

**Keywords:** Ammonia synthesis, Steam reforming, Partial Oxidation, Gasification

## I. INTRODUCTION

Ammonia is primarily used as nitrogenous fertilizer and as a raw material of inorganic compounds including nitric acid, ammonium salts, cyanide and organic compounds, such as amines, sulphanylamide and so on. In addition, ammonia is also an excellent refrigerant. Since ammonia is a key raw material for industry and agriculture, the process of ammonia synthesis gases an extremely important position in any economy.

In the ammonia synthesis, nitrogen is combined with hydrogen in a stoichiometric ratio of 1:3 to give ammonia with no by-products. Ammonia itself is used as a fertilizer. About 85% of ammonia consumptions used for the manufacture of fertilizer. Air contains 79% (volume) of nitrogen. So, nitrogen needed for the reaction can be obtained for air. The difficulty lies in separating the hydrogen needed for the reaction from its source. Hydrogen production method is the main source of distinction between the various ammonia production routes.

Most of the improvements in the technology regarding the ammonia synthesis over the past four decades were concerned with the hydrogen production step. Hydrogen can be produced by steam reforming, partial oxidation, and gasification. The bulk of the world ammonia production is based on steam reforming. The major hydrogen sources are natural gas, naphtha and coal. Most of the steam reforming plants use natural gas as feed stock. Natural gas contains fewer impurities, high hydrogen to carbon ration and less percentage of higher hydrocarbons. So natural gas is superior when compared with other feed stocks.

## II. PROCESS DESCRIPTION

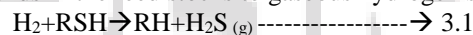
### A. Steam Reforming of Methane

A typical modern ammonia producing plant first converts natural gas or LPG or petroleum naphtha into gaseous hydrogen. The method of producing hydrogen from hydrocarbons is referred to as “steam reforming”. The hydrogen is then combined with nitrogen in the stoichiometric ratio of 3:1 and produce ammonia. The steps involved in this process are (See figure):

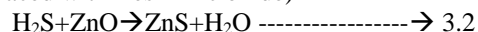
- 1) Feed stock desulfurization
- 2) Primary reforming process
- 3) Secondary reforming process
- 4) Shift conversion
- 5) CO<sub>2</sub> Removal
- 6) Methanation
- 7) Synthesis gas compression and ammonia synthesis

#### 1) Feed stock desulfurization process

The first step in this process is to remove sulfur compounds from the feed stock because sulfur deactivates the catalysts used in the subsequent steps. Sulfur removal requires catalytic dehydrogenation to convert organic sulfur compounds in the feed stocks to gaseous hydrogen sulfide



The gaseous hydrogen sulfide is then passed through a reactor containing zinc oxide (ZnO) where it is converted to solid zinc sulfide (ZnS) in a batch process (i.e., when all the zinc oxide has been converted to zinc sulfide, it is removed and replaced with fresh zinc oxide)

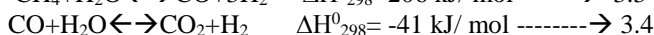


In this way, the sulfur is removed to less than 0.1ppm Sulfur in the gas feed. The zinc sulfide remains in the adsorption bed. The hydrogen for the reaction is usually recycled from the synthesis section.

#### 2) Primary reforming process

The primary reformer is operates at low pressures and high temperatures. The gas from the desulfurizer is mixed with process steam, usually coming from an extraction turbine, and the steam/gas mixture is then heated further to 500°C in the convection section before entering the primary reformer. The primary reformer consists of a large number of high-nickel chromium alloy tubes filled with nickel-containing reforming catalyst. The overall reaction is highly endothermic and additional heat is required to raise the temperature to 800 °C at the reformer outlet. 86% of the CH<sub>4</sub> conversion takes place in the primary reformer.

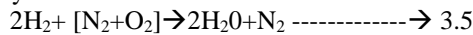
The composition of the gas leaving the primary reformer is given by close approach to the following chemical equilibria:-



### 3) Secondary Reforming Process

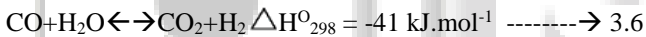
Only 30-40% of the hydrocarbon feed is reformed in the primary reformer because of the chemical equilibrium at the actual operating conditions. The temperature must be raised to increase the conversion. This is done in the secondary reformer by internal combustion of part of the gas with the process air, which also provides the nitrogen for the final synthesis gas. In the conventional reforming process the degree of primary reforming is adjusted so that the air supplied to the secondary reformer meets both the heat balance and the stoichiometric synthesis gas requirement.

The process air is compressed to the reforming pressure and heated further in the primary reformer convection section to around 600 °C. The process gas is mixed with the air in a burner and then passed over a nickel-containing secondary reformer catalyst. The reformer outlet temperature is around 1000 °C, and up to 99% of the hydrocarbon feed (to the primary reformer) is converted, giving a residual methane content of 0.2-0.3% (dry gas base) in the process gas leaving the secondary reformer. The reaction mixture will contact the catalyst at about 1100 to 1200 °C. The process gas is cooled to 350-400 °C in a waste heat steam boiler or boiler/super heater downstream from the secondary reformer.



### 4) Shift Conversion

Carbon monoxide is poisonous the ammonia synthesis catalyst. So it has to be removed. But instead of removing carbon monoxide it is converted to carbon dioxide and then removed. This is known as shift conversion. This not only converts the carbon monoxide but also produces hydrogen. This is exothermic reaction.



The shift conversion reaction is independent of pressure. Shift conversion can be carried out in single stage or in number of stages. If the shift conversion is carried out at high temperature, it is called high temperature shift (HTS) conversion. The outlet mixture of secondary reformer cooled to 360 °C and then enters into the HTS and outlet temperature of HTS is 400 °C. If the shift conversion is at low temperature then it is called low temperature shift (LTS) conversion. For LTS the inlet temperature is 400 °C and products will be obtained at 200 °C. The catalysts used for HTS conversion and LTS conversion are chromia promoted iron oxide and ZnO, Al<sub>2</sub>O<sub>3</sub>, CuO mixture supported on alumina. Since these reactions are exothermic, heat produced must be removed after the reaction. The carbon monoxide conversion is more when employed in multiplied stages rather than a single stage. Isothermal shift conversion is one, where the heat produced due to the reactions is removed within the reactor by passing water through the tubes.

### 5) CO<sub>2</sub> Removal

This process is operated at high pressures and low temperatures. The process gas from the low temperature shift converter contains mainly H<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub> and the excess process

steam. The gas is cooled and most of the excess steam is condensed before it enters the CO<sub>2</sub> removal system.

The carbon dioxide is then removed either by absorption in aqueous ethanolamine solutions or by adsorption in pressure swing adsorbers (PSA) using proprietary solid adsorption media. The CO<sub>2</sub> is removed in a chemical or a physical absorption process. The solvents used in chemical absorption processes are mainly aqueous amine solutions (Mono Ethanolamine (MEA), Activated Methyl Diethanolamine (aMDEA) or hot potassium carbonate solutions. Physical solvents are glycol dimethyl ethers (Selexol), propylene carbonate and others.



### 6) Methanation

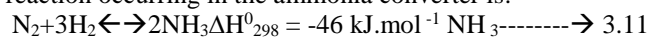
This process is operated at 280 °C to 350 °C, depending on the catalyst activity and gas consumption. The small amounts of CO and CO<sub>2</sub>, remaining in the synthesis gas, are poisonous for the ammonia synthesis catalyst and must be removed by conversion to CH<sub>4</sub> in the methanator before compression of the hydrogen and nitrogen to ammonia synthesis pressure.



