DESIGN OF SHELL AND TUBE HEAT EXCHANGER AND ABSORBER FOR THE MANUFACTURING OF AMMONIA BY LIQUEFIED NATURAL GAS

A PROJECT THESIS

submitted by

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In partial fulfillment for the award of the degree

Of

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BONAFIDE CERTIFICATE

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we hereby declare that the entitled "MANUFACTURING OF AMMONIA BY LIQUIFIED NATURAL GAS" is submitted in partial fulfilment of the requirement for the award of degree in B.E, INDIRA INSTITUTE OF ENGINEERING AND TECHNOLOGY-PANDUR, is record of our own work carried out by us during the academic year of 2021-2022 under the supervision and guidance of Mrs. K.BHAWANI M.Tech., department of petrochemical engineering. The extent and source of information of derived existing literature and have been indicated through the dissertation at the appropriate places. The matter embodied in this work original and has not been submitted for the award of any other degree or diploma, either in this or any other university

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ABSTRACT

The study is carried out in Madras Fertilizers Limited (MFL) for study purpose. Ammonia as a raw material for most of the fertilizers industries for the production of urea. The project deals with Liquefied Natural Gas (RLNG) as a raw material. The Liquefied Natural Gas (RLNG) is receiving from IOCL, Ennore port at 45 Kg at 15 C. Many stage wise section Preheater, Hydro desulphurisation, reformer, removal of CO₂, methanation, synthesis of Ammonia, and refrigeration. Totally the produced ammonia is 954 metric tonne per day.

சுருக்கம்

ஆய்வு நோக்கத்திற்காக மெட்ராஸ் ஃபெர்டிலைசர்ஸ் லிமிடெட் (MFL) இல் ஆய்வு மேற்கொள்ளப்படுகிறது. யூரியா உற்பத்திக்கான உரத்தொழில்களுக்கு பெரும்பாலான மூலப்பொருளாக அம்மோனியா உள்ளது. இந்தத் திட்டம் திரவமாக்கப்பட்ட இயற்கை எரிவாயுவை (RLNG)மூலப்பொருளாகக்கையாள்கிறது. திரவமாக்கப்பட்ட இயற்கை எரிவாயு ஜஓசிஎல், (RLNG) எண்ணூர் துறைமுகத்தில் இருந்து 150°C இல் 45 கிலோவில் வாரியாக பெறப்படுகிறது. நிலைகள் பிரிஹீட்டர், பல ஹைட்ரோடீசல் ஃபரைசேஷன், சீர்திருத்தம், CO2 ஐ அகற்றுதல், அம்மோனியாவின் மெத்தனேஒன், தொகுப்பு மற்றும் குளிர்பதனம். மொத்தமாக உற்பத்தி செய்யப்படும் அம்மோனியா ஒரு நாளைக்கு 954 மெட்ரிக் டன்.

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LIST OF SYMBOL

SYMBOL NAME

P Feed Pressure

Cp Molar Heat Capacity in KJ/ kg mole K

C_p mix Molar Heat Capacity in KJ/ kg mole K

AT Change in Temperature in Kelvin

M Molar flow rate in kg mole/hr

HNH Moisture of Ammonia in dry gas

Hat Saturated moisture in dry gas

Q_{dry} dry stream flow rate

Q Saturated stream flow rate

Q Inlet stream flow rate

Qw Flow rate of water

Velocity at throat Vthroat Area of throat K-empirical constant to account Athroat for energy losses from Calvert's empirical equation Pressure drop in psi A- Area of Duct in m² AP Diameter of the cone in D Overall heat transfer coefficient in W/m²K U Q Enthalpy in KJ Tube inner Diameter in m D Tube outer Diameter in m Do ST Pitch Distance in m n-Number of Tubes Area of A.- Area of all tubes in m²a single tube A in m² Shell Diameter in m D Permissible Stress in N/mm²m F J **Joint Efficiency** Diameter of nozzle in mm D Gasket Contact width in mm N

L/D	Length to Diameter ratio L Height of Adsorbent bed in m
S	Maximum Allowable Stress in Pa
Re	Crown radius in mz
R	Knuckle radius in my
Q	Volumetric flow rate in m'/sec
V	Velocity of gas mixture in m/sec
\mathbf{A}	Nozzle area in m ²

CHAPTER-1

1.1. INTRODUCTION

PROFILE OF MFL

MADRAS FERTILITER LIMITED (MFL) was incorporated in December 1966 initially as a joint venture between the Government of India and Amoco India Corporation of USA with equity share capital contribution of 51% & 49% respectively. In accordance with the participation agreement between the government of India, Amoco India and National Iranian OIL Company (NIOC) and the NIOC had 40% of the share holding of AMOCO was purchased by Government of India and the NIOC in their respective proportion on 27 July 1985. Now the hold 67.55% of shares and NIOC 32.45% shares.

The plant of MFL have been in operation for the last 20 years and have become old. The technology used in ammonia and urea plant is load with low energy efficiency. The proposals of revamping and modernisation project of MFL will certainly cross 415Cr. The economic life of the plant will increase by 15 years and energy consumption will come down below 10 million Kcal per ton of ammonia that is presently as high as 14 million Kcal per ton of ammonia now in MFL Rs.518.50 cr. Expansion cum modernisation project is completed. This leads to a reliable increase in production of fertilizers by 50% from the present level of 7 lakhs tonnes to 10.5 lakhs per annum. The company sales are now reached to nearly RS.1000cr. with sustained increase in the revenue.

PROCESS

The topic "Manufacture of Ammonia by steam reforming of Liquefied Natural gas" was done in MFL which is of great economic step towards urea manufacture. The factor which leads the production of Ammonia is cheap, availability of raw material and the nearness of source. RLNG is the source of H2 which reacts with N2 (from air) to form Ammonia. This takes place in several steps like RLNG Desulphurisation, Reforming shift conversion, CO2 removal, methanator, synthesis of Ammonia and Refrigeration.

Ammonia, a chemical compound of nitrogen and hydrogen is produced using RLNG, steam and air. Feedstock is the source for hydrogen and atmospheric air for nitrogen.

CHAPTER-2

2. PROPERTIES OF AMMONIA:

2.1 Physical properties

Properties

Molecular formula NH3

Molar mass 17.031g/mol

Appearance colourless gas with strong pungent odour

Density 0.86Kg/m³ (1.013 bar at boiling point)

 0.73kg/m^3 (1.013 bar at 15 °C)

681.9Kg/m³ at -33.3 °C (liquid)

817kg/m³ at -80 °C (transparent solid)

Melting point -77.73 °C, 195K, -108 °F

Boiling point -33.44 °C, 240K, -28 °F

Solubility in water 47% $(0 ^{\circ}C)$

31% (25 ℃)

28% (50 °C)

Flash point flammable gas

2.2 Chemical properties

Combustion

Ammonia is neither combustible nor a supporter of combustion. A jet of ammonia can be made to burn in atmospheric oxygen

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$$

Dissociation

Ammonia dissociates in to N₂ and H₂ when electric sparks are passed.

$$2NH_3 \rightarrow N_2 + 3H_2$$

Oxidation

When ammonia is passed on hot copper oxide, oxidation occurs.

$$3CuO+2NH_3 \rightarrow 3Cu+N_2+3H_2O$$

Formation of amides

When ammonia is passed on to heated sodium or potassium at 525 C amides are produced with evolution of hydrogen.

$$2NH_3 + 2Na \rightarrow 2NaNH_2 + H_2$$

Alkaline natural of ammonia

Aqueous solution of ammonia is alkaline in natural due to the presence of hydroxyl ions in the solution on treatment with water.

$$NH_4OH \longleftrightarrow NH_3^+ +OH$$

2.3. Uses

- > Approximately 80% of ammonia is used as fertilizers.
- Household ammonia is a solution of NH₃ in water (i.e., ammonium hydroxide) used as general purpose cleaner for many surfaces.
- Ammonia is used to scrub SO₂ from the burning of fossil fuels, and the resulting product is converted to ammonia sulphate for use as fertilizer.
- Ammonia has been proposed as a practical
- > Liquid ammonia is used for treatment of cotton materials

CHAPTER 3

MATERIAL BALANCE

3.1 MATERIAL BALANCE

The material balance is the fundamental tool of chemical engineering. It is the basis for the analysis and design of chemical processes. So, it goes without saying that chemical engineers must thoroughly master its use in the formulation and solution of chemical processing problems.

Ammonia production = 950 ton/day(43750 kg/hr)

Molecular Weight of ammonia = 17.0306kg/kmol

 $=39.58 \text{ NM}^3/\text{hr}$

Reaction

 $N_2+3H_2 \rightarrow 2 NH_3$

2 Moles of N₂& 1 Moles H₂ Required to Produce 2 Moles NH₁ Mole of H₂ Required to Produce 2568.905 Moles Of NH3 =2568.905x3/2

=3853.358 kg moles

Moles of N₂ Required to Produce 2568.905 Moles of NH₃=2568.905/2

=1284.453 kg moles

RLNG Required Per Day = 950 tons

 $= 39.58 \text{ NM}^3/\text{hr}$

3.1.2 RAW MATERIALS

The raw materials used for the production of ammonia by Haber Bosch process are RLNG, air and steam.

 $RLNG = 2450 NM^3/hr$

Air = 1838.07 kg moles/hr

Steam = 93687 kg/hr

3.1.3 PRE REFORMER

The pre reformer is an adiabatic catalytic reactor placed upstream the reformer in which the higher hydrocarbons contained in the RLNG feed are converted into methane thus preventing the formation of coke in the primary reformer. 262.61 Kg mole of RLNG Are Cracked to Give 1575.392 kg moles of Methane

$CH_4+H_2O \rightarrow CO+3H_2$

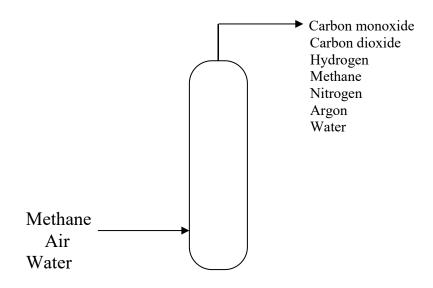


Figure 3.1 PREFOMER

Assuming 27% Conversion

CO Formed=425.36 kg mole

$CO_2\text{+}H_2O \to CO_2\text{+}H_2$

Assuming 97% Conversion CO₂ Formed=412.60 kg mole

Table 3.1 Pre reformer outlet

COMPONENTS	Kg mole/Hr	Kg/Hr	Mole%
H_2	1688.68	3377.36	21.9356
N_2	66.6	1864.8	0.8651
СО	12.76	357.28	0.1657
CO ₂	412.6	18154.4	5.3596
Ar	0.803	32.12	0.0104
CH ₄	1150.032	18400.512	14.9387
H ₂ O	4366.873	78603.714	56.7248
TOTAL	7698.348	120790.18	100

3.1.4 PRIMARY REFORMER

In primary reformer, methane gas and water vapour react into hydrogen, oxygen, carbon monoxide and carbon di-oxide at a pressure of around 30bar and a temperature of 870 °C. Simultaneous measurement of temperature and pressure is made to regulate the process.

