

CL 452 - Design Project
Spring 2019

Group 9

Nitric Acid

Final Project Report

Members

Vishal Jajodia : 15B030014

Abhishek Pawan Sharma : 150020010

Shubhangi Chuhadia : 150020072

Hrishav Ranjan : 150020074

Kshitij Chandrachoor : 150020058



Department of Chemical Engineering
Indian Institute of Technology Bombay

Executive Summary

This report speaks in detail about the manufacturing of Nitric Acid. Chapter 1 is about the molecule, its properties and its uses in the industry. Information about different grades of Nitric Acid is also mentioned in this chapter. We then move on to a market survey in Chapter 2, which provides an insight into the patterns observed over the past decade in worldwide nitric acid production and consumption. Top market producers in both the domestic and global markets were identified and their technology providers were also identified. We then finalise our new plant location to be Hazira, Gujarat, based on factors mentioned and discussed in Chapter 2.

In Chapter 3, multiple production routes for Nitric Acid are discussed, varying from different laboratory methods and the commercially used Ostwald Process. Since the laboratory methods are not feasible, Ostwald Process is discussed in further detail, explaining the stages and the operating parameters for each stage. Variations are available in Ostwald Process, which are useful for plants of different capacities. Processes are differentiated on the basis of the operating pressures in multiple stages of the process. Single Pressure and Dual Pressure processes are explained and compared with each other. Based on our requirement and multiple factors discussed in this section, we finally select the Uhde Dual Pressure Nitric Acid Process to be implemented in our new plant. We choose Thyssenkrupp Industrial Solutions (Uhde GmbH) as our technology model.

To get a better insight into the Uhde Dual Pressure Nitric Acid Process, we visited Deepak Fertilisers and Petrochemicals Corp. Ltd.'s Taloja facility. Chapter 4 discusses this visit in detail. The visit helped us indentify the actual operating parameters for the Uhde Dual Pressure Process and also helped us gather important information, relevant to equipment sizing and costing. Based on the information gathered from our visit, we created our Process Flow Diagram. Chapter 5 discusses the Uhde Dual Pressure Process, as implemented in the PFD. We also identify the intensive Heat Integration already available in this well defined process.

In Chapter 6, we carry out an analytical Mass Balance, providing sample calculations for each major equipment. Chapter 7 provides a look into the flowsheet simulation of the entire process. The simulation was performed on DWSIM. Comparisons between the analytical mass balance and flowsheet results is also done in this section. Chapter 8 shows the sensitivity analysis done on the flowsheet for the reactor, heat exchangers and the absorption column to optimise the process operation.

Equipment Sizing and Costing is done in Chapter 9. Sample calculations are done for each major equipment, and subsequent costing calculations are also tabulated, using costing relations and nomograms for this exercise. The total purchased equipment delivered cost is used to calculate the total capital investment required for our plant, which comes out to be INR 894 Crores. Payback Period calculations are also shown in this section, after total product costs and revenue calculations are carried out. Plant economics for our process was compared with a recently setup Uhde Plant in Donaldsonville, Louisiana, USA.

Finally, Environmental Impact Analysis is shown in Chapter 12, detailing the emission limits in India, process required to bring our emissions within these statutory limits and the economic impact these additions have on our plant.

Acknowledgement

We would like to take this opportunity to thank our panel members for providing us constant support and constructive feedbacks, throughout the Design Project exercise.

We would also like to thank Prof. Sanjay Mahajani, Department of Chemical Engineering, IIT Bombay for setting up a visit to the Deepak Fertilisers and Petrochemicals Corp. Ltd. facility in Taloja, Maharashtra.

At many stages of our project, we acquired guidance from Mr. Amrish Dholakia, Engineering Manager, GM - Processes, Thyssenkrupp Industrial Solutions, India. Many tasks such as Equipment Sizing, Costing, Plant Economics, etc. would not have been possible without his inputs.

Finally, we would like to express our gratitude to the Overall Supervisors, Nitric Acid Process Head and the Staff of Deepak Fertilisers and Petrochemicals Corp. Ltd., Taloja, Maharashtra for helping us understand the intricacies of the Nitric Acid Process during our visit to their facility.

Contents

Executive Summary	ii
Acknowledgement	iv
List of Figures	viii
List of Tables	ix
1 Nitric Acid	1
1.1 Properties	1
1.2 Uses of Nitric Acid	2
1.3 Uses of Intermediates and Byproducts	3
1.4 Grades of Nitric Acid	4
2 Market Survey	5
2.1 World Consumption Patterns	5
2.2 World Production Patterns	6
2.3 Top Market Producers	8
2.4 Technology Providers	9
2.5 Location Selection for New Plant	9
3 Production Process	11
3.1 Production Routes	11
3.2 Ostwald Process	12
3.2.1 Ammonia Oxidation	12
3.2.2 Nitric Oxide Oxidation	12
3.2.3 Absorption	13
3.3 Deviations in Ostwald Process	14
3.3.1 Single Pressure Processes	14
3.3.1.1 Medium Pressure	14
3.3.1.2 High Pressure	14
3.3.2 Dual Pressure Process	15
3.4 Selection of Final Process	15
4 Industrial Visit	18
4.1 Process Highlights	19
4.1.1 Ammonia	19
4.1.2 Ammonia Filters	19

4.1.3	Air Filters	19
4.1.4	Ammonia - Air Mixer	19
4.1.5	Turbine Shaft	20
4.1.6	Reactor	20
4.1.7	Boiler	20
4.1.8	Cooler Condenser	21
4.1.9	Absorption Column	21
4.2	Conclusion	21
5	Process Flow Diagram	22
5.1	Process Flow Diagram	22
5.2	Process Explanation	22
5.3	Process Heat Integration	27
6	Mass Balance	30
6.1	Sample Calculations	30
6.1.1	Reactor - R101	30
6.1.2	Heat Exchangers and Cooler Condenser	32
6.1.3	Absorption Column and Cooler Condenser	33
6.2	Final Mass Balance Table	33
7	DWSIM Flowsheet Simulation	35
7.1	Kinetics and Specifications used in DWSIM	35
7.1.1	Ammonia Oxidation	36
7.1.2	Nitric Oxide Oxidation	36
7.1.3	Absorption Column	37
7.2	Comparisons	38
7.2.1	Ammonia Reactor	39
7.2.2	Heat Exchangers	39
7.2.3	Absorption Column	40
8	Sensitivity Analysis	41
8.1	Reactor Analysis	41
8.2	Heat Exchanger simulated as PFR	42
8.3	Absorption Column Analysis	43
9	Equipment Sizing and Costing	45
9.1	Ammonia Oxidation Reactor	45
9.1.1	Diameter Calculation	46
9.1.2	Catalyst Costs	46
9.1.3	Burner Head Calculation	47
9.2	Storage Tanks	48
9.3	Compressors	49
9.4	Pumps	50
9.5	Heat Exchangers	52
9.6	Columns	54
9.6.1	Shell Calculations	54
9.6.2	Tray Calculations	56

10 Plant Economics	57
10.1 Major Equipment Costing	57
10.2 Capital Investment Estimation	58
10.3 Raw Material Cost	59
10.4 Revenue Calculation	59
10.5 Total Product Cost	60
10.6 Payback Period	60
11 Detailed Design - Absorption Column	63
11.1 Mathematical Model	64
11.2 Tray Selection and Specifications	67
11.2.1 Weeping Check	68
11.2.2 Plate Pressure Drop	68
11.2.3 Perforated Area and Hole Pitch	68
11.2.4 Number of Holes	69
11.3 Head Selection	71
11.4 Tower Thickness	71
12 Environmental Impact	73
12.1 Tail Gas Composition and Emission Limits	73
12.2 Abatement Technology	74
12.3 Tail Gas Post Abatement	75
12.4 Revised Plant Economics	76
12.4.1 Reactor Unit Cost	76
12.4.2 Additional Raw Material Costs	76
12.4.3 Additional Revenue Calculation	77
12.4.3.1 No CER Revenue	77
12.4.3.2 With CER Revenue	78
A Final Process Flow Diagram	79
B MATLAB Code for the Mathematical Model for NO_x Absorption	81
C Detailed Drawing of Absorption Column	84
D DWSIM Flowsheet	86
References	88

List of Figures

1.1	Uses of Nitric Acid	2
2.1	World Nitric Acid Consumption	6
2.2	World Nitric Acid Production	7
2.3	Nitric Acid Top Market Producers	8
3.1	Block Diagram of Ostwald Process	13
4.1	Ammonia Flow through Ceramic Filters	19
4.2	DFPCL Turbine Shaft Structure	20
4.3	Nitric Acid Cooler Condenser	21
5.1	Process Flow Diagram for Dual Pressure Nitric Acid Process	26
5.2	Heat Exchanger Network	29
7.1	DWSIM Flowsheet - Ammonia Oxidation	36
7.2	DWSIM Flowsheet - NO Oxidation and Heat Exchanger Network	37
7.3	DWSIM Flowsheet - Reactive Absorption Column Modelling	38
8.1	Sensitivity Analysis for Reactor	41
8.2	Sensitivity Analysis for Heat Exchanger	42
8.3	Sensitivity Analysis for Absorption Column - 1	43
8.4	Sensitivity Analysis for Absorption Column - 2	43
10.1	Estimated Cash flow from Plant Operation	62
11.1	Sieve Tray Perforated Area with Downcomer	70
11.2	Sieve Tray Cooling Coils	70
12.1	EnviNO _x [®] Process Variant - 2	75

List of Tables

1.1	Nitric Acid Properties	1
2.1	World Nitric Acid Production	6
2.2	Major Producers in Global Market	8
2.3	Major Producers in Domestic Market	8
3.1	Temperature and Pressure Dependence of Ostwald Process	14
5.1	Utility Data after Heat Integration	28
6.1	Reactor Balance	31
6.2	Heat Exchanger Balance	32
6.3	Absorption Column and Cooler Condenser Balance	33
6.4	Final Mass Balance	34
7.1	Mass Balance Comparison for Reactor	39
7.2	Mass Balance Comparison for Heat Exchanger network	39
7.3	Mass Balance Comparison for Absorption Column	40
9.1	Catalyst Costs	46
9.2	Burner Head Design Parameters	47
9.3	Burner Head Costing Parameters	47
9.4	Nitric Acid Storage Tank Costing	48
9.5	Compressor Power Calculation	49
9.6	Costing of Multi Stage Compressors with Turbines	50
9.7	Pump Costing Factors	51
9.8	Pump Factors	51
9.9	Costing of Centrifugal Pumps	52
9.10	Operating Parameters and Costing of Heat Exchangers	53
9.11	Column Parameters and Costing	55
9.12	Sieve Tray Costing	56
9.13	Total Purchased Costs for Columns	56
10.1	Total Purchased Equipment Cost	57
10.2	Total Capital Investment Estimation	58
10.3	Total Raw Material Cost Calculation	59
10.4	Total Revenue Calculation	59
10.5	Total Product Cost Estimation	60
10.6	Cash Flow from Plant production	61
10.7	Plant Economics Comparison with recently setup plant	62

11.1 Mathematical Model Results	65
11.2 Tray Selection Parameters	67
11.3 Final Tray Specifications	69
11.4 Final Column Specifications	72
12.1 Composition of Tail Gas leaving Absorption Column	73

Chapter 1

Nitric Acid

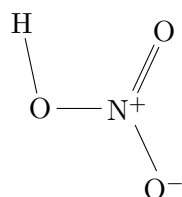
Nitric acid (HNO_3) is a highly corrosive mineral acid and powerful oxidizing agent. It occurs in nature only in the form of nitrate salts. The pure compound is a colorless liquid, but tends to acquire a yellow cast, if stored for long, due to the accumulation of oxides of nitrogen. Most commercially available nitric acid has a concentration of 55-70%, being centrally used in the production of nitrogen fertilisers, nylon and explosives.

1.1 Properties

Property Name	Property Value
Molecular Weight	63.012 g/mol
Colour	Colourless
Boiling point	83°C
Density	1.512 g/cm ³
Azeotropic composition	68% w/w (BP = 120.5°C)
Thermal conductivity (20°C)	0.343 W/m.K
Standard enthalpy of formation	2.7474 J/g (Liquid); 2.1258 J/g (Gas)
Heat of vaporization (20°C)	626.3 J/g
Specific heat (20°C)	1.7481 J/g.K

TABLE 1.1: Nitric Acid Properties

The tabulated data above lists some of the chemical and physical properties of nitric acid, acquired from PubChem¹. Nitric acid is a nitrogen oxoacid, with a nitrogen atom bonded to a hydroxyl group and by equivalent resonating double bonds to the remaining two oxygen atoms, giving the N-atom a +5 oxidation state. This can be seen in the HNO_3 structure shown below:



1.2 Uses of Nitric Acid

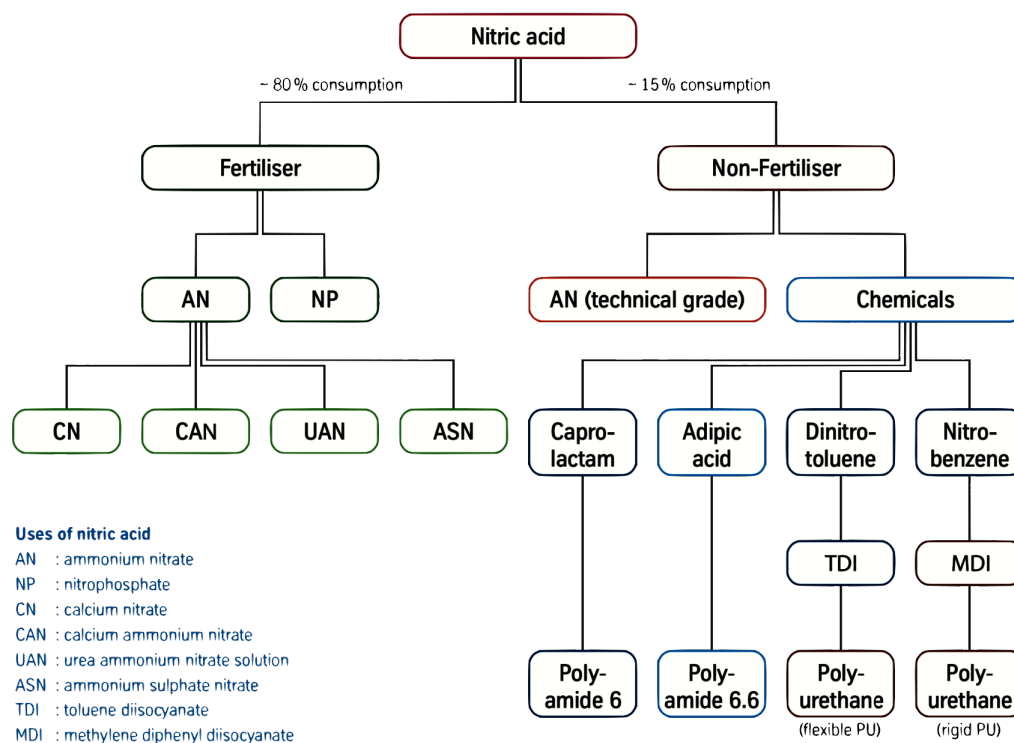


FIGURE 1.1: Uses of Nitric Acid, recreated from Thyssenkrupp Nitric Acid Book [1]

Nitric acid is widely used as an intermediate and its demand majorly depends on the demand of the end product for which it is used as a raw material. About 90% of nitric acid is used for on-site consumption and only 10% accounts for retail market. Nitric Acid is used for following purposes:

¹https://pubchem.ncbi.nlm.nih.gov/compound/nitric_acid#section=Chemical-and-Physical-Properties

- About 80% of the world production is used as raw material in the production of Ammonium Nitrate in the fertiliser industry
- Also used as a raw material in the production of Adipic acid, which is further employed in manufacturing Nylon-6,6 resins and fibres - widely used in the automotive industry
- Also used as a raw material for the production of Nitrobenzene - a precursor to Aniline, which finds widespread use in the pharmaceutical industry
- Used in manufacturing explosives in mining/construction industry
- Used in manufacturing Polyurethane and Polyamide and also as an oxidiser in liquid fueled rockets

1.3 Uses of Intermediates and Byproducts

- **NO** - Nitric oxide is used together with a breathing machine (ventilator) to treat respiratory failure in premature babies. In the human body, nitric oxide expands the blood vessels, increasing blood flow and decreasing plaque growth and blood clotting.
- **NO₂** - Nitrogen Dioxide is used as an oxidising agent in certain oxidation reactions, as an inhibitor to prevent polymerization of acrylates during distillation, as a nitrating agent for organic compounds, as a rocket fuel, as a flour bleaching agent and in increasing the wet strength of paper.
- **N₂O** - Nitrous oxide has significant medical uses, especially in surgery and dentistry, for its anaesthetic and pain reducing effects. Its name "laughing gas" is due to the euphoric effects upon inhaling it, a property that has led to its recreational use as a dissociative anaesthetic.