The reactions take place at around 400 °C in a reactor filled with a nickel containing catalyst. Methane is an inert gas in the synthesis reaction, but the water must be removed before entering the converter. This is done firstly by cooling and condensation downstream of the methanator and finally by condensation/absorption in the product ammonia in the loop or in a make-up gas drying unit.

### 7) Synthesis gas compression and Ammonia synthesis

The gas mixture is now cooled, compressed and fed into the ammonia synthesis loop (see fig 3.1). A mixture of ammonia and unreacted gases which have already been around the loop are mixed with the incoming gas stream and cooled to 5 °C. The ammonia present is removed and the unreacted gases heated in a temperature range of 350-550 °C at a pressure in the range of 100-250 bar and passed over an iron catalyst. Under these conditions 14% of the hydrogen and the nitrogen are converted to ammonia. It is a highly exothermic reaction. The outlet gas from the ammonia converter is cooled from 200 °C to 30 °C. This cooling process condenses more than half the ammonia, which is then separated out. The remaining gases are mixed with more cooled, compressed incoming gas. The reaction occurring in the ammonia converter is:



The ammonia that is formed is separated from the recycle gas by cooling/condensation, and the reacted gas is substituted by the fresh make-up synthesis gas, thus maintaining the loop pressure. The liquid ammonia (which is also contains significant levels of ammonia) is removed and sent to the ammonia recovery unit.

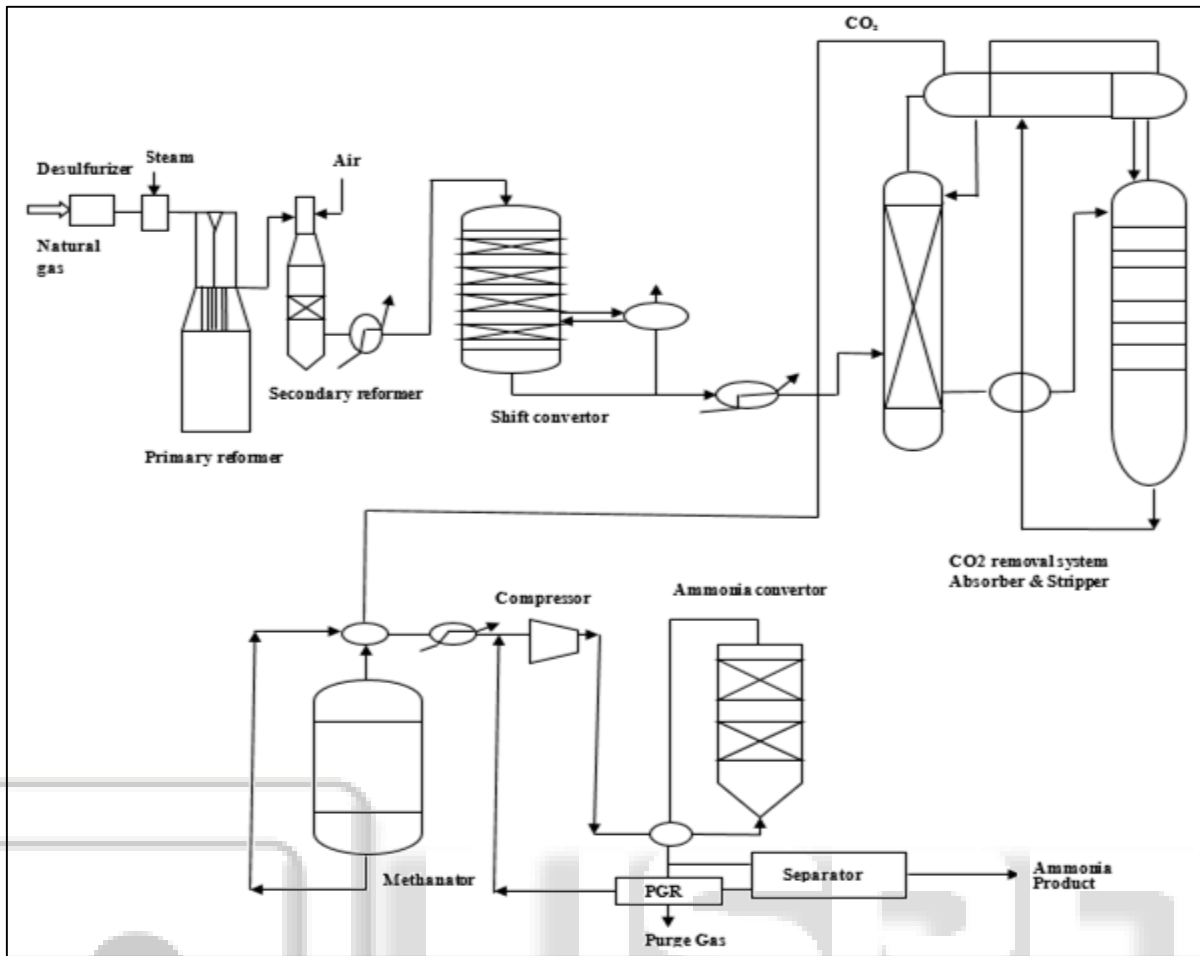


Fig. 3.1: Steam reforming process flow diagram

III. MATERIAL BALANCES

According to conservation of mass theory, mass into the reactor is equal to mass out of the reactor. Here, main objective is to find the flow rates and the unknown compositions. For that overall balance of flow rates and elemental balance are required.

Here this following tables and figures show the elemental and overall balance for every equipment.

A. Feed (i.e. Natural Gas) Composition

S NO	COMPENENT	VOL%
1	O <sub>2</sub>	0.13
2	N <sub>2</sub>	1.24
3	CO <sub>2</sub>	0.11
4	CH <sub>4</sub>	96.98
5	C <sub>2</sub> H <sub>6</sub>	1.01
6	C <sub>3</sub> H <sub>8</sub>	0.23
7	i-C <sub>4</sub> H <sub>10</sub>	0.05
8	n-C <sub>4</sub> H <sub>10</sub>	0.05
9	i-C <sub>5</sub> H <sub>14</sub>	0.02
10	n-C <sub>5</sub> H <sub>14</sub>	0.03
11	C <sub>6</sub>	0.15

Table 4.1: Components volumetric % in Natural Gas

1) Carbon Number:

Average number carbon atoms in a given sample of substance.

$$N_C = \frac{(1 \times 0.11) + (1 \times 96.98) + (2 \times 1.01) + (3 \times 0.23) + (4 \times 0.05) + (4 \times 0.05) + (5 \times 0.02) + (5 \times 0.03) + 6 \times 0.15}{100}$$

= 1.0135

2) Hydrogen number:

Average number hydrogen atoms in a given sample of substance.

$$N_H = \frac{(4 \times 96.98) + (6 \times 1.01) + (8 \times 0.23) + (10 \times 0.05) + (10 \times 0.05) + (14 \times 0.02) + (14 \times 0.03)}{100}$$

= 3.9752

Mole fractions of Carbon and hydrogen:

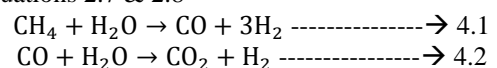
$$X_C = \frac{N_C}{N_C + N_H} = \frac{1.0135}{1.0135 + 3.9752} = 0.203$$

$$X_H = \frac{N_H}{N_C + N_H} = \frac{3.9752}{1.0135 + 3.9752} = 0.797$$

B. Primary Reforming Section

Main reactions in this section:

Use equations 2.7 & 2.8



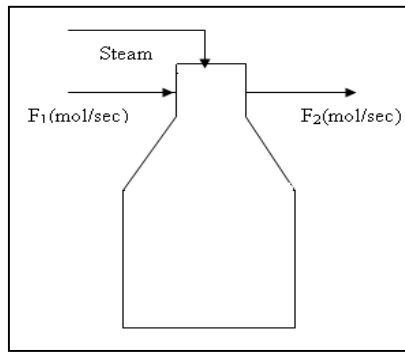


Fig. 4.1: Primary reforming section block diagram

S NO	COMPONENT	Outlet mole fraction
1	$X_{H_2}$	0.6651
2	$X_{N_2}$	0.0082
3	$X_{CO}$	0.0767
4	$X_{CO_2}$	0.1086
5	$X_{Ar}$	0.0001
6	$X_{CH_4}$	0.1413

Table 4.2: Primary reforming section outlet compositions

Carbon balance

$$X_C * F_1 = F_2 * (X_{CO} + X_{CO_2} + X_{CH_4})$$

$$F_1 = 0.6215 F_2 \quad \text{----- (1)}$$

$$\text{Steam added} = 3 * X_C * F_1 = 0.609 F_1$$

### C. Secondary Reformer Section

Here the assumption is, complete conversion of carbon is taking place by adding air.

Main reactions in this section:

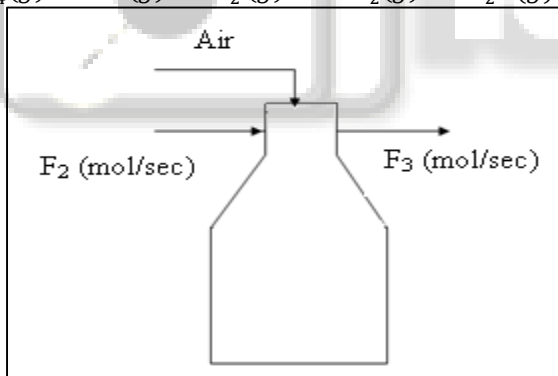
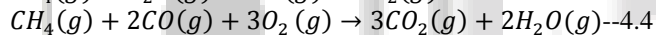
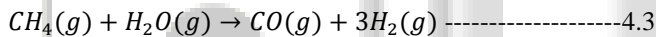


Fig. 4.2: Secondary reforming section block diagram

S NO	COMPONENT	inlet mole fractions	Out let mole fractions
1	$X_{H_2}$	0.6651	0.5533
2	$X_{N_2}$	0.0082	0.2379
3	$X_{CO}$	0.0767	0.1211
4	$X_{CO_2}$	0.1086	0.0788
5	$X_{Ar}$	0.0001	0.0029
6	$X_{CH_4}$	0.1413	0.006

Table 4.3: Secondary reforming section compositions

By adding air,

$$0.21 * A = 2 * X_{CH_4} * F_2$$

$$A = 3.1104 F_2 \implies A = 1.9331 F_1$$

Carbon balance

$$F_2 * (X_{CO} + X_{CO_2} + X_{CH_4}) = F_3 * (X_{CO} + X_{CO_2} + X_{CH_4})$$

$$F_3 = 1.5862 F_2$$

$$F_3 = 0.9858 F_1 \quad \text{----- (2)}$$

### D. High Temperature Shift Conversion Section

Main reaction in this section

Use equation 2.10

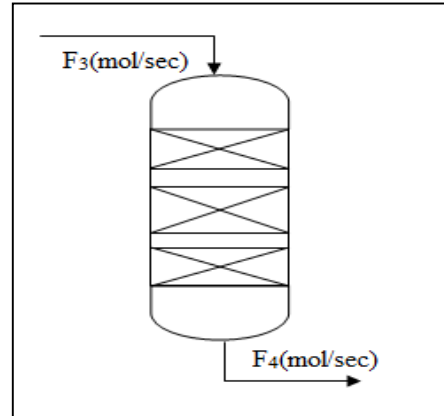
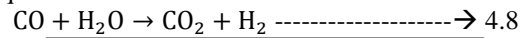


Fig. 4.3: High temperature shift convertor block diagram

S NO	COMPONENT	Inlet mole	Outlet mole
1	$X_{H_2}$	0.5533	0.5888
2	$X_{N_2}$	0.2379	0.219
3	$X_{CO}$	0.1211	0.032
4	$X_{CO_2}$	0.0788	0.1521
5	$X_{Ar}$	0.0029	0.0026
6	$X_{CH_4}$	0.006	0.005
7	$X_{\text{steam}}$	-	0.0005

Table 4.4: High temperature shift conversion section compositions

Carbon balance

$$F_3 * (X_{CO} + X_{CO_2} + X_{CH_4}) = F_4 * (X_{CO} + X_{CO_2} + X_{CH_4})$$

$$F_4 = 1.088 F_3$$

$$F_4 = 1.072 F_1 \quad \text{----- (3)}$$

### E. Low Temperature Shift Conversion Section

Main reaction in this section:

Use equation 2.10

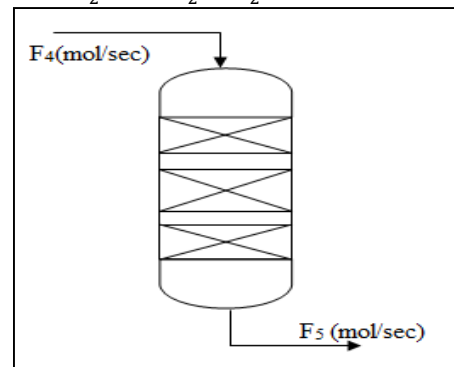
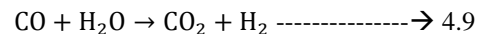


Fig. 4.4: Low temperature shift convertor block diagram

S NO	COMPONENT	Inlet mole	Outlet
1	$X_{H_2}$	0.5888	0.6001
2	$X_{N_2}$	0.219	0.219
3	$X_{CO}$	0.032	0.0036
4	$X_{CO_2}$	0.1521	0.1694

5	$X_{Ar}$	0.0026	0.0025
6	$X_{CH_4}$	0.005	0.0054
7	$X_{steam}$	0.0005	-

Table 4.5: Low temperature shift conversion section compositions

Carbon balance

$$F_4 * (X_{CO} + X_{CO_2} + X_{CH_4}) = F_5 * (X_{CO} + X_{CO_2} + X_{CH_4})$$

$$F_5 = 1.0599F_4$$

$$F_5 = 1.1367F_1 \text{----- (4)}$$

F. CO<sub>2</sub> Absorber section

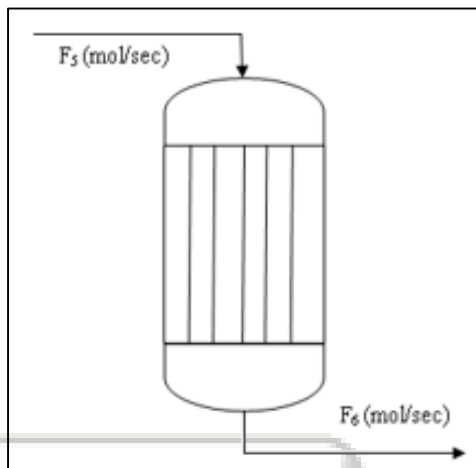


Fig. 4.5: CO<sub>2</sub> absorber section block diagram

S NO	COMPONENT	Inlet mole	Outlet
1	$X_{H_2}$	0.6001	0.7202
2	$X_{N_2}$	0.219	0.262
3	$X_{CO}$	0.0036	0.00425
4	$X_{CO_2}$	0.1694	0.004065
5	$X_{Ar}$	0.0025	0.00299
6	$X_{CH_4}$	0.0054	0.006457