A)
$$CH_4+H_20 \rightarrow CO+3H_2$$

B)
$$CO+H_2O \rightarrow CO_2+H_2$$

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

(Assuming 60.5% conversion) (CH₁ converted)

CO formed: 695.77% kg mole

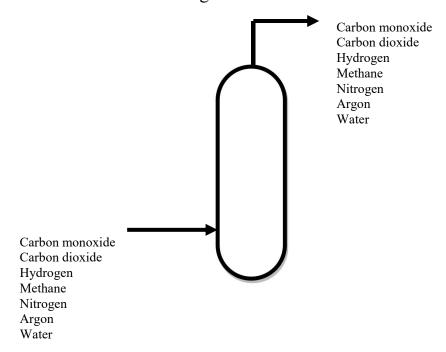


Figure 3.2 PREMARY REFORMER

B)
$$CO+H_2O \rightarrow CO_2+H_2$$

(Assuming 28% conversion) (CO in to CO₂ conversion)

H₂ formed: 191.24 kg mole

Table 3.2 Primary Reformer Outlet

COMPONENTS	Kg Mole/hr	Kg/hr	Mole
H_2	3967.23	7934.46	43.7673
N_2	66.6	1864.8	0.7347
СО	491.77	13769.56	5.4353
CO ₂	603.84	26568.98	6.6617
Ar	0.803	32.12	0.0088
CH ₄	454.262	7268.192	5.0115
H ₂ O	3479.534	62637.534	38.3851
TOTAL	9064.368	120075.626	100

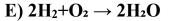
3.1.5 SECONDARY REFORMER

The secondary reformer is a part of a subprocess in a higher scale unit of ammonia synthesis. It is located after the primary reformer where the remaining methane is converted into hydrogen, oxygen, carbon monoxide and carbon dioxide.

Reaction Involved

C)
$$CH_4+H_2O \rightarrow CO+3H_2O$$

D) $CO+H_2O \rightarrow CO+H_2$



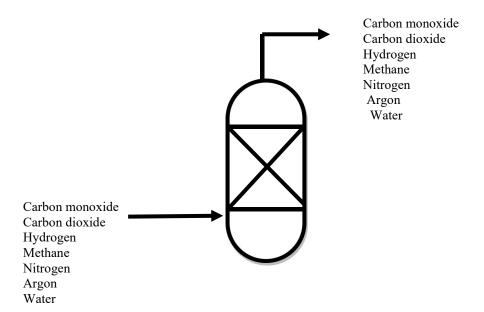


Figure 3.3 Secondary reformer

Process Air Will Contain 352.386 kg moles of O₂

It Is Assumed That All Amount Of O2 Is Converted into H2O

By Reaction (E)

 $352.386 \text{ kg mole of } O_2 \text{ will produce } 704.772 \text{ kg mole of } H_2O$

By Reaction (C)

Assuming 95% Conversion

CO Formed= 431.55 kg mole

By Reaction (D)

The Reaction is Reverse Reaction

Assuming 44.95% Conversion

 CO_2 Inlet + CO_2 in Air = 603.84 +0.535

=604.375kgmole

Amount of CO Converted = 604.375 + 44.95/100

=271.67 kg mole

271.67 kg mole of CO will produce = 271.67 kg mole of CO₂

Table 3.3 Secondary reformer outlet

COMPONENTS	Kg Mole/hr	Kg/hr	Mole
H_2	4285.438	8570.876	38.2349
N_2	1330.814	37262.792	11.8749
СО	1194.99	334.32	10.663
CO_2	332.17	14615.48	2.964
Ar	16.051	642.04	0.1432
CH ₄	22.712	363.392	0.2027
H ₂ O	4024.755	72445.59	35.9131
TOTAL	11206.93	134234.49	100

3.1.6 HTS (HIGH TEMPERATURE SHIFT CONVERTOR)

In most ammonia plants, the shift conversion is carried out in two stages. Usually, a high temperature shift (HTS) catalyst is used as the first stage and typically converts over 80% of the CO.

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

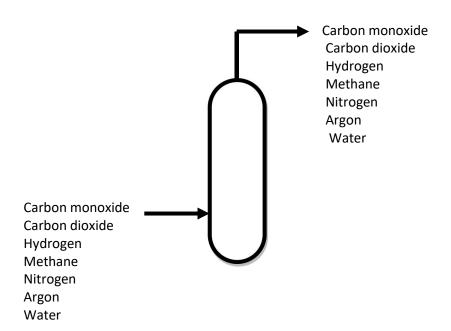


Figure 3.4 High temperature shift converter

Assuming 75% conversion

CO2 formed-896.24 kg mole

Table 3.4 HTS Mass Balance

COMPONENTS	Kg Mole/hr	Kg/hr	Mole
H_2	5181.68	10363.36	46.2446
N_2	1330814	37262.792	11.8770
СО	298.75	8365.21	2.6662
CO_2	1228.41	54050.04	10.9631
Ar	16.051	642.04	0.1432

CH ₄	22.712	363.392	0.2027
H ₂ O	3126.52	56277.36	279031
TOTAL	11204.937	167323.984	100

3.1.7 LTS (LOW TEMPERATURE SHIFT CONVERTOR)

A low temperature shift catalyst (LTS) then converts the majority of remaining CO. As well as maximizing the hydrogen production, the water shift reaction also maximizes the CO₂ production from an ammonia plant.

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

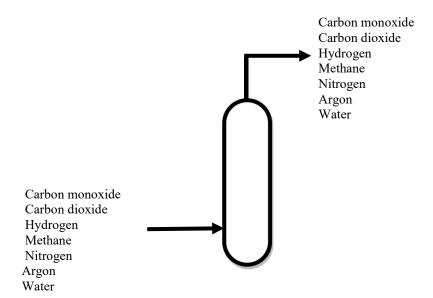


Figure 3.5 Low temperature shift converter

Assuming 54.12% conversion

 CO_2 formed = 18.09 Kg mole

Table 3.5 LTS Mass Balance

COMPONENTS	Kg Mole/hr	Kg/hr	Mole %
H_2	5465.1	10930.2	48.7741
N ₂	1330.81	37262.68	11.877
СО	15.33	429.4	0.1368
CO ₂	1511.83	66520.52	13.4925
Ar	16.051	642.04	0.1432
CH ₄	22.712	363.392	0.2427
H ₂ O	2843.1	51175.8	25.3736
TOTAL	1124.933	167303.992	100

3.1.8 MDEA-ABSORBER

The CO; is removed from the gas by absorption in a MDEA solution of 35 wt% MDEA. It contains 3% piperaizine as activator. Piperaizine increases the mass transfer rate of CO, from the gas phase to liquid phase.

$$R_2NCH_3 + CO_2 + H_2O \rightarrow R_2NCH_4 + HCO_3$$

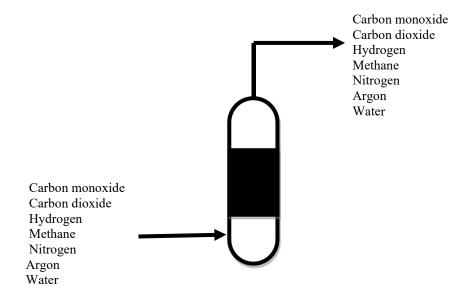


Figure 3.6 MDEA Absorber

MDEA solution inlet flow rate = 2087743.1094 kg/hr

Amount of CO absorbed = 348.45 kg/hr

Amount of CO₂ absorbed = 66393.562 kg/hr

Amount of water absorbed = 50649.3 kg/hr

Flow rate of spent MDEA solution = 2087743.1094 + 348.45 + 66393.562 +50649.3

= 2205134.42 kg/hr

Table 3.6 MDEA Mass Balance

COMPONENTS	Kg Mole/hr	Kg/hr	Mole%
H_2	5465.1	10930.2	79.5538
N_2	1330.81	37262.68	19.3722
СО	2.8854	80.79	0.042
CO_2	2.8854	126.958	0.042
Ar	16.051	642.04	0.2336
CH ₄	22.712	363.382	0.3306
H ₂ O	29.25	526.5	0.4258
TOTAL	6869.69	49549.29	100

3.1.9 METHANATION

Methanation is the conversion of carbon monoxide and carbon dioxide (CO) to methane (CH) through hydrogenation. Methanation is carried out in methanator. Methanation is an important step in the production of synthetic gas (SNG). In ammonia production CO and CO, are considered poisons to most commonly used catalysts.

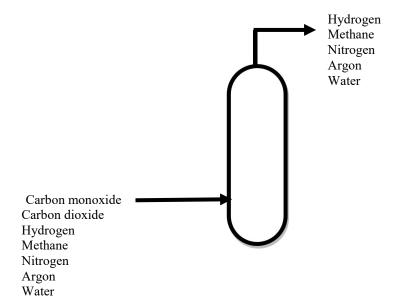


Figure 3.7 Methanator

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

G) CO+
$$4H_2 \rightarrow CH_4 + 2H_2O$$

From reaction (F)

Methane produced = 2.8854 kg mole

From reaction (G)

Methane produced = 2.8854 kgmole

Table 3.7 Methanator Mass Balance

COMPONENTS	Kg Mole/hr	Kg/hr	Mole
H ₂	5444.9	10889.8	79.3931
N ₂	1330.81	37262.68	19.4048
СО	-	-	-
CO ₂	-	-	-
Ar	16.051	642.04	0.2340
CH ₄	28.4828	455.72	0.4153
H ₂ O	37.97	682.38	0.5528
TOTAL	6858.15	49932.62	100

3.1.10 SYNTHESIS SECTION

Ammonia synthesis section is a crucial section in ammonia production unit

Where hydrogen and nitrogen are converted into ammonia.

The reaction is an equilibrium reaction and therefore only part of the hydrogen and nitrogen will be converted into ammonia by passing through catalyst beds.

High pressure and low temperature tend to favour the ammonia synthesis in am effective way

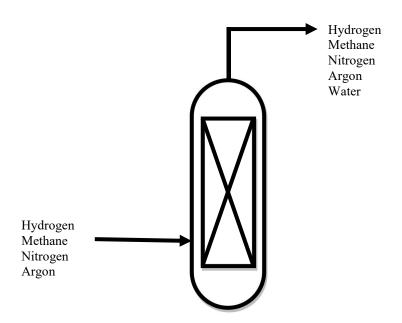


Figure 3.8 Synthesis section

Table 3.8 Synthesis section outlet

COMPONENTS	Kg Mole/hr	Kg/hr	Mole
H_2	12017.375	24034.75	64.32
N_2	3979.479	111425.412	21.29
Ar	713.691	28476.27	3.82
CH ₄	1180.766	18892.256	6.34
H ₂ O	792.15	13466.55	4.23
TOTAL	18683.46	196395.238	100

3.1.11 REACTOR

The ammonia production reactors require a cooling system to achieve a high degree of conversion since it is highly exothermic.