Even though these byproducts find significant uses in multiple sectors of industry, they are major pollutants when produced in large amounts, with NO and NO₂ being the main causes for acid rains and air pollution and N₂O being a major greenhouse gas, contributing to the depletion of the Ozone layer and trapping of heat within the atmosphere, and hence, require to be eliminated as per Government of India norms before being expanded into the atmosphere.

1.4 Grades of Nitric Acid

There are two major commercially available grades of Nitric Acid:

- **Weak Nitric Acid (WNA)** - Nitric acid having a concentration of 55-70% wt.HNO₃. WNA is widely used in the fertiliser industry as the starting raw material for Ammonium Nitrate.
- **Concentrated Nitric Acid (CNA)** - Nitric acid having a concentration of >90% wt.HNO₃. CNA is widely used as a nitration agent in manufacturing explosives, nitroalkanes and nitroaromatics and also as an oxidising agent in multiple industries and laboratories.

Chapter 2

Market Survey

Due to the rapidly increasing population and reduced availability of land for irrigation, there is an increasing demand for fertilisers. The use of nitric acid as an intermediate in the production of ammonium nitrate is a key factor, boosting the production as well as the consumption of HNO_3 . Growing automotive industry drives concentrated nitric acid market as it is utilized in manufacturing of light weight and strong body parts of vehicles. Rising demand for synthetic rubbers, elastomers and polyurethane foams in the automotive industry is anticipated to drive the product demand as well. All the findings of this section were made after referring Nitric Acid Market Research reports provided by Research and Markets[2], Grand View Research[3] and IHS Chemical Economics Handbook[4].

2.1 World Consumption Patterns

The largest market for nitric acid is the production of ammonium nitrate (AN) and calcium ammonium nitrate (CAN), accounting for almost 77% of the total world consumption of nitric acid in 2016. World nitric acid consumption has exhibited a steady upward trend since 2000, with average annual growth rates of 2.0% during 2000-17 [4]. Europe, United States and China account for more than 80% of global demand. Since 2000, the largest increase in consumption has occurred in China, at an average annual growth rate of 7.3%.

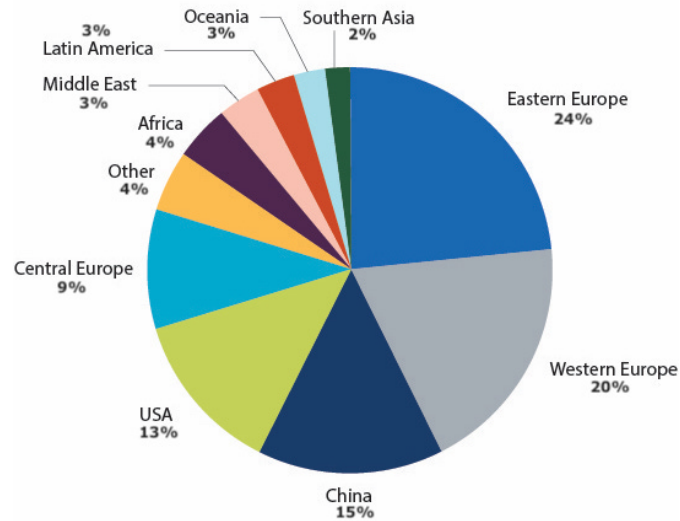


FIGURE 2.1: World Nitric Acid Consumption 2017, recreated from [4]

The presence of large agricultural and industrial market in Asia-Pacific is a key factor responsible for the high growth of the global nitric acid market. Also, the stringent regulations in regions like North America and Europe regarding the use of ammonium nitrate based fertilisers are likely to shift the demand to countries in the Asia-Pacific.

2.2 World Production Patterns

Year	Nitric Acid Produced (tons)	Increase (tons)
2010	7,419,644	—
2011	7,642,233	222,589
2012	7,871,500	229,267
2013	8,107,645	236,145
2014	8,350,874	243,229
2015	8,601,401	250,526
2016	8,859,443	258,042
2017	9,125,226	265,783

TABLE 2.1: World Nitric Acid Production

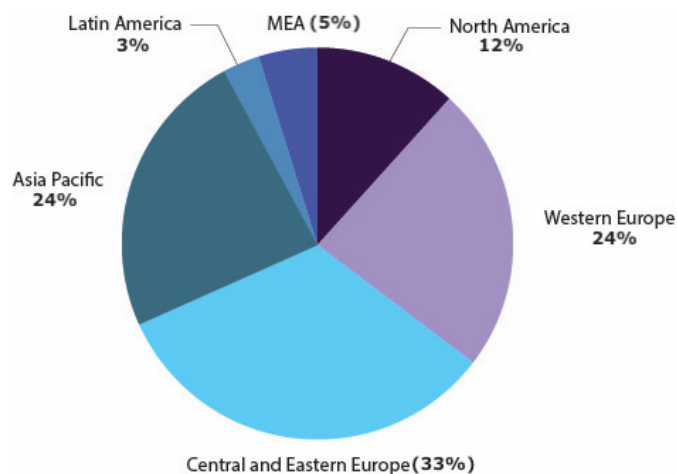


FIGURE 2.2: World Nitric Acid Production 2017, recreated from [2]

Europe and North America account for more than 80% of the global production. In North America, the United States dominated the market with a revenue share of 70% in 2017 and it is estimated to continue the trend over the forecast period of 2018-2025. Robust manufacturing base of chemical, electronics, and automotive industries in the U.S. is anticipated to supplement the growth of the market in the region.

In Western Europe, Germany represented 15% of the overall revenue in 2017. Leading chemical companies such as BASF, Bayer and Henkel have their established manufacturing units intended for the production of application-specific bulk chemicals and speciality polymers in Germany. Aforementioned factors are influencing the growth of the market in Western Europe positively. Presence of advanced fertiliser manufacturing facilities in Russia along with abundant availability of raw materials such as ammonia is projected to be a favorable factor for the market [2].

Ammonia is the key raw material used in the manufacturing of nitric acid. Ammonia production is concentrated mainly in the U.S., China, Eastern Europe and Middle East because of the availability of large natural gas reserves in these regions.

2.3 Top Market Producers

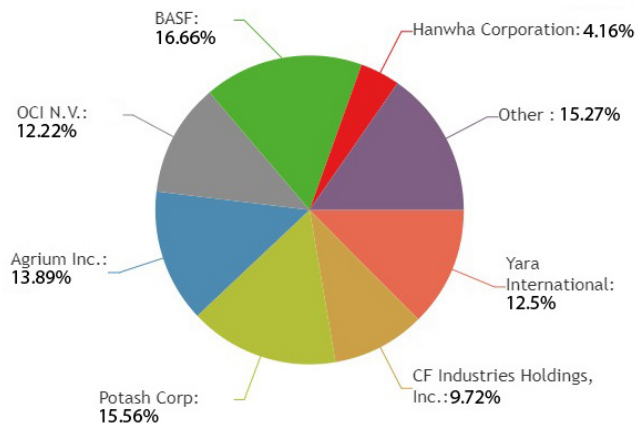


FIGURE 2.3: Nitric Acid Top Market Producers, recreated with data from [2]

TABLE 2.2: Major Producers in Global Market

BASF SE	Germany
Shandong Fengyang	China
Agrium Inc.	Canada
Apache Nitrogen Products, Inc.	USA
Yara International	Norway
OCI NV	Netherlands
CF Industries Holdings, Inc.	USA
Dow Chemicals	USA
Potash Corp of Saskatchewan	Canada
LSB Industries Inc.	USA

TABLE 2.3: Major Producers in Domestic Market

Gujarat Narmada Valley fertilisers Company Ltd.	Bharuch, Gujarat
Vijay Gas Industry Pvt. Ltd	Mumbai, Maharashtra
Rashtriya Chemicals and Fertilisers Ltd.	Raigad & Mumbai, Maharashtra
Deepak Fertilisers and Petrochemicals Corporation Ltd.	Taloja, Maharashtra; Srikakulam, A.P.; Panipat, Haryana; Dahej, Gujarat
Surya Fine Chemicals	Boisar & Palghar, Maharashtra

2.4 Technology Providers

- Weatherly, a company of Chematur Engineering Group of Sweden
- Espindesa, a company of Técnicas Reunidas of Spain
- Borealis of Austria
- Uhde GmbH (now ThyssenKrupp Industrial Solutions) of Germany
- MECS Technology of USA
- KBR of USA
- Technip of France

2.5 Location Selection for New Plant

Option 1: Ukraine

- Cheaper raw material availability (Ammonia - \$250-\$300/ton)
- High demand for Nitric acid in neighboring countries (Nitric Acid - \$300-\$400/ton)
- Ease in exporting products and materials (Bordering Black Sea and close to multiple fertiliser conglomerates)
- Europe being the largest consumer of Nitric Acid provides proximity to desired market

Option 2: India

- Cheaper Labour costs
- Vast import and export opportunities (surrounded by highly populated nations)
- High local demand
- Large agricultural markets of South East Asia provide huge selling outlets for nitric acid products like Ammonium Nitrate fertilisers
- Stringent regulations on Nitrate fertilisers in North America and Europe can cause a shift in the production and selling of these product in and around the Asia Pacific

Reasons for selecting Hazira, Gujarat :

- Raw Material Advantage: close to largest Ammonia plant in India - KRIBHCO
- Proximity to the Hazira Port for importing the raw material and exporting the final product
- Well established industrial area with great connectivity to the rest of world

Based on the above mentioned factors, the final location for the Nitric Acid plant was selected to be **Hazira, Gujarat, India**

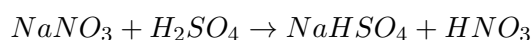
Chapter 3

Production Process

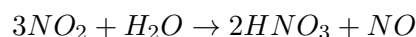
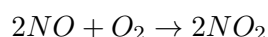
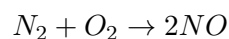
This chapter provides details about various production methods for nitric acid, from laboratory methods to the widely used commercial processes, including their advantages and disadvantages, and finally concluding with determining the right process for the plant and its capacity.

3.1 Production Routes

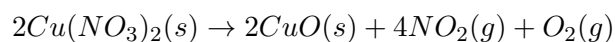
- **From Chile Saltpeter (NaNO_3):**



- **From Electric Oxidation of Air:**



- **From thermal decomposition of Copper(II) Nitrate:**

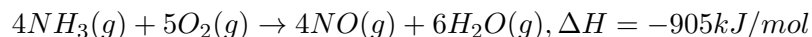


All these processes have become obsolete and the only industry used process is the Catalytic Oxidation of Ammonia by the Ostwald Process and its variants.

3.2 Ostwald Process

Referring to Moulijn et. al. [5], the Ostwald Process involves three steps - (i) Ammonia Oxidation (ii) Nitric Oxide Oxidation (iii) Nitrogen Dioxide Oxidation

3.2.1 Ammonia Oxidation

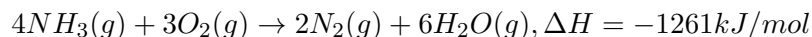
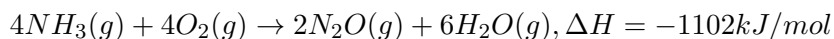


A 1:9 ammonia/air mixture by volume is reacted at a temperature of 750°C to 900°C as it passes through a catalytic convertor.

Catalyst: 90% Platinum - 10% Rhodium gauze constructed from squares of fine wire.

Yield: Under these conditions the oxidation of ammonia to nitric oxide (NO) proceeds in an exothermic reaction with a range of 93 to 98 percent yield.

Side Reactions:

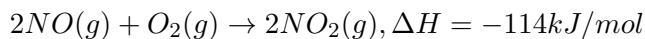


Oxidation temperatures can vary from 750°C to 900°C. Higher catalyst temperatures increase reaction selectivity toward NO production. Lower catalyst temperatures tend to be more selective towards less useful products: nitrogen (N₂) and nitrous oxide (N₂O). Nitric oxide is to be used further in our process, whereas nitrous oxide is known to be a greenhouse gas.

High temperature and low pressure make the reaction more selective towards desired product (NO gas); also owing to the high spontaneity of the reactions, catalytic bed reactor of residence time of 10⁻⁴ to 10⁻³ seconds is used.

3.2.2 Nitric Oxide Oxidation

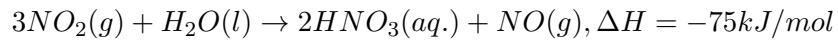
The process stream is passed through a series of heat exchangers and cooler-condensers and cooled to 50°C or less at pressures up to 4 barg. The nitric oxide reacts non catalytically with residual oxygen to form nitrogen dioxide (NO₂)



This slow, homogeneous reaction is highly temperature and pressure dependent. Operating at low temperatures and high pressures promotes maximum production of NO_2 with a reduced reaction time.