Table 4.6: CO<sub>2</sub> absorber section compositions

G. Methanator Section

Main reactions in this section

Use equations 2.13 & 2.14

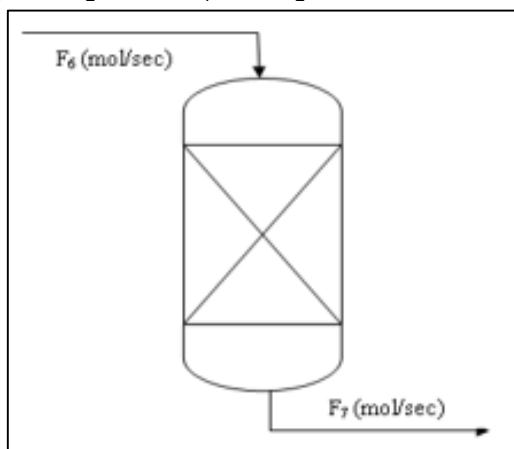
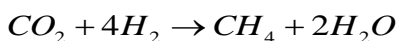
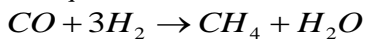


Fig. 4.6: Methanator section block diagram

Hydrogen balance

$$F_6 = 0.9547 F_1 \text{----- (6)}$$

S NO	COMPONENT	Inlet mole	Outlet
1	$X_{H_2}$	0.7202	0.7232
2	$X_{N_2}$	0.262	0.264
3	$X_{CO}$	0.00425	0.011
4	$X_{CO_2}$	0.004065	0.0018
5	$X_{Ar}$	0.00299	
6	$X_{CH_4}$	0.006457	

H. Synthesis loop section

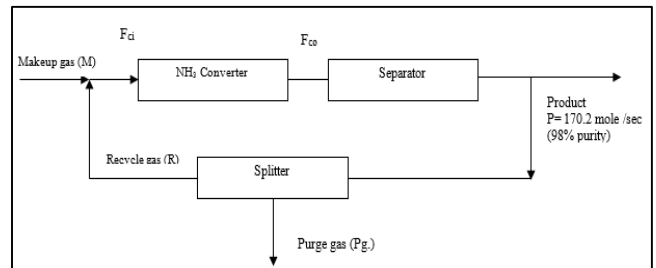


Fig. 4.7: Synthesis loop section block diagram

S NO	COMPONENT	Inlet mole	Purge gas	Recycle	Product
1	$X_{H_2}$	0.7232	0.7225	0.7225	-
2	$X_{N_2}$	0.264	0.2624	0.2624	-
3	$X_{NH_3}$	-	0.012	0.012	0.98
4	$X_{inerts}$	0.0011	0.0031	0.0031	0.02

Table 4.8: Synthesis loop section compositions

I. Overall Balance at synthesis loop

$$M = Pg + P$$

$$M = Pg + 612.74 \text{----- (1)}$$

Overall inert balance

$$M(X_{inert}) = Pg(X_{inert}) + P(X_{inert})$$

$$M(0.0128) = \frac{x}{4}(0.0031) + (170.2 \times 0.02) \text{----- (2)}$$

Form (1) & (2) equations,

$$M = 1061.55 \text{Kmol/hr} ; x = 1819.28 \text{Kmol/hr}$$

$$Pg = \frac{x}{4} = 452.82 \text{Kmol/hr}$$

$$R = \frac{3x}{4} = 378.99 \text{ mole/sec}$$

At Mixing point,

$$M + R = F_{ci} \implies F_{ci} = 2432.01 \text{Kmol/hr}$$

Component balance at mixing point,

$$(X_{H_2})_{F_{ci}} = \frac{MX_{(H_2)} + RX_{(H_2)}}{F_{ci}} = 0.7228$$

$$(X_{N_2})_{F_{ci}} = \frac{MX_{(N_2)} + RX_{(N_2)}}{F_{ci}} = 0.2630$$

$$(X_{NH_3})_{F_{ci}} = \frac{MX_{(NH_3)} + RX_{(NH_3)}}{F_{ci}} = 0.00673$$

$$(X_{inert})_{F_{ci}} = \frac{MX_{(inert)} + RX_{(inert)}}{F_{ci}} = 0.00735$$

S NO	Stream	Flow rate(Kmol/hr)
1	M	1067.55
2	$F_{ci}$	2432.01
3	$F_{co}$	2432.02
4	$P_g$	454.82
5	R	1364.46

Table 4.9: Synthesis loop section flow rates

J. Methanator Section

Its outlet composition is same as inlet composition of make-up gas.

S NO	Stream	Flow rate (Kmol/hr)
1	H <sub>2</sub>	772.05
2	N <sub>2</sub>	281.83
3	Inert	1.366

Table 4.10: Methanator section outlet flow rates

S no	Component	Mole fractions	Inlet flowrate(Kmol/hr)
1	H <sub>2</sub>	0.7202	765.29
2	N <sub>2</sub>	0.262	278.40
3	CO	0.00425	4.516
4	CO <sub>2</sub>	0.004065	4.319
5	Ar	0.00299	3.177
6	CH <sub>4</sub>	0.006457	6.861

Table 4.11: Methanator section inlet flow rates and compositions

K. CO<sub>2</sub> Absorber section

S NO	COMPONENT	Inlet mole fraction	Outlet Flow rate (kmol/hr)	Inlet flow rate (Kmol/hr)
1	X <sub>H<sub>2</sub></sub>	0.6001	765.29	762.75
2	X <sub>N<sub>2</sub></sub>	0.219	278.40	268.19
3	X <sub>CO</sub>	0.0036	4.516	4.575
4	X <sub>CO<sub>2</sub></sub>	0.1694	4.319	215.31
5	X <sub>Ar</sub>	0.0025	3.177	3.051
6	X <sub>CH<sub>4</sub></sub>	0.0054	6.861	6.86

Table 4.12: CO<sub>2</sub> absorber section compositions and flow rates

L. Total Flow Rates of the Process

Flow rate	Kmol/hr
F1	1118.20
F2	694.96
F3	1102.32
F4	1199.27
F5	1271.05
F6	1062.62
A	2161.59
Steam	680.98

Table 4.13: Total flow rates of the ammonia plant

IV. ENERGY BALANCES

A. Primary Reformer

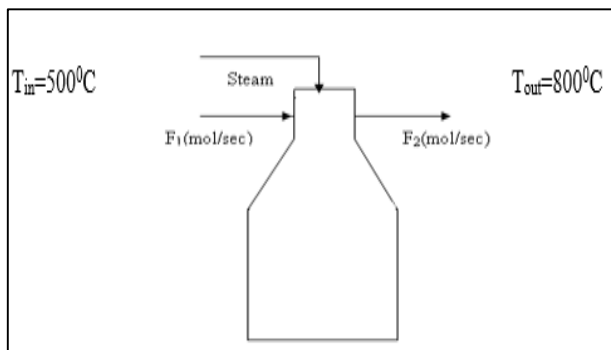


Fig. 5.1: Primary Reformer block diagram

INLET(T <sub>in</sub> =500°C)			OUTLET(T <sub>out</sub> =800°C)		
Component	Phase	Molar flow rate (kmol/hr)	Heat capacity (kJ/mol)	Molar flow rate (kmol/hr)	Heat capacity (kJ/mol)
CH <sub>4</sub>	Gas	1084	H1	98.2	H6
CO	Gas	-	-	53.3	H7
N <sub>2</sub>	Gas	13.86	H3	5.698	H8
CO <sub>2</sub>	Gas	1.23	H4	75.47	H9
H <sub>2</sub> O	Liq	680.98	H5	462.21	H10
H <sub>2</sub>	Gas	-	-	-	-