The reaction is given by.

$$N_2 + 3H_2 \rightarrow 2NH_3$$

(Assuming 30% conversion)

H₂ reacted=3605.213 kg mole

NH, reacted = $3605.213 \times (2/3)$

= 2403.48 k mole

 N_2 reacted = 3605.213 ×(1/2)

= 1802.61 kg mole

Table 3.9 Reactor outlet

COMPONENTS	Kg Mole/hr	Kg/hr	Mole%
H_2	8412.16	16824.32	53.652
N ₂	2176.87	60952.32	13.8839
Ar	713.691	28547.64	4.5519
CH ₄	1180.76	18892.16	7.5308
H ₂ O	3195.63	54325.71	20.3815
TOTAL	15679.11	179542.19	100

3.1.12 OVERALL MATERIAL BALANCE

Table 3.10 Overall material balance

EQUIPMENT	MASS IN kg mole	MASS OUT kg mole
Prereformer	4517.433	6748.348
Primary reformer	6748.34	9757.947
Secondary reformer	9757.947	10256.93
HTSC	10256.93	10254.933
LTSC	10254.933	10254.933
Absorber	10254.933	5919.69
Methanator	5919.69	5908.15
Synthesis Section	5908.15	17733.46
Reactor	17733.46	14729.11

3.2 ENERGY BALANCE

Inlet gas properties,

Reference temperature = 25° C

Inlet gas temperature = 72° C

Enthalpy of inlet gas = mc_P At-----4

Where.

m = 232094.155 kg/hr

C_P can be calculated using the equation,

$$C_P = C_P \text{ VAP A} + C_P \text{ VAPB*T} + C_P \text{VAP C* 2T} + \dots ----5$$

By substituting we get,

 C_P of inlet gas = 19.795+73.436*72 - 5.602*2*72

 $C_P = 0.161 \text{ kcal/kg k}$

By substituting eqn 4,

Enthalpy of inlet gas (232094.155*0.161*47)

 $Q_1 = 1759528.998$ kcal/hr

 C_P of outlet gas = 0.152 kcal/kg k

Enthalpy of outlet gas = $mC_P\Delta t$

Where outlet temperature = 52° c

Enthalpy of outlet gas = (184203.963*0.152*27)

 $Q_0 = 755973.0642$ -(Heat loss or change)

Therefore heat loss is equal to heat gained by the solvent (MDEA)

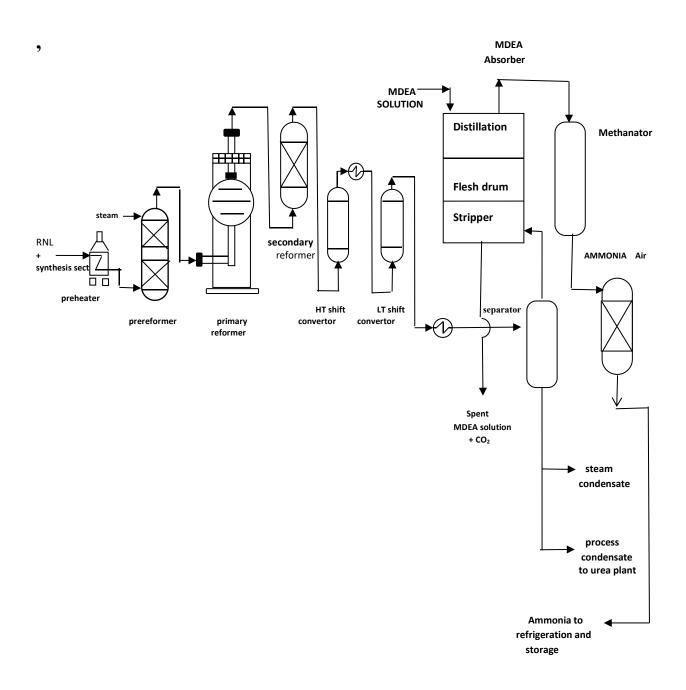
Therefore,

 $Q_1 = 1759528.998 \text{ kcal/hr}$

 $M-1854000 \text{ kg/h}, C_P = 0.62 \text{kcal/kg k}$

3.3 BLACK DIAGRAM **FUEL NG 9013** PROCESS NATURAL GAS FUEL NG 482 NM³/ NH³/HR 25959 NM³ / HR **HRCOMPUSION AIR SECONDARY** HEAT PRIMARY REFORMER HT / LTG / LT -SEC HDS SEC HDS REFORMING PRE **EXCHANGER FURNANCE PREHEATER** CO to CO² **SECTION REFORMER** 116289NM3/HR 38746 NM³/HR PROCESS STEAM 68.1 MT/HR STACK LOSS PROCESS AIR NASA K 1602 AIR COMPRESSOR AMMONIA LIQUOR PURGE GAS 5170 K 1603 & K1604 CO² VENT GAS 964 TO HTD STIPPER NM³/HR NM³/HR **COMPRESSOR** 3425 KG/HR K-1601 CO² REMOVAL **AMMONIA TO** REFRIGERATION COMPRESOR **METHANATOR SYNTHESIS** SECTION (MDEA) STORAGE (SYN GAS) SECTION 7336 KG **AMMONIA TO** PROCESS CONDENSATE **UREA** TO PC BOILER 37825 37716 KG/HR UREA RECYCLE HYDROGEN 1322 NM³/HR KG/HR

3.4 FLOW CHART



CHAPTER-4

4.1 AMMONIA PROCESS AT MFL

4.1.1 INTRODUCTION

In MFL, HALDOR TOPSOE (HTAS) method is currently being processed. RLNG is got from CPCL is stored in the large tank of diameter 12 meter, it is covered by a floating roof which is attached to guide pipe and the circular floating roof is scaled to the storage tank by foam seal. Naphtha source is used for hydrogen and nitrogen from the atmospheric air.

Ammonia is produced from a mixture of hydrogen (H_2) and nitrogen (N_2) , where the ratio of H_2 to N_2 should be 3to 1. Besides these two compounds the mixture will contain inert gases to a limited extent such as argon (Ar) and methane (CH_4) . For the ammonia plant in Madras Fertilizers Limited the source of H_2 is steam and hydrocarbons in the form of naphtha. The sources of N_2 is as in all ammonia plants atmospheric air

The processes which are necessary for producing ammonia from the abovementioned raw materials are as follows

- > Hydrocarbon feed is completely desulphurized in the desulphurization section.
- ➤ The desulphurized hydrocarbon is reformed together with steam and air to raw synthesis gas. This gas contain hydrogen and nitrogen as well as carbon monoxide (CO) and carbon dioxide (CO2) and minor amount of argon (Ar) and reformed methane (CH₄)
- \triangleright Co is converted into CO₂ in two steps. In the shift conversion unit the remaining CO is converted into CO₂ with air. The bulk of the CO₂ is removed in the MDEA unit and the remaining CO and CO₂ is converted into CH₄ in the Methanation section.

➤ In the ammonia synthesis section the purified synthesis gas is, after compression to the pressure of about 200kg/cm²g. Converted into ammonia by a catalytic reaction

4.1.2HYDRO DESULPHURISATION

Liquefied natural gas which is used as feed up to 0.12 wt% sulphur is a poison to the remaining catalyst and has to be removed to a very low level before the feed is passed on to the reforming section. If the sulphur content in the liquefied natural gas to the Hydro desulphurisation vessel is very low, below approximately 2ppm, for a prolonged period, sulphur will tend to be stripped off the hydrogenation catalyst. A reduction to metals of the Co-Mo system in the catalyst may take place. In these circumstances there is a risk that exothermic hydro cracking reactions may occur. The liquefied natural gas from the hydro desulphurisation unit is to contain main. 2-3 vol ppm H₂S. During normal operating condition the sulphur content in the Liquefied natural gas will be removed in the hydro desulphurisation down to below 0.02 vol ppm H₂S.

Liquefied natural gas is mixed with hydrogen gas from the 1st stage of the synthesis gas compressor and the mixture is evaporated and heated to 350 degree centigrade in the steam fired hydro desulphurisation preheater, which is a direct fired in the HDS preheater.

The desulphurisation unit consists of a secondary HDS vessel and sulphur absorbent vessel. In the first reactor containing Co-Mo based catalyst 13.7 M3, 5mm rings. The gas mixture outlet passes over ZnO catalyst 18.8m³, 4mm extrudes, which will absorb H₂S according to the reaction:

$$ZnO \rightarrow ZnS + H_2O$$

Zinc sulphide is not pyrophoric and no special care during unloading is required

4.1.3Reforming section

In the reforming section the desulphurized Liquefied Natural gas is converted into raw ammonia synthesis gas by catalytic reforming with steam and addition of air.

The steam reforming of hydrocarbons can be described by the following reactions:

$$C_nH_m + {}_nH_2O \rightarrow {}_nCO + (m/2+n) H_2-Q$$
 -1

$$CH_4 + H_2O \rightarrow CO + 3H_2 - Q \qquad \qquad -2$$

$$CO_2 + H_2 \rightarrow CO + H_2O - Q$$
 -3

Reaction (1) described a total conversion of higher hydrocarbons into CO and H₂. Methane is reformed to CO and H₂ according to (2)

Reaction (3), the shift conversion reaction, requires a small amount of heat only, whereas the heat required for (1) and (2) will quit dominate the picture.

The reaction place in three steps in the pre reformer and the two reformer, the primary reformer and the secondary reformer. No heat is required for the reaction in the pre reformer as the net reaction is slightly exothermic. The necessary heat is supplied indirectly by firing. In the secondary reformer the heat is supplied as reaction heat by mixing air into the gas. The burning gas provides heat for the rest of the reforming. The reforming taking place in the primary reformer is adjusted in such way that the air supplying the reaction the reaction heat in the secondary reformer will give the required hydrogen/nitrogen ratio of 3 to 1 at the outlet from the methanator

It is desirable to reduce the methane content n the raw synthesis gas to as low a level as possible to maximize the production of hydrogen and to keep the level of inert gases in the synthesis gas low. The methane content in the raw gas is governed by the equilibrium of the reforming reaction (2) and by the approach to the equilibrium obtained in practice. The equilibrium for reaction (2) is so that higher temperature, more steam and lower pressure results in lower methane content. On the other hand, by raising the reforming pressure, a considerable saving in the power consumption for synthesis gas compression can be obtained and the equipment can be made smaller. An operating pressure of 30 to 35 kg/cm2g for the reforming section has been found to give a reasonable economic compromise. In order to compensate for the unfavourable equilibrium conditions thereby encountered, a steam to carbon ratio 3.3 has been chosen.