3.2.3 Absorption

The oxidised gas mixture is fed into the bottom of the absorption tower, while a liquid acid condensate, produced during nitric oxide oxidation, is added at a higher point. Deionized process water enters the top of the column. Both liquids flow counter-current to the NO_x gas mixture. Oxidation takes place in the free space between the trays, while absorption occurs on the trays. The absorption trays used are sieve trays.



A secondary air stream is introduced into the column to re-oxidise the NO that is formed in this reaction. This secondary air also removes NO_x from the product acid. An aqueous solution of 55 to 65 percent (typically) nitric acid is withdrawn from the bottom of the tower. The acid concentration depends upon the temperature, pressure, number of absorption stages, and concentration of nitrogen oxides entering the absorber.

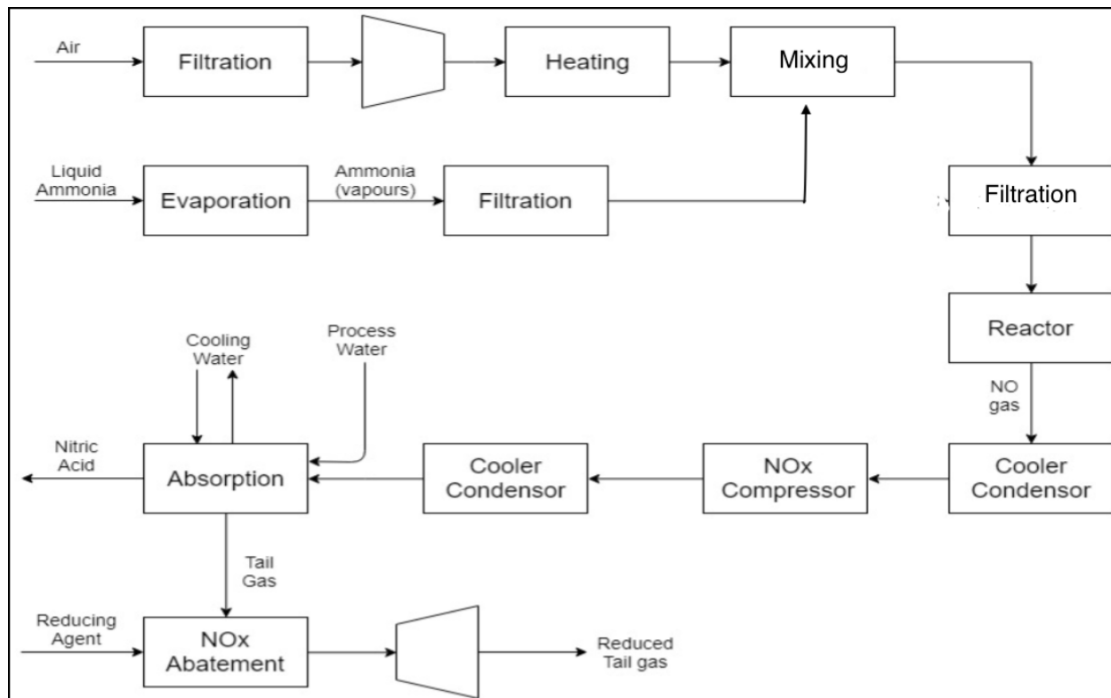


FIGURE 3.1: Block Diagram of Ostwald Process

3.3 Deviations in Ostwald Process

Referring to Moulijn et. al. [5], we found out that the principal design variables for the ammonia oxidation and subsequent stages of the plant are temperature, pressure and gas flow rate, and their effects on the process efficiency is tabulated below:

Process Change	NH ₃ Oxidation	NO Oxidation	Absorption
Temperature Increase	Higher Yield	Lower Yield	Reduced absorption
Pressure Increase	Oxidation rate reduced. Amount of NH ₃ oxidised per unit time increases	Higher Yield	Improved absorption
Flow Rate Increase	Optimum temp. increases; Higher Yield	Higher yield	Minor improvements

TABLE 3.1: Temperature and Pressure Dependence of Ostwald Process

According to Thiemann et. al. [6] and Thyssenkrupp Nitric Acid Book [1], classification of plants is done on the basis of pressure in the oxidation and absorption stages:

3.3.1 Single Pressure Processes

3.3.1.1 Medium Pressure

This type of nitric acid plant operates at around 4–5 bars abs. It can produce up to 700 tonnes/day using a single combustion and a single absorption tower and around 1000 tonnes/day by adding another absorption tower. Using this pressure enhances the oxidation step (NO to NO₂), but reduces the productivity of the final absorption stage.

3.3.1.2 High Pressure

Pressure of around 8–12 bars abs is used. This high pressure forces the nitrogen dioxide gas into water. And thus, a single absorption tower is sufficient to produce 900 tonnes/day of nitric acid. The higher pressure means that other equipment like the burner unit,

pipng can be made smaller so the plant occupies less space, making the initial capital investment less.

3.3.2 Dual Pressure Process

- Low to Medium dual pressure: 1–2/ 4–5 bars abs
- Medium to High dual pressure: 4–5/ 8–12 bars abs

Lower pressure for ammonia oxidation and higher pressure for absorption is favourable. The dual pressure plant uses two different pressures, a lower pressure for the oxidation step and higher pressure to optimize the absorption. This type of plant can produce up to 1600 tonnes/day of nitric acid using single combustion and absorption unit. Lower pressure for the oxidation unit also reduces the catalyst cost.

3.4 Selection of Final Process

The points considered while finalising the actual process to be utilised in the plant are:

- Variable Costs
- Capacity
- Catalyst Life
- Catalyst Performance and Loss
- Environmental Impact
- Absorption Column Efficiency
- Desired Nitric Acid Concentration
- Electric Power

In accordance with the above mentioned points, the following comparisons¹ are documented and are also an industry-wide practice:

¹All comparisons are per tonne Nitric Acid (100%)

- The dual pressure process provides larger capacities (upto 1600 tpd in single train configuration) with relatively lower variable costs, when compared to the mono pressure processes (upto 900 tpd for high pressure, upto 700 tpd for medium pressure - in single train configuration), which require larger variable costs.
- The dual pressure process is designed to accommodate more stringent environmental pollution control requirements, namely to reduce the emissions of NO_x gases into the atmosphere. The process has inherent abilities to reduce the outgoing tail gas to a composition well below the required environmental norms. This reduction in composition is a result of an increased absorption column efficiency due to the increased absorption column pressure incorporated in the dual pressure process.
- Due to a lower load on the burner, the dual pressure process also provides with a longer operation time for a given bundle of catalyst gauzes(> 6–8 months), when compared to the other available processes(upto 6 months). This effect can be seen directly on the total catalyst losses for dual pressure process (0.03g/t of nitric acid produced) when compared to the mono pressure processes (0.04g/t nitric acid produced for medium pressure process and 0.08g/t nitric acid produced for high pressure processes respectively)
- All processes can easily provide the required nitric acid concentration ($\approx 60\%$ wt)
- When comparing all the alternatives, the dual pressure process requires the least amount of electric power per ton nitric acid produced (8.5 kWh), followed by medium pressure (9.0 kWh) and high pressure (13.5 kWh)

Capacity of Proposed plant:

With reference to average plant capacities using dual pressure process, keeping in mind the demand for nitric acid, which is growing at a rate of 3-5% annually, and the incremental production of the plant i.e. 70% in the first year, 80% in the second year and so on, the final plant capacity has been decided to be kept at **1500 TPD of 62% wt nitric acid** (942 TPD in terms of 100% wt nitric acid)

Keeping in mind the desired production from our plant, the final route for the production of nitric was chosen to be the **Dual Pressure Process**, with medium pressure ammonia oxidation over Pt–Rh catalyst and high pressure absorption operations.

Licensor - Uhde GmbH, Germany

Existing plants using this route:

- Abu Qir Fertilisers and Chemical Ind. Co., Abu Qir, Egypt - Capacity - 1850 TPD
- Borealis AG, Linz, Austria - Capacity - 1000 TPD

(As an industry standard, plant capacities are displayed in terms of 100% wt nitric acid)

Hence, our final plant details are as follows: **1500 TPD of 62% wt** (942 TPD in terms of 100% wt nitric acid) nitric acid plant, using the **Uhde Dual Pressure Process**, set up in **Hazira, Gujarat, India**.

Chapter 4

Industrial Visit

In order to gain a better understanding of the selected process and to aid selection of parameters and equipment, a visit to Deepak Fertilizers and Petrochemical Corp. Ltd.(DFPCL) [7] was made on February 6, 2019.

Total Nitric Acid Capacity: 1400TPD

4 nitric acid plants:

2 mono high pressure plants (300TPD each, set up in 1996)

1 mono medium pressure plant (350TPD, set up in 2000)

1 dual pressure plant (Uhde Dual Pressure Process, 450TPD, set up in 1975, Denmark, recommissioned in 2010, India)

The weak nitric acid (59.2% wt) produced here is used further for ammonium nitrate production and concentrated nitric acid (98.5%wt) is sold separately. Since the dual pressure plant is recommissioned, it has a few added features to adjust to the temperature and pressure in India. For example, the compressors used are designed for a lower air temperature (Denmark) whereas the ambient air temperature in India is high. Hence, air chillers are added to reduce the temperature of the air to 20°C before compression.

4.1 Process Highlights

4.1.1 Ammonia

Deepak Fertilisers has a separate plant for ammonia production which usually meets the nitric acid requirement. An alternate of sourcing ammonia externally during off days is also in place. The ammonia obtained is stored in a cylindrical storage refrigerated tank at -33°C and 1 atm pressure.

4.1.2 Ammonia Filters

Ceramic tubes are used to filter oil, water and other impurities from ammonia. The ammonia feed enters radially, is filtered and exits through the axis.

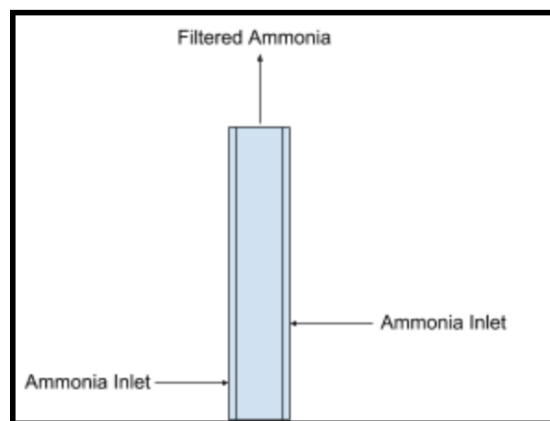


FIGURE 4.1: Ammonia Flow through Ceramic Filters

4.1.3 Air Filters

The air is compressed to 5 bar abs using a centrifugal compressor. Primary and Secondary Filters are used to filter out particulate matter before compression. These filters are made of Stainless Steel and present in huge numbers, incorporated with the cooling network inside the filter rack.

4.1.4 Ammonia - Air Mixer

Mixer used in the industry is a Stainless Steel Static Mixer, where both the gas streams are intermixed, entering perpendicular to each other.

4.1.5 Turbine Shaft

A single steam turbine is used to rotate a shaft which is connected to a series of compressors and expanders. HP steam is used to rotate the turbine at 7000 RPM. The turbine shaft is used to rotate a centrifugal compressor, which compresses air from atmospheric pressure to 5 bar abs pressure. The second equipment on this shaft is an expander; it reduces the pressure of the tail gas from approximately 12 bar abs to 1 atm. A gear (1:14) is used after that to increase the rotations per minute for the NO_x compressor. The energy from steam and tail gas is efficiently used to run the compressor shafts.



FIGURE 4.2: Turbine Shaft Structure, as seen in the DFPCL Dual Pressure Plant

4.1.6 Reactor

A shallow bed reactor with 8 gauzes of 95-5 Pt-Rh is used. The reaction is highly exothermic and takes place at 890°C. For the start-up of the process, hydrogen gas is burned to raise the temperature of the gauzes (around 8 cylinders of hydrogen are kept in the inventory (4 for main use + 4 for extra backup)). After the reaction starts, the heat of the reaction is sufficient to maintain that temperature. 96% of ammonia is converted in a single pass. Catchment gauzes of Palladium are provided to capture catalyst chipped off with outgoing stream.

4.1.7 Boiler

The product stream leaving from the reactor exits at 890°C. This steam is to be cooled before adding to the absorption column. And therefore, a series of heat exchangers and cooler condensers are added. A waste heat boiler is attached just below the reactor setup, with hot water flowing through the tube side. In the boiler, the temperature of the process stream is reduced from 890°C to 410°C. High pressure steam is produced while cooling the process stream, which is used to run the steam turbine.

4.1.8 Cooler Condenser

There were three cooler condensers used instead of the conventional two to reduce the load on condensers.

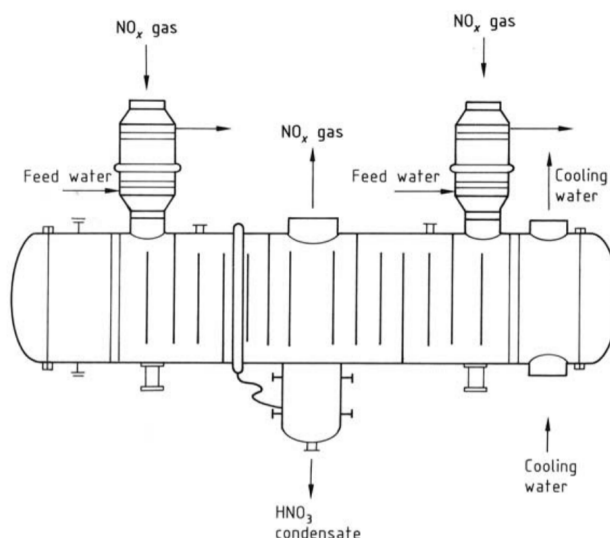


FIGURE 4.3: Nitric Acid Cooler Condenser Structure, provided by DFPCL [7]

4.1.9 Absorption Column

A sieve tray counter-current absorption column (42 m in height) absorbs incoming NO_x into a deionised makeup water stream to form 59% w/w Nitric Acid as bottom product. NO_2 absorption in water occurs on the tray whereas NO oxidation to NO_2 occurs between the trays. Cooling water coils at each stage are used to absorb the heat released by reactions.

4.2 Conclusion

The process studied from literature and the one being used in the plant was very similar. Doubts regarding the type of equipment used, exact conversions and temperature pressure conditions were solved by this visit. The size of the DFPCL Dual Pressure Plant was comparatively low and with reference to findings from the visit, changes were made to scale up the plant capacity for verification with our new plant data.

Chapter 5

Process Flow Diagram

This chapter showcases the Process Flow Diagram (PFD) for the Dual Pressure Nitric Acid Process. The PFD was made with inputs from Moulijn et. al. [5], Thiemann et. al. [6] and DFPCL Staff [7]. The PFD was drawn using an online flowsheet drawing software **Draw.io**¹.