Table 5.1: Molar flow rates of primary reformer

B. Calculation Data for Heat Capacity

Component	Degree	A	B*10 <sup>-2</sup>	C*10 <sup>-5</sup>	D*10 <sup>-9</sup>
CH <sub>4</sub>	C	34.31	5.469	0.3661	-11
	K	19.87	5.021	1.268	-11
CO	C	28.95	0.411	0.3548	-2.22
N <sub>2</sub>	C	29.00	0.2199	0.5723	-2.87
CO <sub>2</sub>	C	36.19	4.233	-2.887	7.464
H <sub>2</sub>	C	28.84	0.00765	0.3288	-0.8698

Table 5.2: heat capacity constants

Temp(K)	CO	N <sub>2</sub>	CO <sub>2</sub>	H <sub>2</sub>
773	13.592	13.481	20.260	13.223
800	15.177	15.046	22.806	14.702
1000	21.690	21.463	33.397	20.680
1073	24.374	23.869	37.402	22.705
1100	25.035	24.763	38.884	23.719

Table 5.3: Ideal gas sensible enthalpies (h<sub>r</sub>-h<sub>298</sub>)(kJ/mol)(perry's,1999)

component	phase	INLET(AT 500°C)		OUTLET(800°C)	
		Molar flow rate M <sub>1</sub> (mol/hr)	Heat capacity H <sub>in</sub> (KJ/mol)	Molar flow rate M <sub>2</sub> (mol/hr)	Heat capacity H <sub>out</sub> (KJ/mol)
CH <sub>4</sub>	Gas	108400	23.09	98200	-54.045
CO	Gas	-	-	53300	-86.156
N <sub>2</sub>	Gas	13860	14.242	5698	23.869
CO <sub>2</sub>	Gas	1230	21.344	75470	-355.898
H <sub>2</sub>	Gas	-	-	462210	22.705
H <sub>2</sub> O	Liquid	680980	-241.841	-	-

Table 5.4: Calculation table for enthalpies at primary reformer

COMPONANT	Q <sub>in</sub> (KJ/sec)	Q <sub>out</sub> (KJ/s)
CH <sub>4</sub>	6952.65	-1474.23

CO	-	-1275.58
N <sub>2</sub>	54.83	37.78
CO <sub>2</sub>	7.292	-7461
H <sub>2</sub>	-	2915.13
H <sub>2</sub> O	-45746.9	-
TOTAL	-38732.128	-7257.9

Table 5.5: components heat energies at primary reformer  
Additional heat required,

$Q = \sum Q_{out} - \sum Q_{in}$   
 $= (-7257.9 + 38732.128) * 10^3 \text{ j/s}$   
 $Q = 3.147 * 10^7 \text{ j/s}$   
 Steam enthalpy = 2802.3 kJ/kg = 50491.9 j/mol  
 Enthalpy content in steam = flow rate \* enthalpy  
 $= 680.98 (\text{k mol/hr}) * 50491.9 (\text{j/mol}) = 9.55 * 10^6 \text{ j/s}$   
 Heat utility of convection zone =  $3.147 * 10^7 - 0.955 * 10^7$   
 $= 2.192 * 10^7 \text{ j/s}$   
 Calorific value of CH<sub>4</sub> = 39383.2 kJ/m<sup>3</sup>  
 Amount of CH<sub>4</sub> required = 0.556 m<sup>3</sup>/s

C. Secondary Reformer

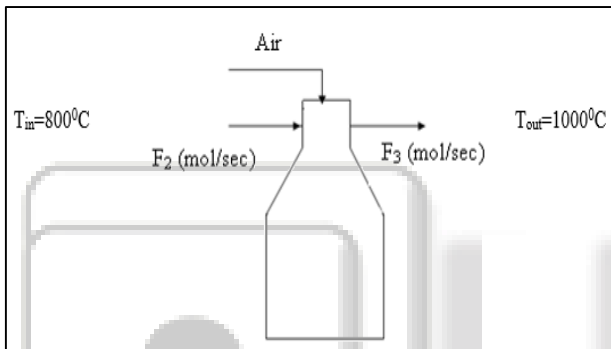


Fig. 5.2: Secondary Reformer block diagram

Component	Input (T <sub>in</sub> =800°C)		Output (T <sub>out</sub> =1000°C)	
	Molar flow rate (mol/hr)	Heat capacity H <sub>in</sub> (kJ/mol)	Molar flow rate (mol/hr)	Heat capacity H <sub>out</sub> (kJ/mol)
CH <sub>4</sub>	98200	-54.045	6613.92	-59.16
CO	53300	-86.156	133490.952	-79.59
O <sub>2</sub>	454000	25.351	45400	32.37
H <sub>2</sub>	462210	22.705	60993.656	29.074
CO <sub>2</sub>	75470	-355.89	86862.816	-344.88
N <sub>2</sub>	1707650	23.869	262241.928	30.596

Table 5.6: heat capacity calculation at secondary reformer

Component	Q <sub>in</sub> (KJ/s)	Q <sub>out</sub> (KJ/s)
CH <sub>4</sub>	-1474227.5	-108688.75
CO	-1492400	-10624544.87
O <sub>2</sub>	3197042.8	4082216.66
H <sub>2</sub>	2915132.79	4925899.875
CO <sub>2</sub>	-7461006.128	-8321578.42
N <sub>2</sub>	11322193.85	2228036.56
TOTAL	7006735.812	-7818658.945

Table 5.7: Heat energies at Primary Reformer

$Q = Q_{out} - Q_{in}$   
 $= -7818658.945 - 7006735.812$   
 $= -1.48 * 10^7 \text{ j/s}$

D. High Temperature Shift Converter

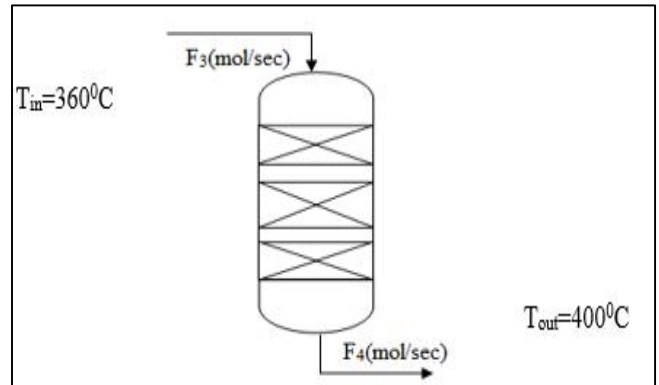


Fig. 5.3: High Temperature Shift Converter block diagram

Component	Inlet (T <sub>in</sub> =360°C)		Outlet (T <sub>out</sub> =400°C)	
	Molar flowrate (Kmol/hr)	Heat capacity H <sub>in</sub> (kJ/mol)	Molar flowrate (mol/hr)	Heat capacity H <sub>out</sub> (kJ/mol)
CO	133.495	-74.85	38.376	1.233
H <sub>2</sub> O	-	-26.04	0.5996	1.479
CO <sub>2</sub>	86.865	-34.127	182.409	1.942
CH <sub>4</sub>	6.614	-44.22	5.996	2.228
H <sub>2</sub>	609.94	-19.296	706.130	1.175
N <sub>2</sub>	262.25	-20.69	262.64	1.218