ADIABATIC PRE-REFORMING

As the process feed has a high content of higher hydrocarbons, it is passed through the reformer before being sent to the primary reformer. Before the process feed enters the pre reformer, process steam is added at a steam/carbon ratio 3.3 and the mixture is heated to 480 degree centigrade in the process feed preheating coil located in the flue gas duct. The pre reformer is simply an adiabatic chemical reactor, containing 18.2m3, 4.3 * 4.3 mm rings of a special reforming catalyst, which has a good reforming activity at low temperatures, well below the kinetic limit for carbon formation.

All higher hydrocarbons will be completely converted, irreversibly, by the first reaction while the other two reactions will be almost equilibrated, i.e. to approximately 52 mol% CH₄ and 0.5 mol% CO (dry basis). The gases leaving the adiabatic pre reformer at approximately 500 degree centigrade is passed directly on to the primary reformer.

PRIMARY REFORMING

The primary reformer is constructed as a duplex furnace, where each radiant chamber contains a single row of 92 (totally 184) centrifugally cast tubes, each 11.4 long, made of high alloy Cr-Ni steel (25/35 NbTi) and is loaded with Topsoe steam reforming catalyst in total 29 m2 of rings in the size 16 * 11 mm/ the reforming catalyst is characterized by a high activity due to a high nickel surface area and a high thermal resistance Thermodynamically carbon formation is not possible when operating the primary reformer at the chosen conditions but if the catalyst loses activity, due to poisoning (sulphur), mal operation or aging carbon formation may occur. Carbon formation itself decreases the activity of the catalyst and therefore it is very important to take immediate action prevent further formation. Carbon deposits normally increase the pressure drop across the reformer and it may be detected by observing hot bands on the reformer tubes. Another consequence of carbon formation is that the catalyst particles lose their mechanical strength.

If the hydrocarbon feed has a high content of olefins, aromatics or naphthenic, this may cause carbon formation. Furthermore, it is important not to operate the reformer with too low steam to carbon ratio, as this gives a thermodynamically possibility for carbon formation, especially inside the catalyst particles. After a slight poisoning, the activity is re-established by operating the reforming for a few hours with pure gas. A severe sulphur poisoning requires n special regeneration procedure. Also salt droplets in steam, for instance NaCl and Na₃PO4 and compounds containing heavy metals are poisonous to the catalyst. For this sort of poisoning no regeneration will work. The gas leaves the tubes and enters the refractory-lined cold collector though the bottom hairpins and hot collectors. At the tube outlet the process gas has a temperature of about 800 degree centigrade. The methane concentration is about 9.5 vol% (dry) at outlet.

When passing the catalyst in the tube, the following reactions take place:

$$CH_4 + H_2O \rightarrow CO + 3H_2 - Q \tag{2}$$

$$CO + H_2O \rightarrow CO_2 + H_2 + Q \tag{3}$$

Both reactions will be close to equilibrium at the outlet temperature,

To compensate for the strongly endothermic reforming reaction (2) the tubes are heated by 288 burners located in each side wall and arranged in 6 horizontal rows at different elevations to provide easy control of a uniform temperature profile along the length of the catalyst tubes: In this manner the optimum utilization of the expensive high alloy tubes is obtained and the risk of local hot spots minimized. The flue gas outlet temperature is about 1020 degree centigrade. The burners are of the forced draught type operating with preheated combustion air at about 360 degree centigrade. In order to ensure complete combustion of the fuel used in the burners, they are operated with an excess of air about 10% which corresponds to 2.0 vol% (dry) of oxygen in the flue gas

Fuel gas from the primary HDS and purge gas from the synthesis section are mixed and preheated to 200 degree centigrade in the steam fired fuel gas preheater. The remaining fuel being raw naphtha is vaporized and heated to 200 degree centigrade in the steam fired RLNG fuel preheater before beingsent to the primary reformer burners. The steam fired RLNG fuel preheater before being sent to the primary reformer burners. The flue gas from each radiant chamber is collected in the flue gas collector of the flue gas heat recovery section where the sensible heat of the flue gas is utilized, in consecutive order, for:

- 1. Preheating of process feed
- 2. Preheating of process air
- 3. HP steam superheating
- 4. Combustion air preheating

The heat recovery section brings down the temperature of the flue gas to about 175 degree centigrade. After the heat recovery section the flue gas fan (ID fan) leads the gas to the stack.

Secondary Reforming

Preheated air at 550 degree centigrade is mixed into the party reformed gas and reacts in the upper empty space of the secondary reformer. The reaction here is mainly a combustion resulting in a temperature rise. From the empty space the gas passes the catalyst bed in the lower part of the reformer where the reforming reaction is completed with simultaneous cooling of the gas. The outlet temperature will be about 970 degree centigrade and the methane concentration approximately 0.3 vol% (dry basis).

The exit gas from the secondary reformer contains about 14 mol % CO and 10 mol % COS. Consequently there is a theoretical risk of carbon formation according to the Boudouard reaction.

$$2CO \rightarrow CO_2 + C$$
 (as soot)

When the gas is cooled at the actual operating conditions the carbon formation can only take place at a temperature below 720'c outlet primary reformer and below 766 e outlet secondary reformer, because of the equilibrium conditions. The lower limit for the reaction is 650'e as the reaction rate becomes too slow at lower temperature. Consequently, it is important to pass the temperature range from 766°c to 650 °c reasonably quickly, and also contact between gas and hot metallic surfaces is to be avoided.

The cooling of the process gas is carried out in the waste heat boiler, where the exchanged heat is used for producing saturated high pressure steam at 45 kg/cm2g being needed in the ammonia plant. The boiler is designed to obtain the rapid cooling, but a too high flux is to be avoided, as it may cause film boiling on the steam side which in turn would decrease the heat transfer coefficient significantly.

The secondary reformer has been charged with a total of 30.1 m3 of catalyst. The dimensions of the catalyst are 20 mm 18 mm high, with seven holes. The catalyst bed rests on a layer of alumina lumps and on top of the catalyst bed a layer of alumina lumps and alumina tiles protects the catalyst from agitation and direct flame contact. The catalyst activation is carried out simultaneously with activation of the primary reformer catalyst. The combustion of the process gas with air gives a gas temperature of 1100-1200 degree centigrade in the upper part, but as the reforming reaction of methane absorbs heat, the outlet temperature of the secondary reformer is approx. 970 degree centigrade. In the temperature range of 1400-1500 degree centigrade, the catalyst starts sintering. The activated catalyst must never be exposed to air at temperature above 100 degree centigrade, as this will cause spontaneous heating, which due to the "snow-balling" effect may lead to overheating and destruction of the catalyst.

4.1.4Gas Purification Section

The gas leaving the reforming section has the following composition expressed in % by volume (dry basis)

Table 4.1 Gas leaving Reforming section

Molecule	Mol formula	Vol%
Hydrogen	H ₂	52.86
Carbon monoxide	СО	14.40
Carbon dioxide	CO_2	10.15
Nitrogen	N ₂	22.02
Argon	Ar	0.27
Methane	CH ₄	0.30
Total		100

Furthermore, the gas contains so much water vapour that steam to dry gas ratio is about 0.59. Of the above compounds argon (Ar) has not yet been mentioned. Argon is an inert gas introduced with the process air which always contain 0.94 vol% Ar.

The purpose of the gas purification section is to prepare a synthesis gas containing hydrogen and nitrogen in the ratio of 3 to 1 and besides this only containing inert gases such as methane and argon in as low a concentration as possible. When leaving the secondary reformer the gas temperature is around 970 degree centigrade. Before entering the shift converter it is cooled in the waste heat boiler, and in the HP BFW preheater, to 360 degree centigrade.

Carbon monoxide is converters.

According to the following reaction:

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

The reacted gas will contain only about 0.12 vol % CO (dry bases). The reached part of the CO increases the H: yield with simultaneous formation of CO₂ which is more easily removable. A further reduction of the CO content in the process gas is taking place in the selectoxo unit, where CO reacts with O₂ (from air) to CO₂. The CO₂ is then removed in the CO₂ removal unit leaving less than 0.05 vol % CO₂ (dry bases) in the gas.

Even small amounts of CO and CO₂ left are severe poisons to the ammonia synthesis catalyst and should therefore be removed down to a concentration of few ppms. This is done in the methanator where reverse of the reforming reaction will take place:

$$CO+3H_2 \rightarrow CH+H_2O+heat$$

$$CO_2 + 4H_2 \rightarrow CH + 2H_2O + heat$$

Resulting in the formation of methane at the expense of hydrogen.

In the ammonia synthesis loop the inert Ar + CH₄ will be built up to a level depending on how much gas is purged from the loop The purpose of whole gas preparation line is to keep the methane concentration reasonably low as nothing can be done to decrease the content of the other inert gas, Argon.

4.1.5 Shift Conversion of CO₂

The shift reaction taking place in the converters will proceed only when process gas contact with a catalyst.

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

The equilibrium is favoured by lower temperature and more water while reaction rate will be higher at higher temperatures. More water may give an apparently lower reaction rate due to the larger total volume resulting in a shorter contact time. This means that for each catalyst will be optimum temperature. Depending on the activity and the quantity this will give optimum conversion. As the reaction results in a temperature rise, the outlet gas will be at an unfavourable equilibrium if removal of heat has not taken place before the conversion is finished.

Thus, the conversion is performed in three steps. The first step takes place in the primary CO converter, where a copper promoted iron/chomium-based catalyst is installed. The inlet temperature is 360 degree centigrade and of the reaction takes place here, causing a temperature rise of 73 degree centigrade. The second step is taking place in two converters, the LT guard vessel and the secondary CO converter. Between the converters the process gas is cooled in 2 HHP BPW pre heater.

Primary CO Converter

The process gas outlet the secondary reformer is cooled to 360'c in the reformed gas waste heat boiler and the 3 HHP BFW preheater before entering the primary CO converter. The primary CO converter contains 39.8m 6 x 6 mm rings of the catalyst. SK-201 is a copper promoted iron oxide catalyst and in the fresh catalyst the iron oxide is at its highest oxidized level and is thus not affected by air, steam, carbon dioxide or nitrogen at elevated temperatures. Normal operating temperature for SK-201 is from 330 °c to 450 "c.

At the start-up of the plant the catalyst must be activated, which is mainly a reduction of Fe:O: to Fe,O4. The reduction will take place simultaneously with start- up or the reformer. When new, the catalyst can operate at a gas inlet temperature of 360 °c. Afterwards the optimum inlet temperature will be higher, but as the outlet temperature has not reached 450°c, the activity will only decrease slowly. The cold catalyst can be heated by steam alone, both when oxidized and reduced. Drops of liquid water on the hot catalyst may result in disintegration of the catalyst. The catalyst is very sensitive to salts which may be introduced with steam. Chlorine concentration of less than 10 vol. ppm in the feed gas will have no effect on the catalyst activity. The catalyst is not influenced by sulphur in the quantities present in this plant. The fresh catalyst contain, however, less than 100 wt. ppm sulphur which will be given off as H-S during the first few days of operation before the LT shift converters are put on line.