5.1 Process Flow Diagram

The final PFD with the stream table for our Dual Pressure Nitric Acid Process is available in [Appendix A](#). All pressures mentioned are in bar abs, unless specified otherwise.

5.2 Process Explanation

- Air (stream-1) is pumped into the plant at ambient conditions (1 atm, 35°C), entirely by the suction force provided by the centrifugal compressor, C101. The Air is filtered using primary and secondary Air Filters in F101 and fed to the compressor (stream-1A).
- The compressor C101 is used to increase the pressure of the air feed to 5 bar, also causing an increase in the temperature to 240-250°C. Stream-1B is split into 2 parts, 85% going into the reaction mixture (Primary Air, stream-1C) and the rest (Secondary Air, stream-1D) is utilised in the bleaching column, B101.

¹<https://www.draw.io/>

- Liquid Ammonia from storage is pumped into the plant at -33°C and 19 bar, into Evaporator E101 by a Centrifugal Pump, numbered stream-2. In the Evaporator, Ammonia is converted to vapor and further superheated to 70°C with the help of LP Steam (4-5 bar, 150°C) in the upper section of Evaporator E101.
- Ammonia Filter, F102 is utilised to filter the superheated Ammonia vapor (stream-2A) of the small amounts of impurities inherent to the Ammonia feed (oils, chlorine, etc.).
- The superheated ammonia vapor and the compressed air stream are mixed in a static mixer, with ammonia to air ratio being 1:9 by volume, giving us stream-3, at 5 bar, $220\text{--}230^{\circ}\text{C}$.
- Stream-3 is fed into the reactor, R101, which is a shallow bed reactor, with around 8-10 catalyst gauzes, made up of 90% Pt and 10% Rh. Hydrogen gas is utilised to heat up the gauzes to the required temperature at startup; once the reaction starts, the heat of the reaction is sufficient to sustain the reaction.
- The catalyst is highly selective, giving a conversion of 96% for Ammonia into Nitric Oxide, with stream-4 exiting at a temperature of 890°C , consisting mainly of Nitrogen and Oxygen from Air feed and Nitric Oxide formed via Ammonia oxidation. Some small amounts of N_2O is also formed (1200 ppmv) due to the occurrence of the side reaction.
- The high heat of reaction is used to make steam and heat other streams throughout the plant. Waste Heat Boiler attached to the reactor is used to produce HP Steam (40 barg), which is used to run the steam turbine, using the energy to run the compressors. Shell and Tube Heat Exchanger, HE102 is used to heat the tail gas (stream-10) coming from Absorption Column to facilitate the abatement process, and HE103 is an Economiser, used to preheat the water to boiler to 80°C , which results in the temperature of stream-5 to drop to 185°C .
- This decrease in the temperature leads to the oxidation of Nitric Oxide to Nitrogen Dioxide (stream-6), with the conversion of the reaction increasing with a decrease in the temperature.
- Cooler Condenser-1 (HE104), is used to cool the stream further, condense water and nitric acid and separate them out for further processing. The temperature

of the outlet streams (7 & 8) is around 50°C. This drop in temperature allows Nitric Oxide to oxidise to Nitrogen Dioxide at a much higher conversion rate when compared to the previous two heat exchangers (HE102 & HE103).

- As Nitrogen Dioxide is produced in HE104, with the drop in temperature and elevated pressures, some of it gets absorbed into the condensed water, which was formed in reactor (R101). Once absorbed, Nitrogen Dioxide combines with Water to form Nitric Acid and Nitric Oxide, which further gets oxidised to Nitrogen Dioxide, which again forms Nitric Acid and so on.
- The Nitric Acid solution in the condensate of the Cooler Condenser-1 (HE104), with a concentration of about 35-40% wt Nitric Acid by weight, is then pumped (stream-7) to the Absorption Column (A101) to increase the Nitric Acid concentration in the solution.
- The vapor outlet of HE104, stream-8, mainly consisting of NO_x gases, is passed through the NO_x Compressor, C102, elevating the pressure of the stream to 12 bar and the temperature to around 260°C.
- C102 outlet, stream 8A, is fed to Cooler Condenser-2 (HE105), where process similar to that in Cooler Condenser-1 (HE104) occurs, providing us with more weak Nitric Acid condensate, which is mixed with HE104 condensate and pumped to the Absorption Column. Stream-9 coming out of HE105 is also fed to the Absorption Column (A101).
- The Absorption Column (A101), has 35-40 stages, with the NO_x gases (stream-9) fed at the bottom-most stage, process water (stream-12) fed at the top-most stage, acid condensate from the Cooler Condensers (stream-7) fed to an intermediate stage (stage 13) and cooling water coils at every stage throughout the column to maintain the column at a reduced temperature.
- Since the Absorption Column is operated at an elevated pressure (12 bar), absorption efficiency is increased, which results in fewer NO_x emissions.
- Inside the column, Nitric Oxide oxidation to Nitrogen Dioxide occurs between stages in the vapor phase, and absorption of Nitrogen Dioxide into water and the formation of Nitric Acid from the absorbed Nitrogen Dioxide occurs in the liquid phase on the sieve trays of the column.

- Top outlet of the column is called Tail Gas (stream-10), with NO_x concentration in the order of 550ppmv. Stream-10 is then preheated in HE106 using secondary air (stream-1D) and further heated in HE102 using stream-4 and sent to the NO_x abatement process where it is expanded to provide 65% of the energy required to run the compressor shafts and then vented into the air.
- Bottom outlet of the column (stream-11) is called Red Fuming Nitric Acid, due to the red color imparted by the dissolved Nitrogen Dioxide.
- Stream-11 is fed to the Bleaching Column, B101, where the secondary air strips away the Nitrogen Dioxide, resulting in a clear, colorless 62% wt. Nitric Acid Solution. The product acid (stream-14) is further cooled and stored in cylindrical storage tanks. The bleaching air is mixed with the NO_x compressor inlet and again fed to the absorption column, to ensure lower NO_x emissions in the tail gas.
- The Tail Gas (stream-10) from the column is first preheated to 130°C , using the secondary air to be fed to the bleaching column, in Tail Gas Preheater, HE106, and further heated to 350°C in HE102.
- The tail gas can now be fed to the abatement process, where the NO_x and N_2O concentration is reduced to below 40 ppmv. Ammonia and Propane are mixed with the tail gas as it enters the abatement unit.
- After the abatement, the tail gas is expanded in the tail gas turbine, EX101, providing around 65% of the energy to drive both the air and NO_x compressors. Once expanded, the tail gas is vented into the air via Stack.

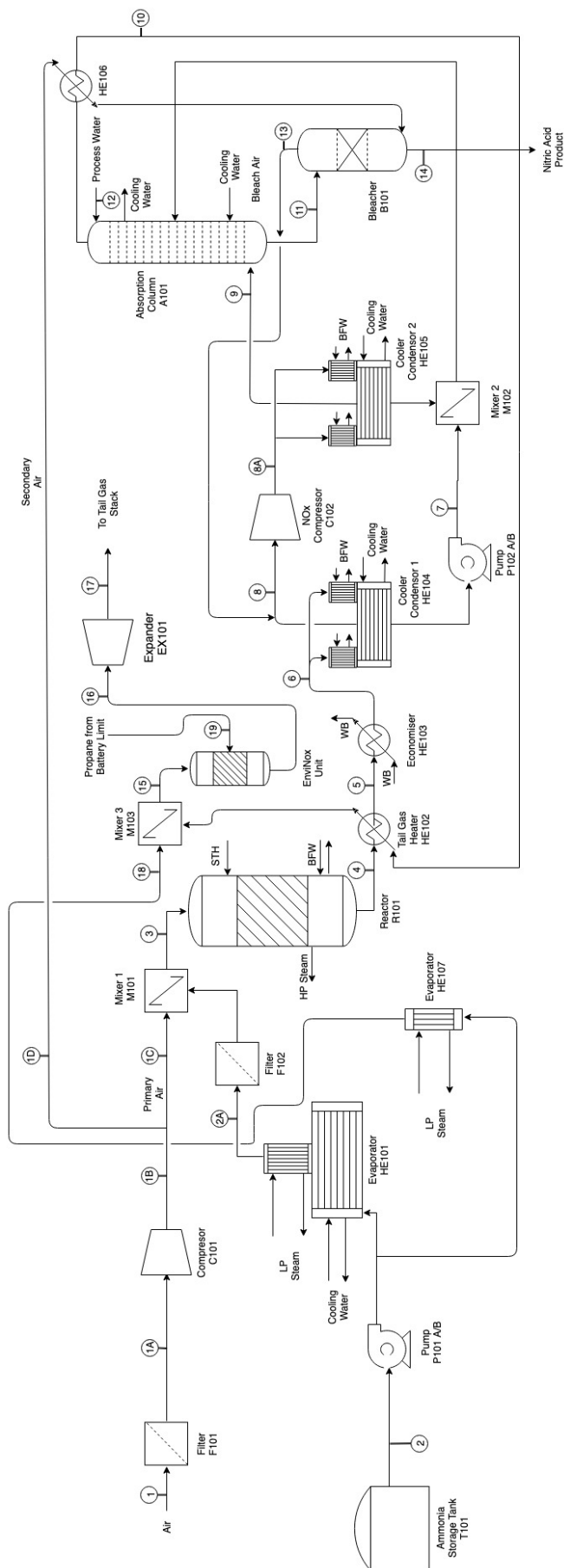


FIGURE 5.1: Process Flow Diagram for Dual Pressure Nitric Acid Process

5.3 Process Heat Integration

Nitric Acid Process is one of the world's oldest and most researched industrial production process. Hence, the intense amount of research that has gone into this process has led to the latest iteration of the process flow to take shape, that we have incorporated into our PFD. This process is highly integrated, from heat to energy. There was no requirement to do a detailed heat integration study as the entire process has been well researched and provided with the ample amount of heat and energy integration required to make any nitric acid plant profitable in the smallest period of time.

The process has one main hot stream - Reactor outlet gas, coming out at a temperature of 890°C. It has to be cooled down to a temperature of 50°C before it enters the absorption column. The first heat exchanger after the reactor is the Waste Heat Boiler, attached directly to the reactor burner head. The gas flows through the shell side of this shell and tube heat exchanger, with boiler feed water passing through the special boiler tubes, made out of SA 192 and SA 213 - T12 Grade, to account for the evaporation and super heating of the High Pressure steam produced in the boiler. This causes the temperature of reaction mixture to drop to 427°C.

This HP Steam is used to run the Steam turbine used to run the common shaft, which in turn drives the compressors. The LP Steam from the turbine is then used to superheat the evaporated ammonia to a temperature of 70°C. Ammonia evaporation utilises cooling water to evaporate the liquid ammonia. The water in turn is cooled down to 7°C, where it can be used as chilled water, used for cooling the top section of the absorption column.

After the Waste Heat Boiler, the NO gas is further cooled down to 300°C in the Tail Gas Heater, by utilising the cold tail gas emanating from the absorption column. This heats the tail gas (stream-10) to 350°C, temperature required by the abatement unit to function properly. The NO gas is further cooled down to 185°C in the economiser. The cooling stream here is the boiler feed water used in the Waste Heat Boiler, whose temperature is increased from 40°C to 80°C.

The next two shell and tube heat exchangers are the largest heat exchanger in the plant. The cooler condensers are utilised to cool down the reaction gases to 50°C, which helps in forming the acid condensate. Cooling water is used in both the cooler condensers, one before and one after the NO_x compression.

The tail gas coming out of the Absorption Column is reduced in order to meet the government norms for NO_x emissions. The abatement process requires temperatures of around 350°C (stream-15), and hence the tail gas, coming out at 10°C, is first preheated in the Tail Gas Preheater to 130°C (stream-10), with the help of the hot secondary air (stream-1D) used in the bleaching column, and further heated in the Tail Gas Heater (HE102) as mentioned in previous points. Once abated, the tail gas is used to drive a turbine, which provides around 65% of the power required to drive the air and NO_x compressors (C101 and C102).

This integration is followed in all Dual Pressure Nitric Acid Processes, with slight variations in stream temperatures for processes from different technology providers. The net utility data is produced in a tabulated form below:

Utility Required	Net Amount Required	Utility Produced	Amount Produced
Electricity	2465 kW	HP Steam (40 barg)	26680 kg/hr
Cooling Water	0.437 MGal/hr		
Make Up Chilled Water	0.0134 MGal/hr		
LP Steam	12600 kg/hr		

TABLE 5.1: Utility Data after Heat Integration

The above mentioned Heat and Energy integration leads to the following heat exchanger network:

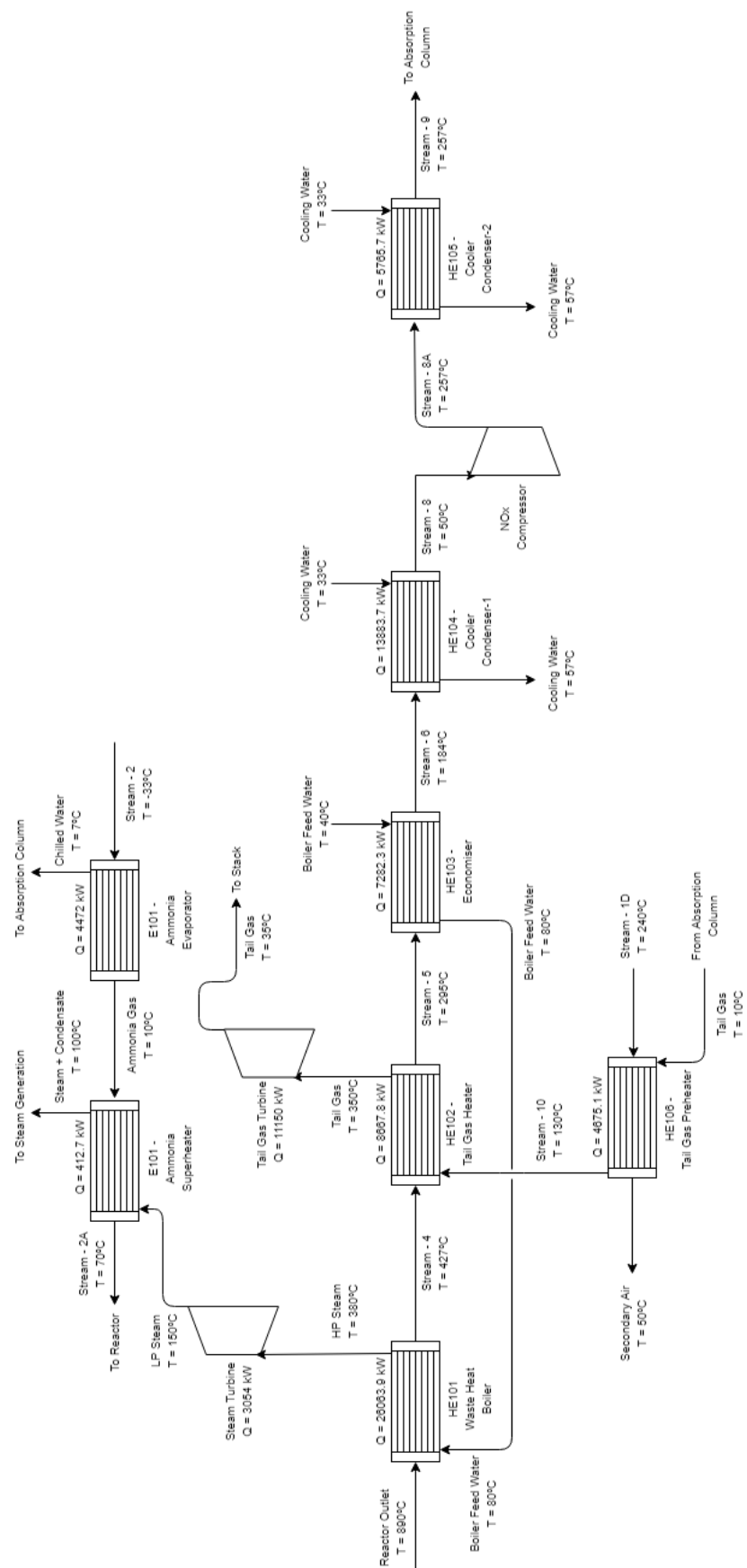


FIGURE 5.2: Heat Exchanger Network

Chapter 6

Mass Balance

This chapter provides a look at the mass balance performed on the process, with inputs from Ray et. al. [8], source of the reference being DFPCL [7]. Some sample calculations are also provided for some major equipment taking 100kmol/hr Ammonia as the basis. All values were scaled up for the desired plant capacity.