Table 5.8: heat capacity calculations at HTSC

$Q_{in} = \sum n\Delta H = (133.495 * -74.85) + (0 * -26.04) + (86.864 * -34.127) + (609.94 * -19.296) + (6.614 * -44.22) + (262.25 * -20.69)$   
 $= -3385600.94 \text{ J/s}$   
 $Q_{out} = \sum n\Delta H = (38.376 * 1.233) + (0.5996 * 1.478) + (182.402 * 1.942) + (706.130 * 1.175) + (5.996 * 2.228) + (262.64 * 1.218)$   
 $= 173931 \text{ J/s}$   
 $Q = Q_{out} - Q_{in}$   
 $= 173931 - (-3385600.94)$   
 $= 3559 \text{ KJ/s}$

E. Low Temperature Shift Converter

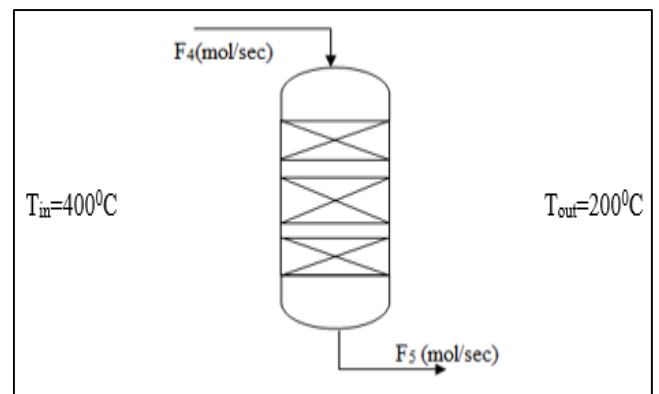


Fig. 5.4: Low Temperature Shift Converter block diagram

component	Inlet(T <sub>in</sub> =400°C)		Outlet(T <sub>out</sub> =200°C)	
	Molar flowrate (kmol/hr)	Heat capacity H <sub>in</sub> (kJ/mol)	Molar flowrate (kmol/hr)	Heat capacity H <sub>out</sub> (kJ/mol)
CO	38.376	1.233	4.578	-6.095
H <sub>2</sub> O	0.5996	1.479	-	-7.204
CO <sub>2</sub>	182.409	1.942	215.42	-9.319
H <sub>2</sub>	706.13	1.175	763.12	-5.86
CH <sub>4</sub>	5.996	2.228	6.867	-10.145
N <sub>2</sub>	262.64	1.218	278.49	-5.996

Table 5.10: Heat capacities at LTSC

$$Q_{in} = \sum n\Delta H = (38.376*1.233)+(0.5996*1.478)+(182.402*1.942)+(706.130*1.175)+(5.996*2.228)+(262.64*1.218)$$

$$=173.931k J/s$$

$$Q_{out} = \sum n\Delta H = (4.578*-6.095)+(0)+(215.42*9.319)+(763.12*-5.86)+(6.867*-10.145)+(278.49*-5.996)$$

$$= -916.310k J/s$$

$$Q=Q_{out}-Q_{in}$$

$$= -0.109*10^7 J/s$$

F. Methanator

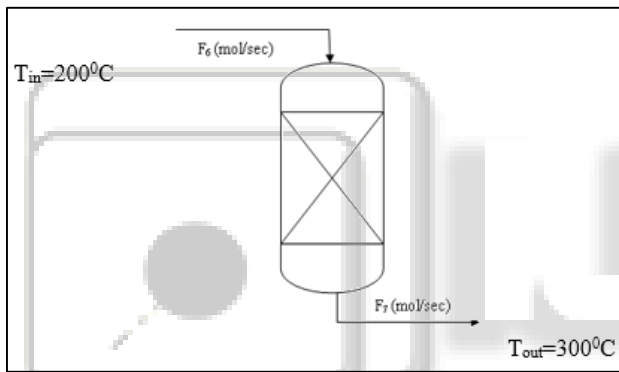


Fig. 5.5: Methanator block diagram

component	Inlet(T <sub>in</sub> =200°C)		Outlet(T <sub>out</sub> =300°C)	
	Molar flow rate (kmol/hr)	Heat capacity H <sub>in</sub> (kJ/mol)	Molar flow rate (kmol/hr)	Heat capacity H <sub>out</sub> (kJ/mol)
CO	4.52	-110.52	-	-
H <sub>2</sub>	762.29	5.86	772.05	-3.251
CH <sub>4</sub>	6.86	10.145	-	-
H <sub>2</sub> O	-	-	-	-
N <sub>2</sub>	278.41	5.996	281.83	-3.026

Table 5.11: heat capacities at methanator

$$Q_{in} = \sum n\Delta H = (4.52*-110.52)+(762.29*5.86)+(6.86*10.145)+(278.41*5.996) = 635998 J/s$$

$$Q_{out} = \sum n\Delta H = (772.05*-3.251)+(281.03*-3.026) = -373639 J/s$$

$$Q=Q_{out}-Q_{in} = -1.009*10^6 J/s$$

V. HEAT RECOVERY

A. Heat Recovery between 2<sup>o</sup> Reformer & HTSC

$$Q = \dot{m}*(C_p \Delta T + \lambda)$$

$$\lambda = c_1(1 - Tr)C_1(1 - Tr)^{c_2+c_3Tr+c_4Tr^2}$$

$$Tr = \frac{T}{T_c}$$

T<sub>c</sub> for steam 374.15 °C or 647.3K (Perry's handbook, 7<sup>th</sup> ed)

C1	C2	C3	C4
5.2*10 <sup>7</sup>	0.3199	-0.212	0.25795

Table 6.1: Constants for latent heat calculation(perry's handbook.7<sup>th</sup> ed)

From table 6.1,  
 $\lambda = 4.0776*10^7 J/kmol$   
 $\dot{m} = 1.48*10^7 / [(4180*75)+(4.0776*10^7)]$   
 $= 0.363 kmol/s$

B. Heat recovery between HTSC & LTSC

$$[Q-(q_{in})_{LTSC}] = \dot{m}[(4180*75)+4.0776*10^7]$$

$$\dot{m} = 0.0862 kmol/s$$

C. Heat Recovery at LTSC

$$Q = mcp\Delta T + \lambda m$$

$$Q = 1.09 \times 10^6 J/sec$$

$$C_p = 4180 j/kmol °C$$

$$\Delta T = 100 - 25 °C = 75 °C$$

$$\Lambda = 4.0776*10^7 J/kmol$$

$$1.09*10^6 = m[(4180*75)+(4.0776*10^7)]$$

$$m = 0.026 kmol/sec$$

D. Heat Recovery at Methanator

$$Q = 1.01*10^6 J/s$$

$$C_p = 4180 J/kmol °C$$

$$\lambda = 4.0776*10^7$$

$$\dot{m} = Q / [C_p \Delta T + \lambda]$$

$$= 1.01*10^6 / [(4180*75 + 4.0776*10^7)] = 0.0245 kmol/s$$

VI. PROCESS DESIGN

A. CO<sub>2</sub> Absorber Design

1) Methodology:

a) Determination of VLE data at operating pressure  
 There are 3 different methods to find equilibrium data among which the suitable will be selected.

b) Experimental VLE Data

This method is appropriate when operating pressure is atmospheric or vacuum. It's not valid for high operating pressures.

c) From Literature

VLE data from literature can be used, if available at operating pressure.

Examples are

- Vapour-Liquid Equilibrium Data by Chu, Ju-chin et al(1956).
- Perry's Chemical Engineers Handbook, 7<sup>th</sup> Edition by Perry and Green, McGraw- Hill, USA, 1998.
- Azeotropic Data, 3 Vol., 2<sup>nd</sup> Ed. By Gmehling, J., Wiley-VCH, Germany, 2004.