LT Shift Converters

The gas outlet is cooled to 210 degree centigrade in the converted gas waste heat boiler producing 45kg/cm g stem and in the primary medium pressure boiler

producing 11 kg/cm³g steam. The CO converter at low temperature is taking place in two reactors, the LT guard vesseland the secondary CO converter. The LT guard vessel contains 47.2m'. 4.3 x 32mm rings of the Topsoe LK-821 catalyst containing of oxides copper, zine and aluminium in two beds. On the top of the LK-821 a layer of 2.6m. 4.5 x 4.5mm rings of Topsoc LSK catalyst is placed as chlorine guard. The LSK catalyst will also protect the main catalyst bad against droplets of condensing steam.

The gas outlet is cooled to 190 degree centigrade in the 2 HHP BFW preheater before entering the secondary CO converter. It contains 512m 43 x 3.2mm rings of the Topsoe LK 821 catalyst. As the catalyst is extremely sensitive to chlorine and sulphur which may be liberated not only form the above-mentioned IT shift catalyst, but to a certain extent also from the refractory in the secondary reformer during the first period of operation are bypassed during this stage until the gas is practically of chlorine as well as sulphur. The chlorine will normally be present in process steam, quench water and process air in very small amounts. Besides chlorides, sulphur and gaseous Si compounds are poisons. When the catalyst is in reduced state, temperature above 250'e must normally be avoided unless the catalyst is old. The normal operating temperature is between 190-275 "c.

A short exposure to 350'e will have no adverse effect on the catalyst. Normal operation. should take place at as low a temperature as possible. However, at temperatures near the dew point, the activity will decrease because of capillary condensation of water inside catalyst pores, thus reducing the free area. During operation the temperature should before be kept min.20°c above the dew point.

4.1.6 CO₂ Removal

The gas leaving the separator unit has a CO₂ content of about 21 vol% (dry bases). The gas enters the CO, absorber at a temperature of about 75 degree centigrade.

The CO₂ is removed from the gas by absorption in a MEDA solution containing 35 wt% MEDA. As an activator for the absorption the MEDA solution contain 3wt% Piperazine. Piperazine increases the mass transfer rate of CO₂ from the gas phase to the liquid phase, the balance solution in water. The overall reactions occurring during the CO₂ absorption are described in the following equations:

1.
$$R_3N+ H_2O + CO_2 \rightarrow R_3NH^+ + HCO_3^- + Q$$
 -1

$$2.2R_2NH + CO_2 \rightarrow R_2NH_2^+ + R_2N-COO^- + Q \quad -2$$

Reaction (1) describes the reaction for a tertiary amine (e.g. MEDA). Reaction (2) describes the reaction for a secondary amine (e.g. piperazine). In the CO₂ absorber the CO₂ is removed from the gas by counter current absorption in two stages. In the lower part (bulk absorber) of the absorber flash- regenerated solution is used for CO₂ removal. In the upper part (lean solution) stripper regenerated solution is used for final CO₂ removal. At the outlet of the absorber the CO₂ content in the gas has been reduced to less than 500 vol ppm on the dry basis. The solution

which enters the absorber at 50°c (stripped solution) and 75°c (flash solution) is heated to 85°c by the exothermic absorption reactions.

High interfacial areas between gas and liquid are provided by 2"CS, IMTP (Intaloz Metal Tower Packing) or cascade mini rings loaded in 2 beds in the bulk absorber and by I" CS IMTP or cascade mini rings loaded in 3 beds lean absorber, respectively. To prevent losses of scrubbing solution by entrainment in the purified gas, the top of the column is provided with 3 bubble cap trays which are fed with approximately 900-1300 kg/h boiler feed water. The energy in the rich solution leaving the bottom of the absorber is utilized in a hydraulic turbine, which together with the steam turbine servers as driver for the flashed solution main pump, thereby reducing the total steam consumption of the process. The flash regeneration of the rich solutionis performed in two stages. In the HP flash drum the main part of the dissolved inert components are liberated at a pressure of 6.2 kg/cm'g. The flash gas is used in the secondary HDS preheater. In the LP flash drum are equipped with the packing, 2" SS and CS pall rings and 2 bubble cap trays in the top.

The CO; released in the LP flash drum is saturated with water at a temperature of 75 degree centigrade. The mixture is cooled to 45.5 degree centigrade in the flash gas cooler and the condensate is separated in the K.O.drum. The condensate is returned to the regeneration system. The flashed solution from the bottom of the LP flash is divided into two streams.

The major part of the solution is transferred to the lower part of the absorber by means of the flash solution split steam pump. Before entering the top of the stripper the semi lean solution is preheated in the solution heat exchanger by means of lean solution coming from the bottom of the stripper. In the CO₂ loading is achieved by using 2" SS pall rings as packing material in two beds.

The CO, leaving the top of the CO₂ stripper at 98 degree centigrade is saturated with water. This vapour is passed though the LP flash drum packed with.

a 1000 mm top layer of 2" SS and the bulk CS pall rings in one bed. The lean solution from the bottom of the CO₂ stripper is cooled in the solution heat exchanger, in the DMW preheater and in the lean solution cooler before it is sent to the top of the CO₂ absorber by means of the lean solution pump.

4.1.7 Methanation

After CO₂ removal unit remaining tracer of CO and CO₂ must be removed since these compounds are poisonous to the synthesis converter, CO + CO₂ are removed in the methanator vessel containing nickel catalyst at the temperature of 320 °c. the reactions involved are:

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

Determining parameters for methanation reactions are besides the activity of the catalyst the temperature, the pressure and the steam content of the process gas. Low temperature, high pressure and low steam content tend to favour the conversion of CO and CO₂ into methane.

However, within the allowable temperature range the equilibrium conditions are so favourable that practically only the catalyst activity determines efficiency of methanation The higher the temperature, better the efficiency, but at the time it means a shorter life of the catalyst. Furthermore, in case of a possible breakthrough CO; or CO to the methanator, which would result in a high temperature rise a low inlet temperature is to be preferred as this limits the temperature rise, low temperature is to be preferred as this limits the temperature rise somewhat in

connection with the lower activity. After the methanator gas normally contain less than 10 ppm CO and CO₂. The temperature rise will normally be about 2-5 "C

The methanator is provided with one catalyst bed loaded with 17.18m of 6mm rings of the catalyst, being a nickel on alumina base. As the reaction takes place at much lower temperature those prevailing in the reformers, the catalyst must be very active at lower temperatures, whereas the performance of the catalyst at higher temp is of minor interest.

Catalyst is very sensitive to sulphur, arsenic and chlorine compounds. Steam without hydrogen will oxidize the catalyst and should therefore not be used in heating, cooling or pursuing. Furthermore, it should not be exposed to condensing steam as the catalyst will disintegrate the catalyst is activated simply by heating it up with gas it should normally treat. The content of CO anCO; in the gas used for activation should be as low as possible preferably close to specific gas.

The adiabatic temperature rise is about 75'c per mole % CO and 60 °e per mole % CO₂. The methanation reaction starts at a temperature of about 240 °c, but in order to ensure a high reaction rate and a sufficiently low content of CO and CO₂ in the effluent gas, the operating temperature would be form 290°c to 350°c, depending on the catalyst activity and the gas composition. The methanator catalyst should not be exposed to catalyst temperature above 450 e for long period of time.

4.1.8 Ammonia synthesis section

The ammonia synthesis in two ammonia converters, 1" NH3 synthesis converter and 2nd NH3 synthesis converter, according to the following reaction formula:

3H2+ N2→2NH3+ heat

i.e. 3 volume of hydrogen +1 volume of nitrogen to give 2 volume of ammonia

The reaction is an equilibrium reaction and therefore only part of the hydrogen and nitrogen will be converted into ammonia by passing through the catalyst beds. The composition of gas at chemical equilibrium is influenced by pressure and temperature. High pressure and low temperature tend to favour the reaction.

However the reaction velocity is very much enhanced by high temperature operation. Therefore, there is a compromise between the theoretical conversion and the approach to the equilibrium in a single pass over the catalyst. This relationship has the result that there is an optimum level for the catalyst temperature at which the maximum production is obtained. At higher temperature the equilibrium percentage (which is the theoretical highest obtainable percentage of ammonia) will be lower, while at lower temperature the reaction rate will be slower. The synthesis unit is designed for a maximum pressure of 240 kg/cm² g, and the normal operating pressure is about 200kg/cm²g the normal operating temperature in the catalyst bed in H 170 is within the range from 395-505 c and in H 1702 from 375 °c to 440 °c

Considerable amount of heat is liberated by the reaction (about 750 k Cal/Kg produced ammonia) and a major part of the heat is utilized for production of HP steam and preheating of Hp boiler feed water.

According to the fact the reaction in an equilibrium reaction only a partial conversion can be obtained and it is necessary to recycle the unconverted synthesis gas to the converters. Approximately 33% hydrogen and nitrogen contained in the synthesis gas at the first converter inlet is converted in to ammonia per pass. In addition to the converter the synthesis loop includes a recirculation compressor (integrated with syn gas compressor) as well as equipment for steam production,

boiler feed water preheating, for cooling and condensation of the synthesis gas as well as separation of the condensed ammonia.

The converter effluent gas is cooled in a number of steps, first in the loop boiler from exit temperature of about 402 °e to 280 °c. Then in the 2nd Hp BFW preheater t 193'e, followed by the feed gas preheater to 193°c followed by the feed gas preheater and the water cooler to about 38°c, and finally in the cold exchanger and NH3 cold exchanger to 1 "c. The condensed ammonia is separated from the circulating synthesis gas in two separators and the secondaryseparator. Make up gas is introduced between exchangers. This make up point has been selected in order to remove any moister and CO, in the makeup gas, as water and CO, is dissolved in the quid ammonia. When entering the ammonia loop, the makeup synthesis gas is saturated with water vapour and contains traces of carbon monoxide and carbon dioxide. (Leakage from methanator). The water vapour cone in the makeup is in the range 400-450 ppm, depending on the operating pressure of the loop. The water is removed by absorption in the condensed ammonia. Any tracer of carbon dioxide in the makeup gas reacts both with gaseous and liquid ammonia, forming ammonia carbamate

The formed carbamate is dissolved in the condensed ammonia. The carbon monoxide is only slightly soluble in ammonia and will pass with reticulating gas to the ammonia converter where it is hydrogenated to water and methane (methanation). As water deactivates the ammonia synthesis catalyst, the carbon monoxide in the makeup synthesis gas should be kept as low as possible.