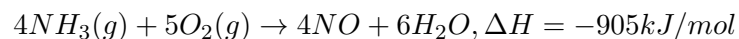
6.1 Sample Calculations

6.1.1 Reactor - R101

Air is passed through a combination of primary and secondary filters and compressed to 5 bar abs (240°C) from ambient conditions. Ammonia is evaporated from sub-zero temperatures using water, passed through a preheater to raise the temperature to 70°C and filtered to remove oils and particulate matter using the ammonia filters. Ammonia & air are mixed in 1:9 ratio and the mixture enters the reactor at 230°C.

Reactor residence time is in few milliseconds where Pt-Rh catalyst provides the site for reaction. Reaction occurs at 890°C which is maintained by the high exothermicity of the reaction.

Main Reaction:



96% ammonia conversion is towards main reaction producing NO and the rest towards side reactions:

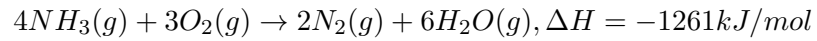
Ammonia entering reactor = 100 kmol

NO formed: $100 \times (96/100) = 96$ kmol

Required O₂ for main reaction: $96 \times 5/4 = 120$ kmol

H₂O formed in main reaction: $96 \times 3/2 = 144$ kmol

Side Reaction 1:



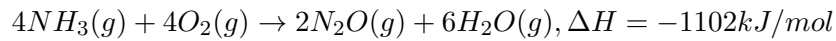
3% ammonia is consumed in side reaction 1:

Amount of N₂ produced = $3/2 = 1.5$ kmol

Amount of O₂ required for side reaction = $1.5 \times 3/2 = 2.25$ kmol

Amount of H₂O produced in side reaction = $2.25 \times 2 = 4.5$ kmol

Side Reaction 2:



1% ammonia is consumed in side reaction 1:

Amount of N₂O produced = $1/2 = 0.5$ kmol

Amount of O₂ required for side reaction = $0.5 \times 3/2 = 0.75$ kmol

Amount of H₂O produced in side reaction = $0.75 \times 2 = 1.5$ kmol

Total water produced = $144 + 4.5 + 1.5 = 150$ kmol

Total O₂ consumed = $120 + 2.25 + 0.75 = 123$ kmol

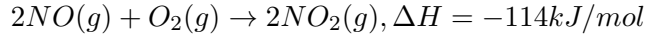
Similar calculations are made for all other equipment using their conversions and desired outputs.

Components	Reactor Feed (kmol/hr)	Reactor Outlet (kmol/hr)
NH₃	100	0
O₂	189	66
N₂	711	712.5
N₂O	0	0.5
H₂O	0	150
NO	0	96

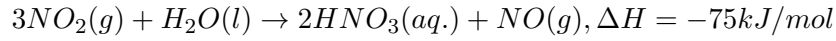
TABLE 6.1: Reactor Balance

6.1.2 Heat Exchangers and Cooler Condenser

The primary reaction that takes place next is the oxidation of nitric oxide to nitrogen dioxide.



This reaction takes place when the process gas is passed through a series of heat exchangers and the conversion increases with reducing temperature. The process gas first passes through Tail Gas Heater-1, where its heat is used to preheat the tail gas exiting from the absorption column. It further passes through an economizer, used to preheat boiler feed water and then through cooler condenser-1. By this point, the temperature of the process gas comes down to 50°C, which is favourable for high nitric oxide conversion. Simultaneously, water formed in the ammonia oxidation condenses, thereby dissolving NO₂ and forming HNO₃ in small amounts as condensate.



The conversion of NO in Tail gas heater-1 is $\approx 15\%$, in the economiser is $\approx 27\%$ and the concentration of acid condensate is $\approx 38\%$. These figures are similar to the DFPCL data [7].

Component	Reactor Outlet (kmol/hr)	HE102 Outlet (kmol/hr)	HE103 Outlet (kmol/hr)	NO _x Comp. Inlet (kmol/hr)	Acid Condensate (kmol/hr)
O ₂	66	59	48	20	0
N ₂	712.5	712.5	712.5	712.5	0
H ₂ O	150	150	150	0	138
N ₂ O	0.5	0.5	0.5	0.5	0
NO ₂	0	14	36	56	0
NO	96	82	60	16	0
HNO ₃	0	0	0	0	24

TABLE 6.2: Heat Exchanger Balance

6.1.3 Absorption Column and Cooler Condenser

The process gas (known as NO_x gas) is compressed to 12 bar abs (260°C) and fed to cooler condenser 2. The gas stream is then fed to the absorption column at the bottom and acid condensate from cooler condenser 1 is fed at the middle of the column for further concentration. Process water added at the top of the column at 10°C absorbs the NO_2 forming HNO_3 and NO formed as a side product gets oxidised back to NO_2 by excess air added to the column.

The acid leaving the column from the bottoms is 55%-60%wt which then passes through the bleaching column to be stripped off of dissolved NO_x gases. The tail gas leaving from the tower of the tower is further sent for NO_x abatement process to bring down the NO_x content to permissible levels. The basis for calculations on the column was the empirical concentration of different NO_x gases in the tail gas as 550ppmv.

Component	Cooler Condenser 2 Outlet (kmol/hr)	Acid Condensate (kmol/hr)	Tail Gas (kmol/hr)	Nitric Acid Bottom (kmol/hr)
NH_3	0	0	0	0
O_2	12.5	0	19.5	0
N_2	713	0	808	0
H_2O	0	138	0	202.54
N_2O	0.5	0	0.5	0
NO_2	71	0	0.06	7.82
NO	1	0	0.6	0
HNO_3	0	24	0	94.42

TABLE 6.3: Absorption Column and Cooler Condenser Balance

6.2 Final Mass Balance Table

Above calculations were scaled to our desired production of 1500TPD of 62% Nitric Acid Solution, providing us with the following results ¹:

¹All values are in kg/hr

Line No.	Stream Comp.	Phase	NH ₃	O ₂	N ₂	H ₂ O	N ₂ O	NO ₂	NO	HNO ₃	CO ₂	C ₃ H ₈	Total	Pressure(bar abs)	Temperature (°C)
1	Air feed	g	0	43519	145541	0	0	0	0	0	0	0	189060	1	35
1C	Primary Air	g	0	39005	128387	0	0	0	0	0	0	0	167391	5	240
1D	Secondary Air	g	0	4514	17154	0	0	0	0	0	0	0	21669	5	240
2	Ammonia Feed	l	11003	0	0	0	0	0	0	0	0	0	11003	1	-33
2A	Evaporated NH ₃	g	10963	0	0	0	0	0	0	0	0	0	10963	5	70
3	Reactor Inlet	g	10963	39005	128387	0	0	0	0	0	0	0	178355	5	230
4	Reactor Outlet	g	0	13570	128658	17412	142	0	18573	0	0	0	178355	5	427
5	HE102 Outlet	g	0	12125	128658	17412	142	4153	15865	0	0	0	178355	5	300
6	HE103 Outlet	g	0	9856	128658	17412	142	10680	11608	0	0	0	178355	5	185
7	Acid Condensate	l	0	0	0	16019	0	0	0	9751	0	0	25770	12	50
8	NO _x Comp. inlet	g	0	8591	145812	0	142	18932	3096	0	0	0	176573	5	50
8A	NO _x Comp. Outlet	g	0	8591	145812	0	142	18932	3096	0	0	0	176573	12	260
9	Absorption Inlet	g	0	7043	145812	0	142	23382	193	0	0	0	176573	12	50
10	Tail Gas	g	0	3307	145812	0	142	18	58	0	0	0	149336	12	130
11	Absorption Outlet	l	0	0	0	23816	0	2320	0	38858	0	0	64993	12	50
12	Process Water	l	0	0	0	11987	0	0	0	0	0	0	11987	12	10
13	Bleaching Air	g	0	4514	17154	0	0	2320	0	0	0	0	23988	5	80
14	Nitric Acid Pdt	l	0	0	0	23816	0	0	0	38858	0	0	62673	5	50
15	Mixed Tail Gas	g	40	3307	145812	0	142	18	58	0	0	0	149376	12	350
16	Reduced Tail Gas	g	0	3292	145966	87	2	1	2	0	42	0	149391	12	350
17	Tail Gas Out	g	0	3292	145966	87	2	1	2	0	42	0	149391	1	35
18	Reducing Ammonia	g	40	0	0	0	0	0	0	0	0	0	40	12	350
19	Propane	g	0	0	0	0	0	0	0	0	0	15	15	12	350

TABLE 6.4: Final Mass Balance

Chapter 7

DWSIM Flowsheet Simulation

We employed the DWSIM Chemical Process Simulator for process simulations of the Nitric Acid plant. DWSIM is a multiplatform, CAPE-OPEN compliant chemical process simulator featuring a rich graphical interface with many features previously available only in commercial simulators. DWSIM being a free and open source software provides everyone with the opportunity to simulate process free of cost. The direct benefit of this is that DWSIM can directly replace commercial simulators like ASPEN or can at the least be used for multiple simultaneous test-simulations in companies where there is a shortage of ASPEN licenses. The simulations helped us not only validate our data from linear mass balance and the visited DFPC plant, but also optimize process operating conditions.

Our DWSIM flowsheet is available online on the FOSSEE Flowsheeting Project portal - <https://dwsim.fossee.in/flowsheeting-project/dwsim-flowsheet-run/335>

7.1 Kinetics and Specifications used in DWSIM

The process explained in Chapter 5 is used to simulate a DWSIM flowsheet. Due to unavailability of a few equipment in DWSIM, their modelling is done using different alternatives. Centrifugal compressors and shell and tube heat exchangers are used where ever required.

7.1.1 Ammonia Oxidation

Ammonia oxidation reaction in presence of Pt-Rh catalyst is highly selective and occurs almost instantaneously, with residence time in the order of 10^{-4} - 10^{-3} seconds. Hence, the available Conversion Reactor is used as an equivalent for the Shallow Bed Reactor for optimised temperature and pressure conditions, giving a conversion of 96% for the desired reaction. It is also assumed that almost all ammonia is consumed in the reactor, either in the main reaction or in one of the side reactions.

The instantaneous nature of the reactions call for a millisecond reactor, which is why it is difficult to use a kinetic model of this reaction in the simulation of the reactor. Only one of the side reactions is considered in the DWSIM Flowsheet.

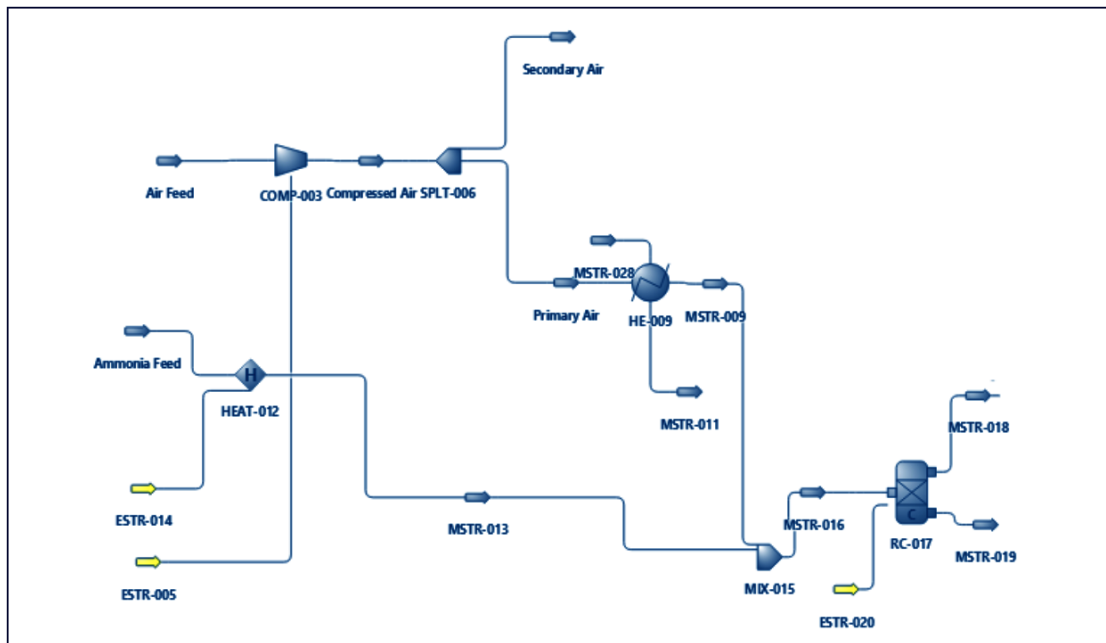
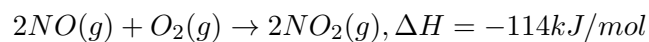


FIGURE 7.1: DWSIM Flowsheet - Ammonia Oxidation

7.1.2 Nitric Oxide Oxidation

In this step, the temperature of the stream is reduced which leads to the kinetic oxidation of NO to NO₂ to move in the forward direction. Since the heat exchangers cannot be modelled to include a reaction in them, plug flow reactors are used instead. DWSIM PFRs give us the ability to calculate the heat duty for our required process, while enabling us to model kinetic reactions, satisfying our requirements of reactive heat exchangers.