2) Theoretical VLE Data

For the ideal VLE, Raoult's Law is applicable.

$$y_i P_t = x_i P_i^{sat}$$

Where,

y<sub>i</sub> - Mole fraction of component i in vapor phase

P<sub>t</sub> - Operating pressure, Kpa

x<sub>i</sub> - Mole fraction of component i in liquid phase

P<sub>i</sub><sup>sat</sup> - Vapour Pressure of pure liquid i at the given temperature, Kpa



**B. Method:**

Bubble point Calculations for binary system,

$$P_t = X_1 P_1^{sat} + (1-X_1) P_2^{sat}$$

$P_1^{sat}$ ,  $P_2^{sat}$  can be calculated using Antoine equation at given temperature,

Antoine equation is:

$$\ln P_1^{sat} = A - \frac{B}{T+C}$$

A,B,C values are taken for particular components in temperature ranges.

$y_i$  can be calculated using Raoult's law.

For non-ideal system,

$$y_i \theta_i P_t = x_i P_i^{sat} \gamma_i$$

Where,

$\theta_i$ -Fugacity coefficient of component i

$\gamma_i$ -Activity coefficient of component i

**C. Procedure for Calculating tower Diameter**

$F_{LG}$  factor can be calculated as,

$$F_{LV} = \frac{L_1}{G_1} \sqrt{\frac{\rho_G}{\rho_L}}$$

Where,

$L_w$ ,  $G_w$  = Mass velocity of liquid, gas (lb/hr.)

$\rho_G$ ,  $\rho_L$  = Density of gas, liquid (lb/ft<sup>3</sup>)

From Graph  $F_{LV}$  Vs CSB, get the value of Capacity parameter for corresponding  $F_{LG}$ .

Gas velocity through the net area at flooding

$$U_{nf} = C_{SB} \left( \frac{\rho_G}{\rho_L - \rho_G} \right)^{0.5} \left( \frac{\sigma}{20} \right)^{0.2}$$

Linear Design gas velocity

$$U_n = \% \text{ flooding} * U_{nf}$$

$$\text{Volumetric flow rate} = \frac{\text{mass flow rate}}{\text{density}} \text{ ft}^3/\text{s}$$

Cross-sectional area of tower

$$\text{Area} = \frac{\text{volumetric flow rate}}{\text{vapor velocity}} \text{ ft}^2$$

Column Diameter,

$$D_c = \left( \frac{\text{Area} * 4}{\pi} \right)^{1/2}$$

**D. Provisional Area calculation**

Downcomer area

$$A_d = \% A_T$$

Net area

$$A_n = A_T - A_d$$

Active area

$$A_a = A_T - 2A_d$$

Hole area

$$A_h = \% A_a$$

Hole diameter

$$\frac{A_h}{A_p} = 0.906 \left[ \frac{d_h}{p'} \right]^2$$

Pressure drop

$$h_t = h_d + h_r + h_w + h_{ow}$$

Dry plate pressure drop

$$h_d = 51 \left[ \frac{U_h}{C_0} \right]^2 \frac{\rho_g}{\rho_l}$$

$U_h$  hole velocity m/s

$C_0$  Orifice coefficient

Residual head

$$h_r = \frac{12.5 * 10^3}{\rho_l}$$

Weir liquid crest

$$h_{ow} = 750 \frac{L_w}{\rho_l l_w}$$

$L_w$  liquid flow rate

$l_w$  weir length

$\rho_l$  liquid density

Calculation of column diameter

**E. Assumptions**

Triangular pitch

Weir height – 50mm

Pressure drop 100mm

**1) Material Balance**

Here balance is used to determine the liquid flow rate at the bottom section of the absorption tower

S NO	X	Y
1	0	0
2	0.1	0.002
3	0.2	0.004
4	0.25	0.008
5	0.3	0.016
6	0.35	0.03
7	0.4	0.052
8	0.48	0.08
9	0.49	0.09

Table 8.1: Equilibrium data for absorption of CO<sub>2</sub> in MEA

Slope  $m = 0.2259$

Equilibrium equation

$$Y = 0.2259 X$$

Material balance

$$G_s(y_1 - y_2) = L_s(x_1 - x_2)$$

$$1055.73(0.169 - 0.0039) = L_s(0.7481 - 0)$$

$$(L_s)_{min} = 232.99 \text{ k mol/hr}$$

Actual liquid flow reate is 1.25 times the original

$$L_s = 1.25 * 232.99$$

$$= 291.24 \text{ k mol/hr}$$

The liquid at the bottom of the tower

$$L_1 = L_s + \text{flow rate of CO}_2 \text{ absorber}$$

$$= 291.24 + 210.95$$

$$= 502.19 \text{ k mol/hr}$$

**2) Number of stages**

S NO	X	Y
1	0	0
2	0.1	0.0245
3	0.2	0.0535
4	0.3	0.0883
5	0.4	0.131
6	0.5	0.184
7	0.6	0.253
8	0.7	0.345
9	0.8	0.475
10	0.9	0.67
11	1	1

Table 8.2: Equilibrium data for finding no of stages

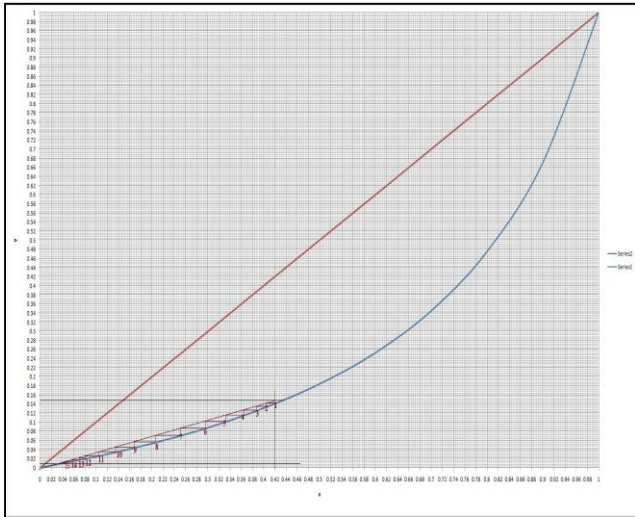


Fig. 8.1: finding No of theoretical plates

F. Diameter Calculations

Gas density  $\rho_g = 0.452 \text{ kg/m}^3$

Liquid density  $\rho_L = 930 \text{ kg/m}^3$

$L_1 = 502.19 \text{ k mol/hr}$

$G_1 = 1271.05 \text{ k mol/hr}$

Flow parameter

$$F_{LV} = \frac{502.19}{1271.05} \sqrt{\frac{0.452}{930}}$$

$$= 0.0099 \approx 0.01$$

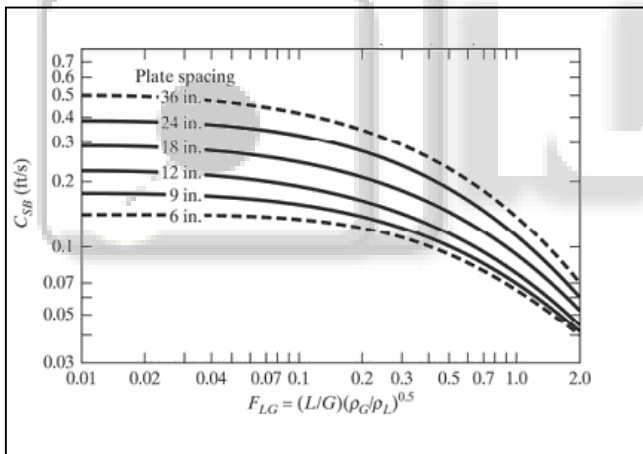


Fig. 8.2: Souder-Brown constant ( $C_{SB}$ ) at flooding condition as a function of the flow parameter

From the graph  $F_{LV}$  Vs.  $C_{SB}$  for particular plate spacing  
That is let the plate spacing be 36 in.