The converters are radical type converters with gas flowing though the catalyst beds in radical direction.converter, containing two catalyst beds, an inter bed heat exchanger and a feed effluent heat exchanger in the bottom. The converter contains Topsoe type KMIR catalyst. The nominal diameters of the catalyst

granules are 1.5mm to 3mm catalytic activity of the small particles is very high and the special advantage of the radical converter is to allow the use of small particles without a prohibitive pressure drop.

4.1.9 Refrigeration

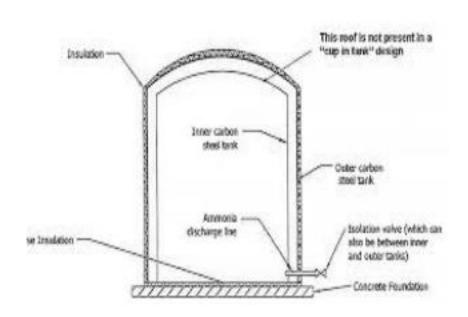
The multistage flash drum consists of five compartments operating at different pressures from .05 to 8.7 kg/cm and refrigeration compressor forms the major part of the system. The vapours flashed at the flash drum are sent to a refrigeration compressor. The compressor compresses the vapours to 15.2kg/cm pressure and discharge is sent to ammonia condenser

Condensed ammonia is separated in NH, receiver and sent to multistage flash drum. The inert from the refrigeration system is mixed with purge gas from synthesis section and is used as fuel in primary reformer.

4.1.10 STORAGE OF AMMONIA

Ammonia was initially stored in pressurized systems, such as bullets and Horton spheres. Typically, spheres were used to store up to 2,000 tonnes. Due to its explosion risk, store ammonia in a fire-rated chemical storage building. Regulators may require this depending on how far the ammonia storage location is from an occupied building. Use an ammonia gas detector in the building to pick up the release of ammonia vapours. Today, atmospheric ammonia storage tanks are used to store up to 50,000 tonnes of ammonia at plant sites and distribution terminals. Low-pressure ammonia storage has been widely accepted for two reasons. First, it requires much less capital per unit volumeEnergy storage – ammonia is easily

stored in bulk as a liquid at modest pressures (10-15 bar) or refrigerated to -33°C. This makes it an ideal chemical store for renewable energy. Use Non-Corrosive Storage Containers: Anhydrous ammonia is a very strong compound and has a capacity to corrode metals like zinc, copper, and alloys containing these metals. Zinc is used to galvanize steel, and thus these containers are not suitable to store anhydrous ammonia. Ammonium hydroxide should always be stored in well-ventilated areas. Glass, plastic or rubber containers can be used, but they must be stopped and only partially filled. Never store ammonium hydroxide at any solution with or near food or food-type products. Consequently, the use of ammonia in a conventional engine is not possible to use without power losses. However, when it is taken into consideration that being carbon-free fuel and its potential to reduce carbon emissions, ammonia is still a worthwhile and significant alternative fuel for internal combustion engines. Ammonia is not highly flammable, but containers of ammonia may explode when exposed to high heat.



CHAPTER-5

ABSORBER

A long vertical column used in industry for absorbing liquid, often water, passes in at the top and falls down against the counter current of gas. The towers are also known as scrubbers. Gas-liquid absorption columns are primarily used to clean gas streams from chemicals that should not be released into the environment. Sulphur dioxide (SO₂), carbon dioxide (CO₂) and other gases are found in industrial waste streams and contribute to air pollution and acid rain

This water will be enriched with ammonia and is pumped to the absorber or boiler, where a heat source is used to separate ammonia and water by evaporation. As in conventional refrigeration systems the high pressure refrigerant gas is liquefied and sent to An absorber tower, also referred to as a contact tower, is where natural gas contacts the system's triethelyne glycol in order to release the entrained water and hydrocarbons. This glycol "absorbs" the water from the gas and caries it out of the absorber.

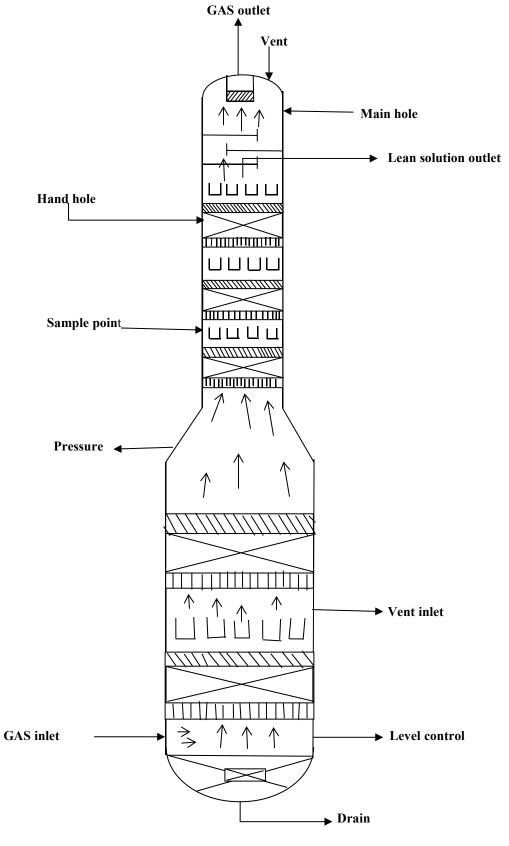


FIGURE 5.1 ABSORBER

5.1. DESIGN OFABSORPTION COLUMN:

DESIGN DATA FOR ABSORBTION COLUMN: BOTTOM COLUMN:

BOTTOM COLUMN:

FLOW RATE OF SEMI LEAN SOLUTION =1824500 Kg/hr

FLOW RATE OF LEAN SOLUTION =269600 Kg/hr

INLET GAS FLOW RATE =164714 Kg/hr

GAS OUTLET FLOW RATE =127994 Kg/hr

TOTAL INLET LIQUID FLOW RATE = FLOW RATE OF SEMI LEAN

SOLUTION + FLOW RATE OF LEAN SOLUTION

=1824500+269600

=2094100 Kg/hr

INLET GAS FLOW RATE =164714 Kg/hr

DENSITY OF MDEA = 1070 Kg/m

SPECIFIC HEAT OF MDEA =3.18 KJ/Kg C

PRESSURE OF GAS = 26.9 kg/cm^2

SPECIFIC GRAVITY OF MDEA =1.103

ACCELERATION DUE TO GRAVITY =9.81 m/s

TEMPERATURE OF INLET GAS =75 $^{\circ}$ C

TEMPERATURE OF OUTLET GAS =50 $^{\circ}$ C

GAS CONSTANT = 0.08206 1 atm/mol k

DENSITY OF GAS:

PV=nRT

Inlet gas density =26.9*16.99/346*0.08206

=16.10 Kg/m

CROSS SECTIONAL AREA A = GAS MASS FLOW

RATE / MASS VELOCITY

A = 2.69/0.985

 $A = 2.731 \text{ m}^2$

DIAMETER D= $(4A/\Box)$

D (4*2.731/3.14)0.5

D = 1.865 m.

 $X_1 = ?$

X2 0.0395

 $y_1 = 0.2138$

 $y_{\text{\tiny 2}}=0.04$

 $X_1 =$ mole fraction of solute in liquid outlet

x2= mole fraction of solute in liquid inlet

y₁= mole fraction of solute in gas inlet

y2= mole fraction of solute in gas outlet

INERT GAS FLOW RATE

$$Gs=G*(1-y_1)$$

=(164714*(1-0.2138)

=129498.14 k mol/h

INERT LIQUID FLOW RATE Ls = $L*(1-x_2)$

$$=(2094100*(1-0.0395)$$

$$= 2011383 \text{ k mol/h}.$$

FROM MATERIAL BALANCE EQUATION

$$L_s/G_s = y_1-y_2/x_1-x_2$$

$$1.4x_1 = 0.2138 - 0.04$$

$$X_1 = 0.15$$

EQUILIBRIUM RELATION y = 0.8x

m = 0.8

$$y1* = mx_{1=} 0.8* 0.15 = 0.12$$

$$y2*=mx_2=0.8*0.0395=0.0316$$

NUMBER OF TRANSFER UNIT CALCULATION:

$$NTU = (yl-y2)$$

$$(yl-yl^*)-(y2-y2^*)/In((yl-yl^*)/(y2-y2^*))$$

$$=(0.2138-0.04)$$

 $(0.2138 \hbox{-} 0.12) \hbox{-} (0.04 \hbox{-} 0.0316) / \ In((0.2138 \hbox{-} 0.12) / (0.04 \hbox{-} 0.0316))$

NTU = 3.81 m.

HEIGHT OF TRANSFER UNIT CALCULATION:

$$HTU = Q_g/K_{ya}$$

$$K_{ya} = K_{ga} * P_t$$

 $K_{ga} = b(Q_1)^r (Q_g)^p$

FOR TWO INCH INTALAX SADDLE

b = 0.0085, r = 0.4, p = 0.4

 Q_1 = mass flow rate of liquid/cross sectional area

=581.69/1.62

 $=359.06 \text{ Kg/m}^2 \text{ sec}$

Qg= mass flow rate of gas/ cross sectional area

=45.75/1.62

=28.24 Kg/m sec

Kga=0.0085 (359.06)^{0.4}* (28.24)^{0.4} =0.3402

Kya = 0.3402 * 25.5 = 8.677

HTU 28.24/8.677 = 3.25

HTU = 3.25 m

HEIGHT OF COLUMN:

Z=HTU* NTU

Z = 3.25*3.81

Z = 12.38 m

HEIGHT OF BOTTOM TOWER $z_1 = 12.38 \text{ m}$

TOP COLUMN:

FLOW RATE OF LEAN SOLUTION = 269600 Kg/hr

INLET GAS FLOW RATE = 129498 Kg/hr

TOTAL INLET LIQUID FLOW RATE =269600 Kg/hr

INLET GAS FLOW RATE = 129498 Kg/hr

DENSITY OF MDEA $= 1070 \text{ Kg/m}^3$

SPECIFIC HEAT OF MDEA = $3.18 \text{ KJ/Kg} ^{\circ}\text{C}$

PRESSURE OF GAS = 26.9 Kg/cm^2

SPECIFIC GRAVITY OF MDEA = 1.103

ACCELERATION DUE TO GRAVITY =9.81 m²/s

TEMPERATURE OF INLET GAS = 348K (75 °C)

TEMPERATURE OF OUTLET GAS = $323K (50 \degree C)$

GAS CONSTANT =0.08206 1 atm/mol k

DENSITY OF GAS:

PV=nRT

Inlet gas density = 26.9*16.99/346*0.08206

=16.10 Kg/m

Outlet gas density = 26.9*8.63/323*0.08206

 $=8.608 \text{ Kg/m}^3$

Average gas density = $(16.10+8.608)/2=(12.354) \text{ Kg/m}^3$

FLOODING CORRELATION:

$$(L/g)(\rho_g/\rho_t)\; Vs\; (U_t^{\,2}/g)(a/F^3)(\rho g/\rho_l)(\mu^{0.2})$$

$$(L/g)(\rho g/\rho_l) = 0.03$$

CROSS SECTIONAL AREA A= GAS MASS FLOW RATE / MASS VELOCITY

$$A = 2.69/0.985$$

$$A=2.731 \text{ m}^2$$

DIAMETER $D = (4A/\Box)$

 $D = (4 * (2.731)/3.14)^{0.5}$

D=1.865 m.