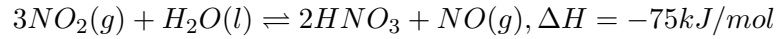
NO Oxidation is a third order reaction, with reaction rate and constant as,

$$Rate = 2k_p C_{NO}^2 C_{O_2}$$

$$\log k_p = \frac{530}{T} + 7.09$$

Hence, the Arrhenius parameters required become, $A = 1200$ and $E = -4406.42$, values taken from Tsukahara et. al. [9]

Water formed in the ammonia oxidation reaction reacts with absorbed NO_2 to form HNO_3 . Since the reaction is mass transfer controlled, the kinetics involved in this reaction are very difficult to model and therefore a simpler alternative used for this reaction was to model an equilibrium reactor, with the equilibrium reaction,



with K_p being the equilibrium constant, given by Thiemann et. al. [6] as,

$$\log K_p = -7.35 + 2.64/T$$

Cooler Condenser is modelled using a PFR to take into account the NO Oxidation, followed by an Equilibrium Reactor to model the Nitric Acid formation and a Gas-Liquid Separator to produce Acid Condensate and NO_x gas.

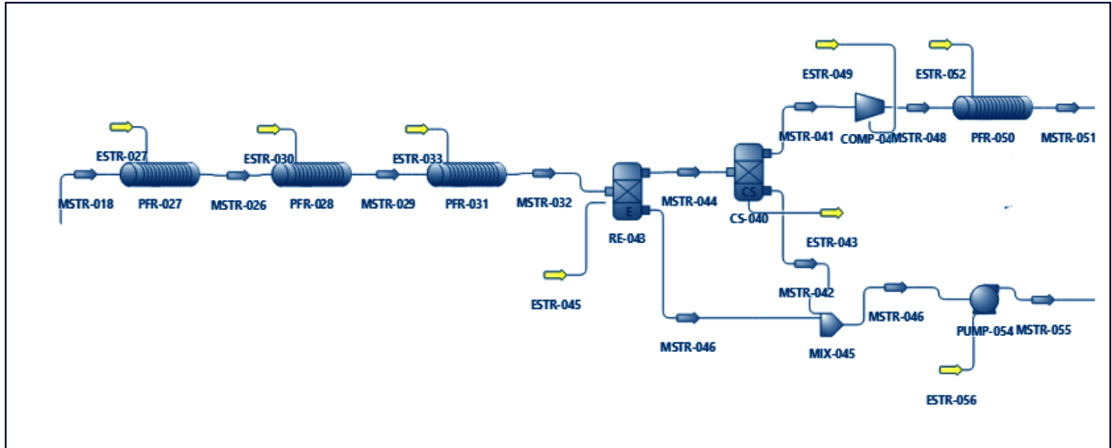


FIGURE 7.2: DWSIM Flowsheet - NO Oxidation and Heat Exchanger Network

7.1.3 Absorption Column

The separated streams are sent to the absorption column. In the absorption column, the NO_2 is absorbed in water and reacts to form HNO_3 and NO , which is again oxidised to form NO_2 , and so on. Modelling of a reactive absorption column was done using a ChemSep column, with the specified reactions used in the unit. Issues propped up as

7.2.1 Ammonia Reactor

	Reactor Inlet		Reactor Outlet	
	Manual	DWSIM	Manual	DWSIM
NH₃	10963	11000	0	0
NO	0	0	18573	18605
NO₂	0	0	0	0
HNO₃	0	0	0	0
H₂O	0	0	17412	17452
N₂	128387	128397	128658	128775
O₂	39005	38993	13570	13568
Total	178353	178400	178353	178400

TABLE 7.1: Mass Balance Comparison for Reactor

7.2.2 Heat Exchangers

	Reactor Outlet		Cooler Condenser Inlet	
	Manual	DWSIM	Manual	DWSIM
NH₃	0	0	0	0
NO	18573	18605	11608	12024
NO₂	0	0	10680	10044
HNO₃	0	0	0	0
H₂O	17412	17452	17412	17452
N₂	128658	128775	128658	128775
O₂	13570	13568	9856	10069
Total	178355	178400	178353	178400

TABLE 7.2: Mass Balance Comparison for Heat Exchanger network

7.2.3 Absorption Column

	Gas Inlet		Combined Outlet	
	Manual	DWSIM	Manual	DWSIM
NH₃	0	0	0	0
NO_x	22288	22068	76	100
HNO₃	0	0	38858	38800
H₂O	17412	17452	23816	24000
O₂	9856	10069	3307	3500
Total Inlet/Outlet Flow rate	178355	178400	178355	178400

TABLE 7.3: Mass Balance Comparison for Absorption Column

Chapter 8

Sensitivity Analysis

8.1 Reactor Analysis

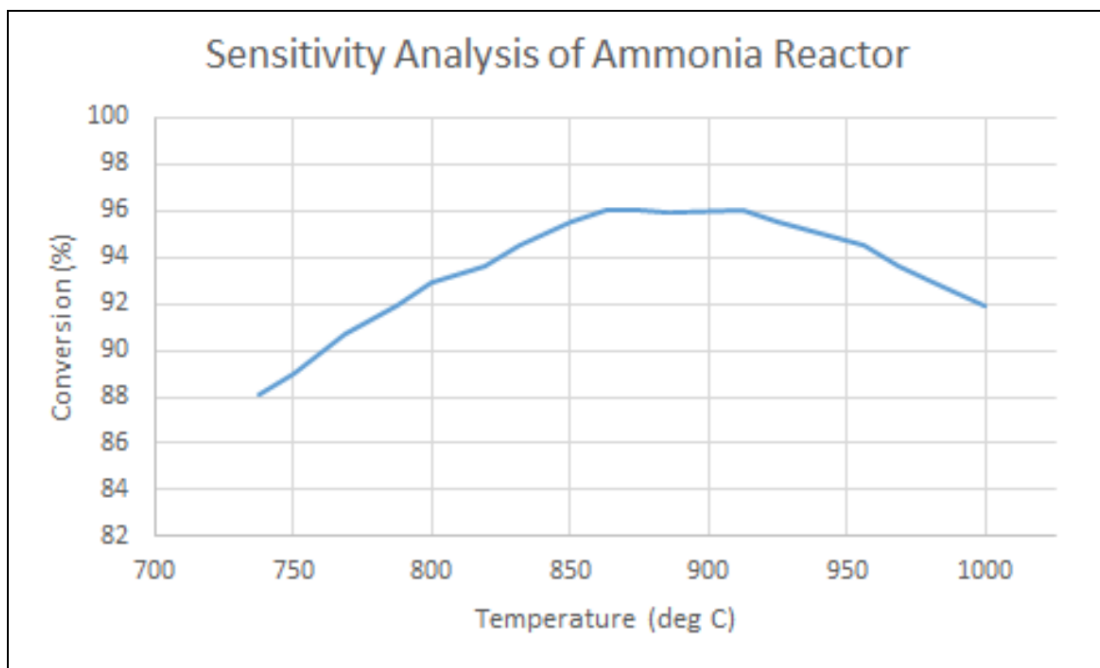


FIGURE 8.1: Sensitivity Analysis for Reactor

The above results are produced for the operation of the reactor at 4 barg pressure. To get high values of conversion for our reaction, the optimum temperature at which the reaction should be done is between 860 - 920°C. The highest possible conversion at 4barg is 96%, which occurs when the reactor is operated at 890°C. Hence, 890°C was chosen as the operating temperature of the Ammonia Oxidation Reactor.

8.2 Heat Exchanger simulated as PFR

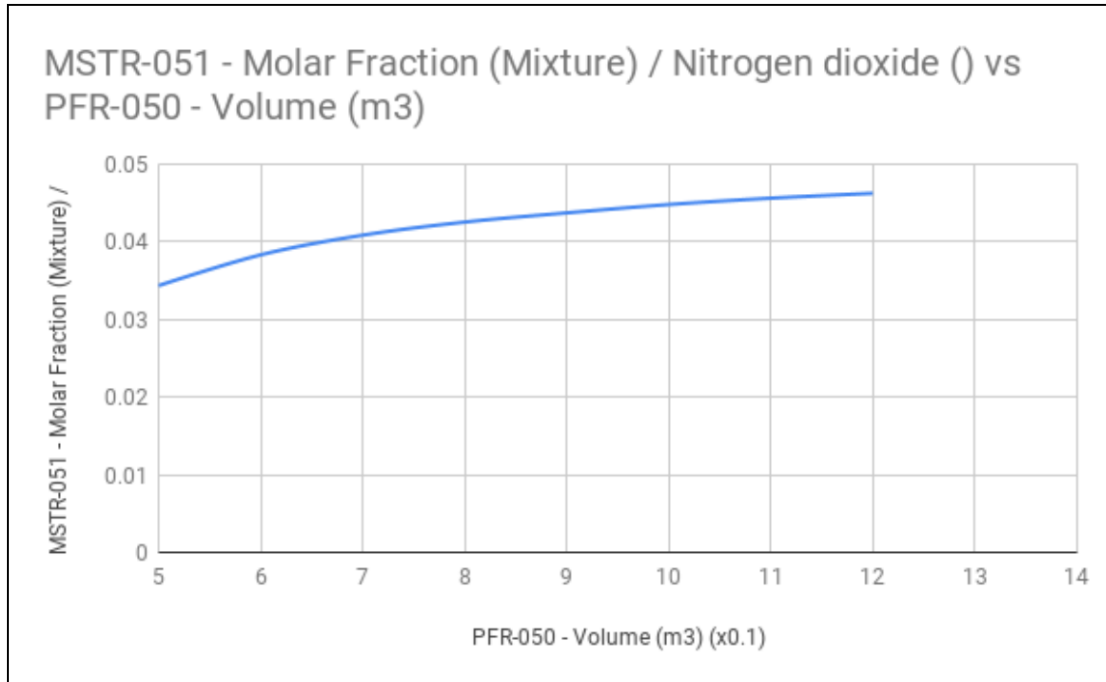


FIGURE 8.2: Sensitivity Analysis for Heat Exchanger

As explained in Chapter 7, modelling of reactive heat exchangers is difficult in any simulation software, hence to ease this process, they were modelled as PFRs. The above results are produced for the amount of NO_2 in the Absorption Column inlet. We want to achieve a high conversion of NO to NO_2 in the heat exchangers, but also want to reduce the cost involved in doing so. On increasing the volume of the PFR, the mole fraction of NO_2 increases to a certain value, and becomes constant after around 0.9 m^3 . Hence, a volume of 0.9 m^3 is used for this particular heat exchanger, to give us optimum operation.

8.3 Absorption Column Analysis

Extra O₂ Flow rate(kg/s) and NA Conc(% wt)

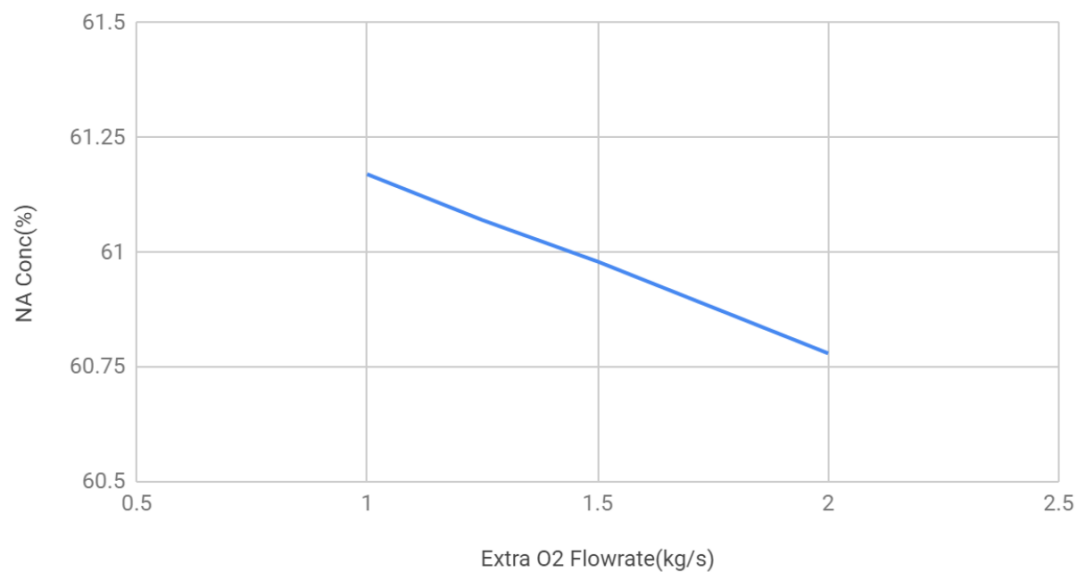


FIGURE 8.3: Sensitivity Analysis for Absorption Column - 1

Extra O₂ Flow rate(kg/s) vs NA Sol Flow rate(kg/s)

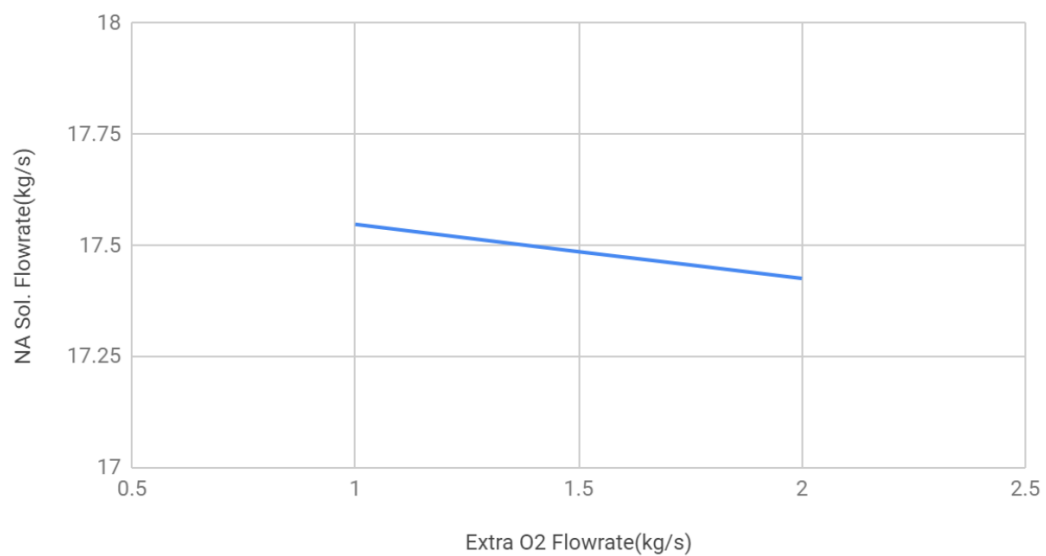


FIGURE 8.4: Sensitivity Analysis for Absorption Column - 2

The above analysis compares the Nitric Acid Solution Flow rate and Concentration as a function of extra added air. The minimum amount of extra O₂ required is 1kg/s which provides us with the best results, the selected O₂ rate was set at 1.25 kg/s, which

provided us with the **least amount of NO_x in the tail gas** as well. The mentioned comparisons are for the said extra O₂ values, which are obtained from the secondary air, and can be manipulated using the split ratio and intake of air.