$C_{SB} = 0.5$

Gas velocity through the net area at flooding

$U_{nf} = 8.047 \text{ ft/s}$

Linear design gas velocity  $U_n$  based on net area

Let the flooding be 80%

$U_n = 23164.11 \text{ ft/hr} = 6.43 \text{ ft/s}$

Volumetric flowrate  $q = G_1 / \rho$

$= 1055.73 * 44 / 0.452$

$= 3368461.94 \text{ ft}^3/\text{hr}$

Area = Volumetric flow rate /  $U_n$

$= 3368461.94 / 23164.11$

$= 145.42 \text{ ft}^2$

Tower Diameter  $D_c = 13.6 \text{ ft} = 4.14$

1) Provisional Area Calculation

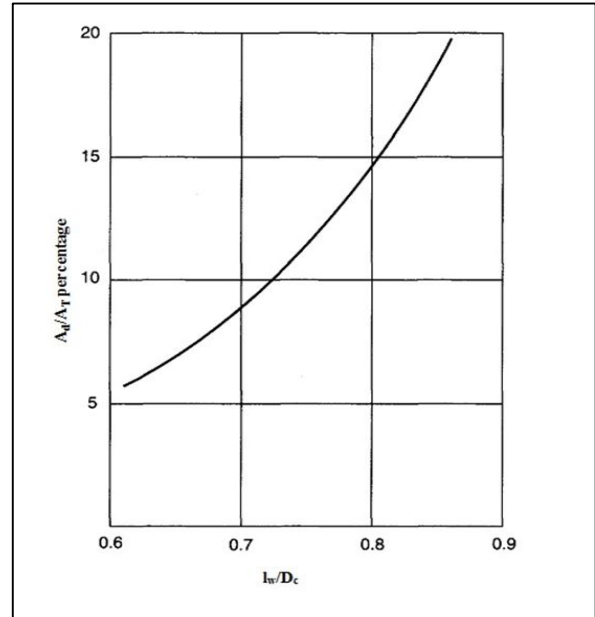


Fig. 8.3: Relation between downcomer area and weir length

2) Downcomer area

Let  $A_d = 10\% A_T$

$A_d = 14.542 \text{ ft}^2$

$A_n = A_T - A_d$

$= 145.42 - 14.542$

$= 130.878 \text{ ft}^2$

3) Weir length

Let  $A_d / A_T = 10\%$

From fig 8.2

$Lw/D_c = 0.73$

$Lw = 90928 \text{ ft}$

$= 3.026 \text{ m}$

4) Active area

$A_a = A_T - 2A_d$

$= 145.42 - 2 * 14.542$

$= 116.336 \text{ ft}^2$

5) Hole area

Considering triangular pitch

$A_h = 10\% A_a$

$$\frac{A_h}{A_p} = 0.906 \left[ \frac{d_h}{p'} \right]^2$$

$d_h = 0.0136 \text{ ft}$

$A_h = 11.6336 \text{ ft}^2$

Area of one hole  $A_{h1} = 1.4548 * 10^{-4}$

Number of holes  $N = A_h / A_{h1} = 79967$

6) Pressure drop

Total Head

$h_t = h_d + h_w + h_{ow} + h_r$

Dry plate pressure drop

Velocity through hole

$$U_h = \frac{q}{A_h}$$

$$U_h = \frac{3368461.94}{11.6336}$$

$= 28954.96 \text{ ft/hr}$

$= 24.514 \text{ m/s}$

From fig 8.4

Taking the ratio of plate thickness to hole diameter 1

$C_0 = 0.845$

Dry plate pressure drop

$$h_d = 51 \left( \frac{24.514}{0.845} \right)^2 \frac{0.452}{930} \implies h_d = 20.862 \text{ mm}$$

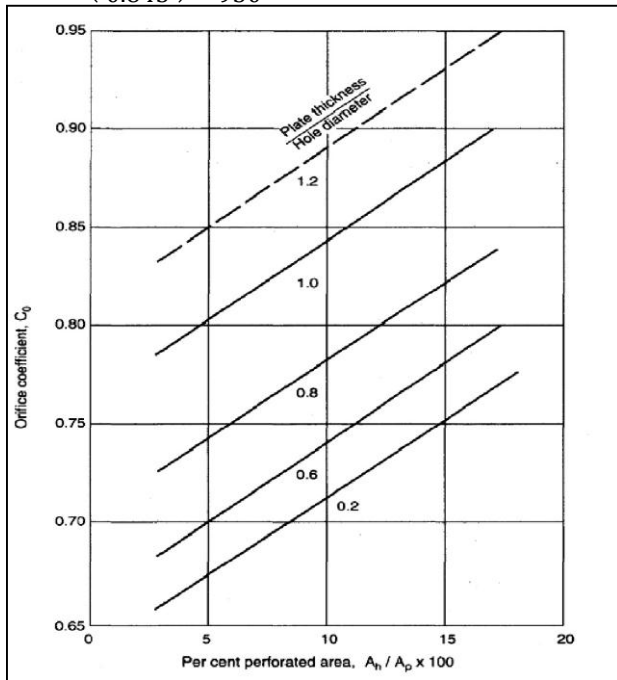


Fig. 8.4: Discharge Coefficient, sieve plate

7) Residual Head

$$h_r = \frac{12.5 * 10^3}{930}$$

$$h_r = 13.3 \text{ mm}$$

8) Weir liquid crest

$$h_{ow} = 750 \frac{2454.321}{3600 * 930 * 9.928}^{2/3} \implies h_{ow} = 1.32 \text{ mm}$$

9) Total Pressure drop

$$h_t = 21.862 + 1.32 + 13.3 = 85.483 \text{ mm}$$

Diameter = 4.14 m, Total Area $A_T = 13.509 \text{ m}^2$						
S N O	Downcomer area $\text{m}^2$	Net Area $\text{m}^2$	Active area $\text{m}^2$	Hole Area $\text{m}^2$	Weir length h m	Pressure Drop m
1	1.3509	12.158	10.807	1.0807	3.026	85.483

Table 8.3: Considerations for adsorption column design

## VII. CONCLUSION AND FUTURE SCOPE

The present work include material and energy balance over the entire ammonia plant. The heat in the plant is integrated through a network of heat exchangers so that minimum amount of steam is to be produced and the number of stage of shift conversion is decided by the activity of catalyst over the temperature range. Here two stages of shift conversion are used, one at high temperature and the other one at lower temperature. Using aspen plus simulation package  $\text{CO}_2$  absorber has been designed.

A. Scope of Future Work:

- Identification of more active methane steam reforming catalysts in future will lead to the increased conversion of methane in the reformer.

- Isothermal shift conversion is normally employed for higher capacity plants. Since it is very costly, it is not employed in all the plants. Improvement in design and operation of the isothermal shift conversion reactors will lead to the use of this in all plants and it will also be economical.
- The conventional  $\text{CO}_2$  removal process and methanation are replaced by the pressure swing adsorption process, since it is economical when compared with others. Design of a pressure swing adsorption system for air separation is carried out and it is found that poly bed PSA systems are required for the separation.

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