 $x_1 = ?$

 $X_{2} = 0$

 $y_1 = 0.04$

 $y_2 = 0.005$

 x_1 = mole fraction of solute in liquid outlet

x₂= mole fraction of solute in liquid inlet

 y_1 = mole fraction of solute in gas inlet

y₂= mole fraction of solute in gas outlet

INERT GAS FLOW RATE

$$Gs = G*(1-y_1) = (129498*(1-0.04))$$

= 124318.08 kmol/hr

INERT LIQUID FLOW RATE Ls = $L*(1-x_2)$

=(269600*(1-0)

=269600 kmol/h

FROM MATERIAL BALANCE EQUATION

 $L_S/G_S = y_1-y_2/x_1-x_2$

 $2.16x_1 = 0.04 - 0.005$

 $X_2 = 0.0162$

EQUILIBRIUM RELATION y = 0.8x

m = 0.8

 $y1*=mx_1=0.8*0.0162=0.0129$

 $y2*=mx_2=0.8*0=0$

NUMBER OF TRANSFER UNIT CALCULATION:

$$NTU = (yl-y2)$$

$$(yl\hbox{-}yl\hbox{*})\hbox{-}(y2\hbox{-}y2\hbox{*})/In(\ (yl\hbox{-}yl\hbox{*})/(y2\hbox{-}y2\hbox{*}))$$

=(0.04 - 0.005)

(0.04 - 0.0129) - (0.005 - 0) / In((0.04 - 0.0129) / (0.005 - 0))

NTU= 3.1 m.

HEIGHT OF TRANSFER UNIT CALCULATION:

HTU=Q_g/Kya

$$K_{ya} = K_{ga} * P_t$$

$$K_{ga} = b (Q_1)^r (Q_g)^p$$

FOR TWO INCH INTALAX SADDLE

 $Q_1 = mass flow rate of liquid / cross sectional area$

=74.88/1.02

 $= 73.41 \text{ Kg/m}^2 \text{ sec}$

Qg= mass flow rate of gas / cross sectional area

=35.97/1.02

 $= 35.26 \text{ Kg/m}^2 \text{ sec}$

Kga=0.0085 (73.41)^{0.4}* (35.26)^{0.4}

=0.197

Kya = 0.197*25.5 = 5.02

HTU = 35.26/5.02

HTU = 7.02 m

HEIGHT OF COLUMN:

z=HTU*NTU

z=7.02*3.1

Z = 21.76 m

HEIGHT OF TOP TOWER 22 = 21.76 m

TOTAL HEIGHT OF COLUMN:

 $Z = z_1 + z$

Z=12.38+21.76

Z=34.14 m

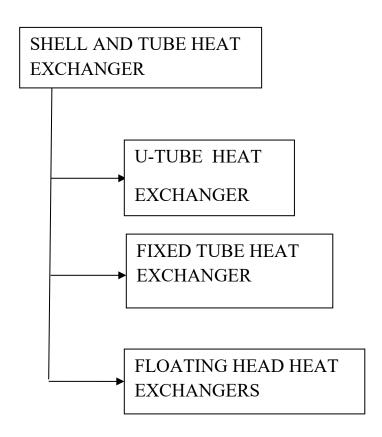
5.2.1 SHELL AND TUBE HEAT EXCHANGERS

Shell and Tube heat exchanger make it possible to pump materials as soon as possible, and they transfer temperature efficiently so you can ensure the material are at the necessary temperature without expending extra energy to do so.

Shell and Tube heat exchanger is used in various industrial process applications because they can perform tasks such as: Removal of heat and feed water preheating. Cooling of hydraulic and lube oil. Cooling of turbine, compressor, and engine.

Smeller designs can be lower cost. Mush easier to service.0ring seal also make them cheap to service. A better solution for sea water coolant, or other fluids at risk of clogging in narrow spaces

- Are the most commonly used heat exchangers in oil refineries and other large chemical processes.
- ➤ Are used when a process requires large amounts of fluid to be heated or cooled.
- ➤ Provide transfer of heat efficiently.
- > Use baffles on the shell-side fluid to accomplished mixing or turbulence



5.3 U-TUBE HEAT EXCHANGER

Heat exchanger systems consisting of straight length tubes bent into a U-shape surrounded by a shell.

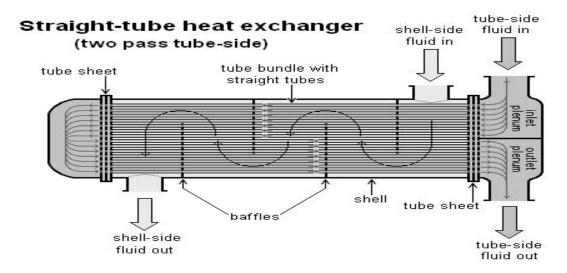


FIGURE 5.2 HEAT EXCHANGER

U-TUBE HEAT EXCHANGERS

- ➤ Both initial and maintenance costs are reduced by reducing the number of joints.
- > They have drawbacks like inability to replace individual tubes except in the outer row and inability to clean around the bend.

U-TUBE HEAT EXCHANGERS

- Examples: Reboilers, evaporators and Kettle type.
- They have enlarged shell sections for vapor-liquid separation. mixing with each other.

• One fluid runs through the tubes, and another fluid flows over the tubes (through the shell) to transfer heat between the two fluids.

Why shell-and-tube?

STHE accounted for 85% of new exchangers supplied to oil-refining, chemical, petrochemical and power companies.

Why?

- ➤ Can be designed for almost any duty with a very wide range of temperatures and pressures
- > Can be built in many materials
- Many suppliers
- > Repair can be by non-specialists
- ➤ Design methods and mechanical codes have been established from many years of experienc

Scope of shell-and-tube

> Maximum pressure

- Shell 300 bar (4500 psia)
- Tube 1400 bar (20000 psia)

> Temperature range

- Maximum 600°C (1100°F) or even 650°C
- -Minimum-100°C (-150°F)

> Fluids

- -Subject to materials
- Available in a wide range of materials

> Size per unit 100-10000 ft (10-1000 m²)

Can be extended with special designs/materials

Shell and tube heat Exchanger

- ➤ Main Parts
- ➤ 1.Tubes
- ➤ 2.Shell
- ➤ 3.Baffle
- ➤ 4.Tube Sheets
- ➤ 5.Head
- ➤ 6.Tube Bundle
- Consist of two mainthings as it's name implies Shell & Tubes
- The shell is a large vassel with a number of tubes inside it
- ➤ The principle of operation is simple enough: Two fluids of different temperatures are brought into close contact but they are not mixing with each other.
- ➤ One fluid runs through the tubes, and another fluid flows over the tubes (through the shell) to transfer heat between the two fluids.

Why shell-and-tube?

STHE accounted for 85% of new exchangers supplied to oil-refining, chemical, petrochemical and power companies.

Why?

- ➤ Can be designed for almost any duty with a very wide range of temperatures and pressures
- > Can be built in many materials
- ➤ Many suppliers
- > Renair can be by non-specialists

5.4 DESIGN OF SHELL AND TUBE HEAT EXCHANGER:

Shell and tube heat exchanger details:

FLUID CIRCULATED	UNIT	SHELL SIDE CO ₂	TUBE SIDE WATER
Fluid (in/out) Temprature(T)	°C	(75/41)	(30/35)
Specific heat (C _{p)}	KJ/Kg C	0.846	4.187
Thermal conductivity (K)	W/m C	0.0746	0.58
Viscosity (μ)	Ср	0.07	1
Density (ρ)	Kg/m ²	0.1	1000
Fouling resistance	Kg/m ³	1.76 * 10-4	1.76*10

HEAT DUTY OF HEAT EXCHANGER:

 $Q = m_h C_{ph} \, \Delta T$

Cooling water flow rate:

$$Q = m_c C_{pc} \Delta T$$

$$514 = m*4.187* (40-30)$$

$$m = 6.63 \text{ kg/s}$$

considering the end conditions of the heat exchanger the flow is counter current

TO FIND LMTD:

$$Th_1 = 75 \text{ C} \quad Th_2 = 41 \text{ C}$$
 $Tc_2 = 40 \text{ °C} \quad Tc_2 = 30 \text{ C}$
 $\Delta T_1 = 30 \text{ °C} \quad \Delta T_2 = 11 \text{ °C}$
 $LMTD =$

= (30-11)/ In (30/11) = 18.93 c

$$\begin{split} \Delta T_m &= F_T *LMTD \\ P &= (Th_1 - Th_2)/(Tc_2 - Tc_1) \\ &= 0.33 \\ R &= (Tc_2 - Tc_1)(T_{h1} - T_{h2}) \\ &= 2.2 \\ Fr &= 0.89 (from graph) \\ For 1 shell and 2 tube pass \end{split}$$

 $\Delta T_m=18.44$ C

TO FIND NUMBER OF TUBES:

Assumed unit:

Let as assume overall heat transfer co-efficient.

 $U_0 = 90 \text{ w/m}^2 \text{ C}$

W.k.t

$$A = Q/U_0AT$$

= 277.89 / 18.44* 90
=167.44 m²

Assume:

OD =20 mm, ID= 16 mm, L=4.5 m

 $P_T = 25$ mm square pitch.