Another important parameter to take care of while designing the absorption column is the total pressure drop across the column. Since we want to use the pressurised tail gas to generate energy, low pressure drops are desired. The pressure drop is a function of the diameter of the column, which in turn is a function of the tray spacing. Lower spacing (0.3-0.6 m) require smaller diameters and hence a relatively lower capital cost, but cause a larger pressure drop. Whereas larger spacing (1.0-1.2 m) require larger diameters but cause smaller pressure drops, helping us reduce our operating costs by providing higher amounts of energy. Hence, a diameter of 5 m, with spacings of 1.0 m in the bottom part (trays 1-13) and 1.2 m in the top part (trays 13-36) is chosen for the column.

Chapter 9

Equipment Sizing and Costing

In this chapter, we size the major equipments used in the plant and also estimate the cost of each of the equipment. They are listed in the following sections. The following data is used in the cost estimation:

- India location index w.r.t US = **0.7**
- Dollar to INR = **70**
- Cost Index - Chemical Engineering Plant Cost Index
- All equipment cost are delivered cost (1.1*fob cost)
- Direct and Indirect Costs in FCI are calculated using percentage normalisation from Peters et. al. [10]
- Equipment Cost is estimated using Nomograms from Peters et. al. [10] and Cost relations from Walas et. al. [11]
- All equipment are mapped to the average 2018 Cost Index - **603.1** (As of Dec 18), data acquired from ChemEngOnline Website[12]

9.1 Ammonia Oxidation Reactor

The Ammonia Oxidation Reactor is a shallow bed reactor, with a burner head and 90-10 Pt-Rh gauzes as its main parts. Since Pt-Rh Gauzes have a lifetime of 6-8 months, only

first 24 months of the catalyst gauzes will be capitalised and the rest will be incorporated into the Operating Costs. The burner head is a pressure vessel head, with a conical shape and operating pressure of 5 bar abs. Since the burner head doesn't come under the direct heat of the reaction gases (890°C), we don't require any special material of construction for the said equipment.

9.1.1 Diameter Calculation

The diameter of the gauzes and that of the burner head are calculated using the following data provided by Krupp Uhde[13]

1. Gauze Density - 400g Pt/m² of gauze
2. Amount of Nitrogen allowed on Gauze to provide desired conversion - 10 Tonnes per day of N/m² of gauze
3. Platinum required for given Nitrogen - 320g Pt/Tonne per day Nitrogen

NH_3 consumed = 3.056 kg NH_3 /s = 0.17974 kmol NH_3 /s = 179.74 mol N/s
 = 2.516 kg N/s = **219.608 tonnes N/day**

From 2., we get, Area required, $A = 21.961 \text{ m}^2$

Hence, **Diameter = 5.288 m**

From 3., we get, Pt required = 70.275 kg

From 1., we get, Pt/gauze = 8.784 kg

Hence, we get, **Number of Gauzes = 70.275/8.784 = 8 gauzes**

9.1.2 Catalyst Costs

Platinum and Rhodium prices were acquired from [14] and [15] respectively. Since the catalyst life is 6 months, we are using 2 batches of catalyst gauzes per year. We are also capitalising 24 months worth of catalyst.

Catalyst Required / year (kg)	Catalyst Cost / kg (USD)	Catalyst Cost / year (INR)
140.55	34,750	48.837 Lakhs

TABLE 9.1: Catalyst Costs

$$\begin{aligned}\text{Capitalised Catalyst Cost} &= 140.55 * 2 * 34750 * 70 \\ &= \text{INR } 97,67,475 = \text{INR } \mathbf{97.675 \text{ Lakhs}}\end{aligned}$$

9.1.3 Burner Head Calculation

The burner head is vertical, conical vessel with the following specifications:

$\alpha(^{\circ})$	D_i (m)	MoC	Corrosion Allowance (c)	Milling Tolerance (m)	S_a (MPa)	Design Temp. (C)	Design Pressure (barg)(P)	Weld Joint Efficiency (E)
45	5.3	SS 321	0.5 mm	12.5	190	500	4.4	1

TABLE 9.2: Burner Head Design Parameters

According to the Internal Pressure Vessel calculations, to find the regulation thickness, t , referring to CL 407 Handouts [16],

$$t = \frac{PD_i}{2 \cos \alpha [S_a E - 0.6P]}$$

Hence we get, $t = 11.7$ mm. Now to get the t_{rec} , we have,

$$t_{rec} = \frac{t + c}{1 - \frac{m}{100}} = 14mm$$

Hence, weight of the Burner head = **6,336.2 lbs**

From Walas et. al. [11], we have Vertical Pressure Vessels cost, C as (The formula provides values for 1984 in US\$ with CE Cost Index = 315),

$$C = F_M C_b + C_a$$

$$C_b = 1.672 \exp[9.1 + 0.2889(\ln W) + 0.04576(\ln W)^2]$$

$$C_a = 480 D^{0.7396} L^{0.7066}$$

where W - shell weight in lbs, D - Diameter in ft and L - Height in ft. On using the required values we get the following results:

W (lbs)	D (ft)	L (ft)	C_b	C_a	F_M (SS 321)	Cost (\$, in 1984)	Cost (\$, in 2018)	Cost (INR)
6,336.20	6.6	8.7	23805.9	4562.2	1.87	49,079.10	105,883.20	72.36 Lakhs

TABLE 9.3: Burner Head Costing Parameters

Hence, cost to construct the burner head = **INR 72.36 Lakhs**

9.2 Storage Tanks

We produce 62% Nitric Acid solution at 1500 tonnes/day, which corresponds to 45.2 m³/h. Referring to Walas et. al. [11] we will require a Field Erected Storage Tank of height 20 m and diameter 33 m with a capacity of 4.5 million gallons, keeping an inventory of 15 days of Nitric Acid. Nitric Acid Solution is stored under ambient atmospheric conditions. We also require an Ammonia Storage Tank to store our Ammonia for a period of one month to account for imports and procurement of the raw material. Ammonia is stored at -33°C and 1 atm abs. For this, special Double walled Tanks are constructed on site with a refrigeration unit accompanying the same. Ammonia required is 267 tonnes/day, which corresponds to 16.5 m³/h. All the calculations include pumps installed in the tank farm as a factor of the total equipment cost [13]. Referring to Fertilizers Manual [17], we will require a LT Carbon Steel Refrigerated Double Walled Storage Tank, of height 20 m and diameter 28 m with a capacity of 3.25 million gallons. Suggestions for inventory were given by Krupp Uhde [13]. Referring Fertilizers Manual [17], Refrigerated Double Walled Ammonia Storage Tank incurred a capital cost of \$ 3.22 million in 1992-1994. Using CE Cost Index of 360 for the said period, multiplying CE Cost Index of 2018, 603.1, and multiplying \$ to INR conversion factor of 70 and 1.1 we get,

Refrigerated Ammonia Storage Cost = **INR 41.52 Crores**

The following relation is used for costing of Field Erected Storage Tanks (C calculated in \$, all values for 1984 with CE Cost Index = 315):

$$C = F_M \exp[11.662 - 0.6104(\ln V) + 0.04536(\ln V)^2]$$

where V - Volume in Gallons and FM - MoC Factor

Storage Tank	Dim. (m)	Temp. And Pressure	Volume (gal)	MoC	F _M	C (\$, 1984)	C (\$, 2018)	Cost (INR)
Nitric Acid Storage	D = 33 H = 20	T = 30°C P = 1 atm	4.52 million	SS 304L	2.4	1,019,978.60	1,952,854.30	15.04 Crores

TABLE 9.4: Nitric Acid Storage Tank Costing

Hence, the total cost required for Storage Tanks = **INR 56.56 Crores**

9.3 Compressors

There are two compressors in the plant - C101 to compress the Air feed from ambient conditions to 5 bar abs before the Ammonia Oxidation Reactor and C102 to compress the oxidised NO_x gases to a pressure of 12 bar, for the high pressure absorption column.

Both the compressors are Two Stage Centrifugal Compressors with turbines, with the Air Compressor, C101 having a compression ratio of 2.236 and the NO_x Compressor, C102 having a compression ratio of 1.549. The choice to use a multi-stage compressor was made because the temperature increase due to compression in one single stage could have damaged the compressor in both the cases and also due to the fact that the power requirements and the flow rates were in the range of the operating conditions for centrifugal compressors. [13]

Calculations are shown for the first stage of the C101, Air Compressor, with Air coming at 189.06 tonnes/hour.

$$\text{Power} = \text{Work rate} / \text{Isentropic Efficiency} = W / \eta$$

$$W = P_1 V_1 \frac{n}{n-1} \left[\left(\frac{P_2}{P_1} \right)^{\frac{n-1}{n}} - 1 \right]$$

P₁ - Inlet Pressure = 1 bar abs

P₂ - Outlet Pressure = 2.266 bar abs

V₁ - Volumetric Flow = 49.21 m³/s

n - Heat Capacity Ratio = 1.4

Isentropic Efficiency, $\eta = 0.85$ [13]

On solving the given equation, we get, Power = **5307.05 kW**

Similar calculations for other stages and compressors yield the following results:

Compressor	Stage	Inlet Pressure (bar abs)	Outlet Pressure (bar abs)	Power Required (kW)
C101	1	1	2.236	5237.5
C101	2	2.236	5	7042.9
C102	1	5	7.745	2037.2
C102	2	7.745	12	2350.1

TABLE 9.5: Compressor Power Calculation

For cost estimation, Nomograms from Peters et. al. [10] are used. Referring the nomograms, we get the following results for the compressor cost estimation:

**** Note that both the compressors are Two Stage Centrifugal Compressors with Turbines**

Equip. No. - Stage	P _{in} - P _{out} (bar abs)	Process Fluid	Power Required (kW)	MoC	Cost (\$, 2002)	Cost (\$, 2018)	Cost INR
C101 - 1	P1 = 1 P2 = 2.236	Air	5237.5	CS	3.1 million	4.789 million	36.88 Crores
C101 - 2	P1 = 2.236 P2 = 5	Air	7042.9	CS	4.2 million	6.488 million	49.96 Crores
C102 - 1	P1 = 5 P2 = 7.745	NO _x Gas	2037.2	SS 304L	1.4 million	2.163 million	16.65 Crores
C102 - 2	P1 = 7.745 P2 = 12	NO _x Gas	2350.1	SS 304L	1.6 million	2.472 million	19.04 Crores

TABLE 9.6: Costing of Multi Stage Compressors with Turbines

Hence, total cost required for Compressors = **INR 122.53 Crores**

9.4 Pumps

There are a total of 6 estimated pumps in the plant. Including standby pumps, we have a total of 12 pumps. Out of these 12, 6 are part of the cooling circuit of absorption column and their cost is incorporated into the costing of the absorption column using the data provided by Krupp Uhde [13]. Out of the remaining pumps, one set is used to pump liquid ammonia into the plant, one set is used to pump the acid condensate to the absorption column and the last set is used to pump the required water into the boiler for production of steam. Sample calculation for the liquid Ammonia pump is shown below.

Liquid Ammonia is fed at 19 bar to the Ammonia evaporator from the Ammonia Storage, which stores ammonia at 1 bar and -33°C. Since the temperature is so low, LT Carbon Steel is used as the MoC of this pump.

Flow rate = 3.056 kg/s; Pressure difference = 18 bar; Density of liquid = 610 kg/m³

We know that, Pump Work,

$$W_P = \frac{\Delta P}{\rho} + g\Delta z + \frac{\Delta P_f}{\rho}$$

Hence we get, Pump Work, $W_P = 2.992 \text{ kJ/kg}$

Power required = $W_P \times \text{Flow Rate/pump efficiency (assumed to be 0.85)} = \mathbf{10.757 \text{ kW}}$

All pumps used here fall under the zone of Centrifugal Pump considering the flowrate and the head required. The following relations from Walas et. al. [11] are used to estimate individual pump costs, C (Calculated values in \$ for 1984, with CE Cost Index = 315):

$$C = F_M F_T C_{b, \text{base cast} - \text{iron}, 3550 \text{ rpm}, VSC}$$

$$C_b = 3 \exp[8.833 + 0.6019(\ln Q \sqrt{H}) + 0.0519(\ln Q \sqrt{H})^2]$$

$$F_T = \exp[b_1 + b_2(\ln Q \sqrt{H}) + b_3(\ln Q \sqrt{H})^2]$$

Type	b_1	b_2	b_3
One-stage, 1750 rpm, VSC	5.1029	-1.2217	0.0771
One-stage, 3550 rpm, HSC	0.0632	0.2744	-0.0253
One-stage, 1750 rpm, HSC	2.029	-0.2371	0.0102
Two-stage, 3550 rpm, HSC	13.7321	-2.8304	0.1542
Multistage, 3550 rpm, HSC	9.8849	-1.6164	0.0834

TABLE 9.7: Pump Costing Factors

Type	Flow Range (gpm)	Head Range (ft)	HP (max)
One-stage, 3550 rpm, VSC	50-900	50-400	75
One-stage, 1750 rpm, VSC	50-3500	50-200	200
One-stage, 3550 rpm, HSC	100-1500	100-450	150
One-stage, 1750 rpm, HSC	250-5000	50-500	250
Two-stage, 3550 rpm, HSC	50-1100	300-1100	250
Multi-stage, 3550 rpm, HSC	100-1500	650-3200	1450

TABLE 9.8: Pump Factors

Based on the tables and cost relations provided above, we get the following results for the pump cost estimations:

**** Note - All the above mentioned Pumps are Centrifugal pumps. Cost include the costing of both A/B pumps for each set**

Pump	Process Fluid	Flow rate (gpm)	Head (ft)	Type - MoC	Cost (\$, 1984)	Cost (\$, 2018)	Cost INR
P101 (A/B)	Liquid Ammonia	79.5	1001.2	Two-Stage, 3550 rpm, HSC - CS	17,233.40	32,995.10	25.41 Lakhs
P102 (A/B)	Nitric Acid	127.7	250.1	One-Stage, 3550 rpm, HSC - SS 304L	17,495.30	33,496.50	25.80 Lakhs
P103 (A/B)	Boiler Feed Water	52.6	322.5	One-Stage, 3550 rpm, VSC - CS	7,721.50	14,783.60	11.39 Lakhs

TABLE 9.9: Costing of Centrifugal Pumps

Hence, the total cost required for Pumps = **INR 62.60 Lakhs**

9.5 Heat Exchangers

There are a total of 8 Heat Exchangers in the plant. All the heat exchangers are Shell and Tube Heat Exchangers, as cross checked with Krupp Uhde [13] and DFPCL [7]. The waste heat boiler is sized below.