Area per tube = $\pi D_o Le$

= 3.14 *0.02* 4

 $=0.251 \text{ m}^2$

N_T=Area/ surface area of the tube

 $=A/\pi D_0 Le$

=167.44/0.251

= 668 tubes

From the tube count table the exchanger assumed will have 787.4 mm shell ID(31"inches) with 668 tube of 20mm OD*16mm ID 4.5 m long placed at 25mm square pitch 1-shell and 2-tube pass

FILM CO-EFFICIENT TUBE SIDE:

$$h_i di/k = 0.023 (Re)^{0.8} (pr)^{0.33} (\mu/\mu_w)^{0.14}$$

$$Re = (D_iG_t/\mu)$$

$$G_t = m_c/A_t$$

$$A_t = \pi/4 * D_i^2 * (N_t/N_p)$$

$$=0.201 \text{ m}$$

$$m_c = 6.63 \text{ kg/s}$$

$$G_t = 6.63/0.201$$

$$=30.13 \text{ kg/sm}^2$$

Viscosity (μ)=ICp,

Thermal conductivity (k) = 0.58 W/m C,

Specific heat $(C_p) = 4.187 \text{kJ/kg}$ C

$$Re = 482.08$$

$$Pr = C_p \mu/k \,$$

$$=7.21$$

Let as assume $(\mu/\mu_w) = 1$ for low viscous fluids

$$h_iD_i\!=\!0.023(400)^{0.8}\,(7.2)^{0.33}$$

$$h_1 = 224.2 \text{ W/ } m^2 \text{ C}$$

Wall thickness 'based on ID and OD:

$$h_{io} = hi *(ID/OD)$$

$$= 224.2*(16/20)$$

$$=180 \text{ W/m}^2 \text{ C}$$

FILM CO-EFFICIENT SHELL SIDE h₀:

$$h_0D_e = 0.36 \text{ (Re)}^{0.55} \text{ (Pr)}^{0.33} (\mu/\mu_w)^{0.14}$$

D_e= shell side equivalent tube dia (m) for

Sq.pitch

$$=4[p_T^2 - (\pi/4)D_o^2/\pi D_0]$$

$$=4((0.025)^2-\pi/4 (0.020))^2/\pi^* 0.020)$$

$$=0.01979 \text{ m}$$

Shell side, $Re = (D_eG_s)/\mu$

Shell side mass velocity, $G_s = m_h / A_s (kg/m^2s)$

Cross flow area, $A_s = (D_s c' B)/P_T$

D=Shell ID

$$A_s = D_s C'B / P_T$$

$$= (0.7874*0.005*0.7874)/0.025$$

$$= 0.1239 \text{ m}^2$$

$$As=0.1239 \text{ m}^2$$

$$G=77.96 \text{ kg/m}^2\text{s}$$

Viscosity of
$$CO_2(\mu)=0.07$$

Thermal conductivity of $CO_2(k) = 0746$

$$P_r\!=C_p\mu/K$$

$$=(0.846 *0.07* 10^{-3})/0.0746$$

=0.79
=0.36
$$(21160)^{0.55} (0.79)^{0.33} (1)^{0.14}$$

 h_o =313 w/m 2 C

TUBE WALL RESISTANCE (Rw):

$$R_w = {}_{D0/2Kw} In (D./D_i)$$

=0.5189*10 -4 m²° C/W

Assuming fouling resistance value:

Shell side fluid $R_{do} = 1.76 \ 10^{-4} \ m^{2o} \ c/w$

Tube side fluid $R_{di} = 1.76 \cdot 10^{-4} \text{m}^2 \cdot \text{C//W}$

$$R_{dio} = R_{di} * (OD/ID)$$

= 2.2*10⁻⁴m² C/W

OVERALL HEAT TRANSFER COEFFICIENT:

Heat transfer area available in the assumed unit:

$$A_a = \pi^* OD^* L_e N_T$$
 (L_e=length of tube)
=3.14 *0.02*4*668

 $=167.8 \text{ m}^2$

For safer design the heat exchanger area in assumed unit should have a value 10 to 20 % higher than the heat exchanger area required as per the calculation.

% excess area =
$$(A_a-A_r)/A_r *100$$

= $(167.8-138.6)/138.6*100$
= 21%

RESULT SHEET:

PROPERTIES	SHELL SIDE	TUBE SIDE
Fluid	CO ₂	Cold water
Heat duty (kw)	277.89	277.89
Temp in/out (°c)	75/41	30/40
Reynolds no	21160	482
Prantl no	0.79	7.21
Film co-efficient (w/m ²⁾	313	180

No of pass: 2

No of tube: 668

Overall heat transfer co-efficient: 108.7 w/m² C

Required heat transfer area: $140 \ m^2$

Tube OD 20mm, ID 16mm, L=4.5m

CHAPTER-6

6.1 PLANT SAFETY

Historical data show that the major accidents in ammonia plants are explosions and fires. In addition there is also a potential of toxic hazard due to the handling and storage of liquid ammonia.

The following credible major hazards events are identified in an ammonia production plant:

1. Fire/explosion hazard due to leaks from the hydrocarbon feed system. 2. Fire/explosion hazard due to leaks of synthesis gas in the CO removal/synthesis gas compression areas (75% hydrogen). 3. Toxic hazard from the release of liquid ammonia from the synthesis loop.

In ammonia storage the release of liquid ammonia (by sabotage) is a credible major hazard event.

Confined explosions in ammonia plants appear to be limited to explosions equivalent to a few hundred kg TNT. Such explosions are normally not fatal for humans at 50-60m distance, and thus in most cases not severe for people outside. the plant fence. The same is true for fireballs equivalent to 500kg hydrogen. Fires and explosions are usually not a hazard or only a minor hazard to the local population although potentially most severe for the plant operators. Appropriate precautions to protect both the operators and the local population are taken in the design and operation of the plants.

The toxic hazard of a potential large release of liquid ammonia (ie. from a storage tank) may be much more serious for the local population. An emergency plan for this event, covering the operators and the local population must be maintained.

HAZARDS IDENTIFICATION

Human helth:

Ammonia is toxic by inhalation, corrosive to all parts of the body and liquid splashes can cause severe cold burns.

Skin contact:

Liquid ammonia splashes may produce severe cold burns to skin. Vapour in presence of moisture is an irritant to the skin.

Eye Contact:

Liquid ammonia splashes may cause permanent damage to eyes with the full effects not being apparent for several days. Vapours can cause irritation and watering of eyes and at high concentrations can cause severe damage.

Ingestion:

Will immediately cause severe corrosion and damage to the gastro-intestinal tract.

Inhalation:

Ammonia odour threshold 5-25ppm. Concentrations in the range 50-100ppm may cause slight irritation following prolonged exposure. Immediate eye, nose and throat irritation may occur with ammonia levels between 400 - 700ppm with symptoms of slight upper respiratory tract irritation persisting beyond the period of exposure. At higher concentrations, above 1000ppm, severe eye and upper respiratory tract irritation can develop following a short period of exposure. Exposure to ammonia in excess of 2000ppm for even short periods may result in severe lung damage and could be fatal. Fluid build up on the lung (pulmonary dema) may occur

up to 48 hours after exposure and could prove fatal. Exposure to concentrations grossly in excess of the occupational exposure limit may lead to permanent respiratory impairment.

No evidence of adverse effects at exposure below occupational exposure limits

Long term effects

Environment:

Free (non-ionised) ammonia in surface water is toxic to aquatic life, however the ammonium ion which predominates in most waters is not toxic. In the event of water contamination with ammonia, ammonium salts which may be formed will not present a toxic hazard. Increases in pH above 7.5 leads to an increased level of non-ionised ammonia.

Studies in fish have shown that repeated exposures produce adverse effects on growth rate at concentrations greater than 0.0024mg/l

Other:

Fire, heating and explosion

Flammable but difficult to ignite in open air. In enclosed space ammonia air mixtures may be flammable/explosive.

Danger of tank or cylinder bursting when heated.

Large leaks of liquid ammonia may produce a dense cloud, restricting visibility.

FIRST-AID MEASURES

Speed is essential. Remove affected person from further exposure. Give immediate first aid and obtain medical attention.

Skin Contact

Drench with large quantities of water. In case of frost bite (freeze burns) clothing may adhere to the skin. Defrost with care using comfortable warm water. Remove clothing and wash affected parts. Obtain immediate medical attention.

Eye contact

Immediately irrigate the eyes with eyewash solution or clean water for at least 10 minutes. Continue irrigation until medical attention can be obtained. Hold eyelids open during flushing.

Ingestion

Do not induce vomiting. If the person is conscious, wash out mouth with water and give 2 or 3 glasses of water to drink. Obtain immediate medical attention.

Inhalation

Move the injured person to fresh air at once. Keep the patient warm and at rest. Administer oxygen if competent person is available. Apply artificial respiration, if breathing has stopped or shows sign of failing. Obtain immediate medical attention.

Further medical advice

Keep under medical review for possibility of rapid or delayed tracheal, bronchial and pulmonary edema. Progressive ocular damage may arise.

FIRE-FIGHTING MEASURES

Ammonia vapour and liquid spills are difficult to ignite, particularly in the open air. In an enclosed space, mixtures of ammonia and air within the limits (16-27%), might cause explosion if ignited. Cold, dense cloud of ammonia may impair visibility.

- Attempt to isolate source of leak.
- ➤ Use foam, dry powder or CO,.
- ➤ Use water sprays to cool fire-exposed containers and structures, to disperse vapours and to protect personnel. Do not spray water into liquid ammonia.
- ➤ Wear self-contained breathing apparatus and full protective clothing.

ACCIDENTAL RELEASE MEASURES

- ➤ Those dealing with major releases should wear full protective clothing including respiratory protection.
- Evacuate the area down-wind of the release, if it is safe to do so. If not, then stay indoors, close all windows and switch off any extraction fans or electrical fires.
- ➤ Isolate source of leak as quickly as possible by trained personnel.
- ➤ Ventilate area of spill or leak to disperse vapours. Remove ignition sources.
- ➤ Consider covering with foam to reduce evaporation.
- ➤ Contain spillages if possible.

- ➤ Use water sprays to combat gas clouds. Do not apply water directly into large ammonia spills.
- Take care to avoid the contamination of watercourses.
- ➤ Inform appropriate authority in case of accidental contamination of watercourses or drains.

HANDLING AND STORAGE

- Avoid skin and eye contact and inhalation of vapours.
- Provide adequate ventilation.
- ➤ Control atmospheric levels in compliance with occupational exposure limits.
- Wear full protective equipment where there is a risk of leaks or splashes.

Storage:

- > Store containers tightly closed in a cool, well ventilated area.
- > Keep away from heat, ignition sources and incompatible substances.
- ➤ Do not permit smoking in the storage area.
- Follow appropriate Industry or National codes for bulk and container (cylinder) storage.

EXPOSURE CONTROL / PERSONAL PROTECTION

Recommended occupational exposure limits:

ACGIH [4] occupational exposure limits for ammonia and other components associated with ammonia production are given in the table below. All the figures are ppmv:-

COMPONENT	TLV – TWA (8hr)	TLV –STEL (15 min)
NH ₃	25	35
NO ₂	3	5
SO_2	2	5
H ₂ S	10	15
СО	50	400
CO ₂	5000	30000

The figures are subject to updating and may vary between countries.

Precautionary and engineering measures

- Provide local exhaust ventilation where appropriate.
- ➤ Provide safety showers and eye washing facility at any location where skin or eye contact can occur.

Personal Protection

- Wear suitable breathing apparatus if exposure levels exceed the recommended limits.
- ➤ Wear cold insulating PVC gloves, rubber boots, PVC suit

CHAPTER - 7

7.1. CONCLUSION

In this project I have studied the manufacture of ammonia process bymeans And also detailed study is done on the Reforming Section and MEDA selection where CO₂ absorbed from the process gas because CO₂ acts as a catalytic poison to the ammonia synthesis and "Design verification of absorption column and Shell and Tube Heat exchanger".

CHAPTER - 8

8.1. REFERENCE

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