Cooling Agent - Water at 80°C, 6 bar

NO_x Gas from Reactor is cooled from 890°C to 427°C

Water boils and is converted to steam, which is superheated to 380°C

$$T_{LMTD} = 405.4^{\circ}\text{C}$$

Overall Heat Transfer Coefficient for Gas-Water Heat Exchange, $U = 150 \text{ W}/(\text{m}^2.\text{K})$

$Q = 26063.9 \text{ kW}$ and we know that, $Q = U A \Delta T_{LMTD}$. Hence, we get,

$$A = Q / (U * T_{LMTD}) = \mathbf{428.62 \text{ m}^2}$$

The cost estimate for heat exchangers is performed using the nomograms available in Peters et. al. [10], where the cost from nomogram was in \$ for 2002, with CE Cost Index = 390.4:

HX No.	HE101-AE	HE101-AS	WHB	HE102	HE103	HE104	HE105	HE106
Hot Stream	Cooling Water	LP Steam	NO Gas	NO Gas	NO Gas	NO Gas	NO Gas	Air
T _{hot, in} (K)	306	423	1123	700	568	457	530	493
T _{hot, out} (K)	280	372	700	568	457	323	323	323
Cold Stream	Ammonia	Ammonia	BFW/Steam	Tail Gas	BFW	Cooling Water	Cooling Water	Tail Gas
T _{cold, in} (K)	240	283	353	403	313	306	306	283
T _{cold, out} (K)	283	343	653	623	353	330	330	403
Q (kW)	4472	412.7	26063.9	8667.8	7282.3	13883.7	5765.7	4675.1
U (W/m ² .K)	150	300	150	95	150	150	150	95
Area (m ²)	970.5	16.3	428.7	790.2	274.1	1692.1	517.8	798.2
Shell Side Fluid	Ammonia	LP Steam	NO Gas	Tail Gas	BFW	NO Gas	NO Gas	Air
Shell Side MoC	LT CS	CS	SS 321	SS 321	SS 304L	SS 304L 2Re10	SS 304L 2Re10	SS 304L
Tube Side Fluid	Cooling Water	Ammonia	BFW/Steam	NO Gas	NO Gas	Cooling Water	Cooling Water	Tail Gas
Tube Side MoC	LT CS	SS 321	SA 192/SA 213	SS 304L	SS 304L	SS 304L 2Re10	SS 304L 2Re10	SS 304L
Pressure (bar abs)	6.5	5	5	5	5	5	12	Tube:12 Shell:5
Cost (\$, 2002)	54,150	5,054	197,534	191,301	60,078	704,968	346,418	177,650
Cost (1000\$, 2018)	83.7	7.8	305.2	295.5	92.8	1,089.10	535.2	274.4
Cost INR Crores	0.65	0.061	2.35	2.28	0.72	8.39	4.12	2.11

TABLE 9.10: Operating Parameters and Costing of Heat Exchangers

**** Note - SS 304L 2Re10 is a special material provided Sandvik Materials Technology. The cost factor of this material is used as 3X of SS 304L according to the data provided by Krupp Uhde. Also SA 192 and SA 213 are high**

temperature corrosion resistant Alloys, for which cost factor used is 2X SS 304L according to the data provided by Krupp Uhde [13].

Hence, the total cost required for Heat Exchangers = **INR 20.67 Crores**

9.6 Columns

We have two Absorption Columns in our plant, one is a 47 m tall reactive absorption column and the second one is a 10 m tall bleaching column. Since the absorption column has a height greater than 10 m, we need to make thickness calculation based on stresses produced due to wind at heights. We can ignore this for the shorter bleaching column. We use internal pressure vessel and wind force calculations to find out the thickness required for the column body and heads.

9.6.1 Shell Calculations

Using Internal Pressure Vessel calculations, referring to CL 407 Handouts [16], we have,

$$t = \frac{PD_i}{2[S_a E - 0.6P]}$$

$P = 12.1$ bar, $D_i = 4$ m, S_a for MoC SS 304L = 180MPa, $E = 0.9$. Hence we get, $t = 15$ mm. Now to get the t_{rec} , we have,

$$t_{rec} = \frac{t + c}{1 - \frac{m}{100}} = 14mm$$

Using $c = 1$ mm and $m = 12.5$, we get $t_{rec} = \mathbf{18.3 \text{ mm}}$

Both the columns have ellipsoidal heads, using details from CL 407 Handouts [16], similar calculations are done for the heads and the skirt. The details of the calculations are provided in the detailed design of the absorption column. Following the thickness calculations, weights of the columns were calculated, skirts and heads included.

**** Note - The bottom closure of the absorption column, A101 has a separate vessel attached inside, with its weight being 0.25 times that of the closure itself, according to the data provided by Krupp Uhde [13].**

**** Note - The Absorption Column comes with a cooling system, inclusive of a piping network and 6 pumps. According to the data provided by Krupp Uhde**

[13], once the entire column cost is calculated, including trays, multiplying a factor of 1.25 will give a rough estimate for the entire column cost including the cost of the cooling system.

Nomograms from Peters et. al. [10] are used, where the cost from nomogram was in \$ for 2002, with CE Cost Index = 390.4:

Column	A101 - Absorption Column	B102 - Bleaching Column
Height (m)	44.6	9
Diameter (m)	4	1.75
Tray Spacing	1 m / 1.2 m	0.6 m
t _{rec} for Body (mm)	18.3	4.55
t _{rec} for Heads (mm)	18.24	4.54
t _{rec} for Skirt (mm)	3.77	3.77
Skirt Height (m)	3.4	1
Fluids Processed	NO-NO _x Gases, Nitric Acid	Air, NO _x Gases, Nitric Acid
Operating Pressure (barg)	11	4
Operating Temp. Range (°C)	10 - 50	30 - 50
Design Pressure (barg)	12.1	4.4
Design Temp. (°C)	80	80
MoC	SS 304L	SS 304L
Weight (Tonnes)	88.46	2.006
Cost (\$, 2002)	700,000	52,000
Cost (\$, 2018)	1,081,378	80,331
Cost INR	8.33 Crores	0.62 Crores

TABLE 9.11: Column Parameters and Costing

9.6.2 Tray Calculations

Sieve trays are used in both the absorption columns due to their many benefits. Selection process, the tray specification and calculations for number of trays for absorption column are all specified in the detailed design of the absorption column.

Nomograms from Peters et. al. [10] are used for cost estimation, where the cost from nomogram was in \$ for 2002, with CE Cost Index = 390.4:

Column	Diameter (m)	Number of trays	MoC	QF	Per Tray Cost (\$, 2002)	Total Tray Cost (\$, 2018)	Cost INR
A101	4	36	SS 304L	0.98	4,000.00	239,807.00	1.68 Crores
B102	1.75	12	SS 304L	1.4	1,400.00	42,823.00	0.30 Crores

TABLE 9.12: Sieve Tray Costing

Column	Shell Costs (INR, 2018)	Tray Costs (INR, 2018)	Total Purchased Cost (INR, 2018)
A101	8.33 Crores	1.68 Crores	12.51 Crores
B102	0.62 Crores	0.30 Crores	0.92 Crores

TABLE 9.13: Total Purchased Costs for Columns

Hence, the total cost required for Columns, including the cooling system = **INR 13.43 Crores**

Chapter 10

Plant Economics

This chapter focuses on an overview of the plant economics, by estimating the capital investments, production costs and finally the payback period for the Nitric Acid Plant.

10.1 Major Equipment Costing

The Dual Pressure Nitric Acid plant has many major equipments including storage tanks, compressors, pumps, heat exchangers, reactor and columns. We used costing relations provided by Peters et. al. [10] and Walas et. al. [11] to determine the total purchased cost of each of these equipments, using CE Cost index to find their costs in 2018. A dollar to INR factor of 70 is used and an India location factor of 0.7 is also used. The following is the final result of our calculations in Chapter 9:

TABLE 10.1: Total Purchased Equipment Cost

Equipment	Total Purchased Cost, INR (2018)
Reactor	1.700 Crores
Storage Tanks	56.56 Crores
Compressors	122.53 Crores
Pumps	62.60 Lakhs
Heat Exchangers	20.67 Crores
Columns	13.43 Crores
Total Purchased Equipment Cost	215.51 Crores

10.2 Capital Investment Estimation

Total purchased equipment costs calculated in the previous section are used to calculate the total capital investment in the plant. Working capital is calculated as 15% of the total capital investment. The plant is considered to be a Fluid-Fluid Processing plant (F-FPP) and the percentage of delivered equipment cost is implemented for this cost estimation. The results of the estimation are provided in the table below:

Direct Costs	F-FPP	Normalized %	Cost (Cr. INR)
Purchase Equipment Delivered	100	0.1984	215.51
Purchased Equipment Installation	47	0.0933	101.29
Instrumentation and controls	36	0.0714	77.58
Piping	68	0.1349	146.54
Electrical Systems	11	0.0218	23.71
Buildings	18	0.0357	38.79
Yard Improvements	10	0.0198	21.55
Service Facilities	65	0.1290	140.08
Land	5	0.0099	10.78
Total direct plant cost	360	0.7143	775.82
Indirect Costs			
Engineering and Supervision	33	0.0655	71.12
Construction Expenses	41	0.0813	88.36
Legal Expenses	4	0.0079	8.62
Contractor's Fee	22	0.0437	47.41
Contingency	44	0.0873	94.82
Total indirect plant cost	144	0.2857	310.33
Fixed Capital Investment	504	1.0000	1086.15
Working Capital (15% of total capital investment)	89		191.67
Total Capital Investment			1277.82

TABLE 10.2: Total Capital Investment Estimation

Peters et. al. [10] is used as the reference for this costing exercise, using the ratio factors provided by it for our cost estimation.

Using an India Factor of 0.7, we get,

Total Capital Investment = INR 894.48 Crores

10.3 Raw Material Cost

The estimation of the total product cost comes from raw material cost. We require Liquid Ammonia as a raw material, which is acquired via imports and from KRIBHCO, and we also require 140.55 kg of Pt-Rh catalyst gauzes every year, taken from Johnson Matthey India Pvt. Ltd. Ammonia cost is acquired from data provided by DFPCL [7]. Raw material cost calculation is provided below:

Raw Material	Amount	Cost/kg (\$/kg)	Cost/year (\$/year)
Ammonia	267 tonnes/day	0.429	37.35 Million
Pt-Rh Gauze	140.55 kg/year	34,750	4.884 Million
Total Raw Material Cost			42.24 Million

TABLE 10.3: Total Raw Material Cost Calculation

Hence, the Total Raw Material Cost = \$ **42.24 Million / year**

10.4 Revenue Calculation

The plant revenue is calculated from the untaxed prices of 62% Weak Nitric Acid (WNA) Solution, sold at INR 20/kg, with 1\$ = INR 70, cost taken from data provided by DFPCL [7]. The results are tabulated below:

Product	Amount	Cost/kg (\$/kg)	Cost/year (\$/year)
62% WNA Solution	1520 tonnes/day	0.286	141.82 Million

TABLE 10.4: Total Revenue Calculation

Hence the Total Revenue = \$ **141.82 Million / year**

10.5 Total Product Cost

Total Product cost is calculated using the normalised percentage method from Peters et. al. [10]. The result is reproduced in the following tabulated form:

Category	Factor	Norm	Cost (\$/yr)
Raw material	45	0.3460	42.23 Million
Operating Labour	10	0.0769	6.569 Million
Supervising Labour	3	0.0231	1.971 Million
Utilities	15	0.1153	14.08 Million
Repairs and Maintenance	7	0.0538	6.569 Million
Operating supplies	1.05	0.0081	0.986 Million
Laboratory charges	1.5	0.0115	1.408 Million
Patents	3	0.0231	2.815 Million
Fixed charges	15	0.1153	14.08 Million
Plant overhead	12	0.0923	11.26 Million
Admin costs	1.5	0.0115	0.985 Million
Distribution and marketing	11	0.0846	10.32 Million
RnD cost	5	0.0384	4.692 Million
Total	130	1.0000	117.965 Million

TABLE 10.5: Total Product Cost Estimation

Hence, the Total Product Cost = **\$ 117.965 Million / year**

Please note that since the plant is setup in India, India factor of 0.7 is applied to Operating Labour, Supervising Labour and Admin costs.

10.6 Payback Period

The following assumptions were made while making the payback period calculations:

- 90% of FCI excluding the land costs is considered to be depreciable over a period of 10 years.
- Average depreciation is calculated using linear depreciation model.

- Bank interest rate of 6% over the total capital is also used.
- Final Product and Raw Material costs are assumed to be constant for profit calculations.

Total Depreciable FCI = **INR 677.49 Crores**

Total Depreciation per year = **INR 67.749 Crores / year**

Taxation Rate, including surcharge and education cess = 28.3% = 0.283

Total Product Cost = \$ 117.965 Million = **INR 825.76 Crores / year**

Revenue = \$ 141.82 Million = **INR 992.74 Crores / year**

Bank Interest Rate = 6%

Gross Profit = Revenue - Total Product Cost - Depreciation per year
= **INR 99.234 Crores**

Net Profit = Gross Profit * (1 - Taxation Rate) = **INR 71.151 Crores**

Interest on TCI = Bank Interest Rate * TCI = **INR 53.669 Crores**

$$\text{Payback Period} = \frac{\text{Depreciable FCI} + \text{interest on TCI}}{\text{Avg. Profit/yr} + \text{Avg. Depreciation/yr}}$$

Using 70% production capacity for year 1, 80% for year 2, 90% for year 3 and 100% thereafter, the following cash flow diagram was generated,

Year	Investment	Cost	Revenue	Gross Profit	Depreciation	Net Profit	Cash Flow	Cumulative Position	Capacity (%)
0	-760.31						-760.31	-760.31	
1		-554.10	694.92	140.82	56.46	60.49	116.94	-643.36	70
2		-633.26	794.19	160.93	56.46	74.91	131.37	-511.99	80
3		-743.18	893.47	150.28	56.46	67.27	123.73	-388.26	90
4		-825.76	992.74	166.98	56.46	79.25	135.70	-252.56	100
5		-825.76	992.74	166.98	56.46	79.25	135.70	-116.86	100
6		-825.76	992.74	166.98	56.46	79.25	135.70	18.85	100
7		-825.76	992.74	166.98	56.46	79.25	135.70	154.55	100
8		-825.76	992.74	166.98	56.46	79.25	135.70	290.26	100
9		-825.76	992.74	166.98	56.46	79.25	135.70	425.96	100
10		-825.76	992.74	166.98	56.46	79.25	135.70	561.66	100

TABLE 10.6: Cash Flow from Plant production, all values in INR Crores

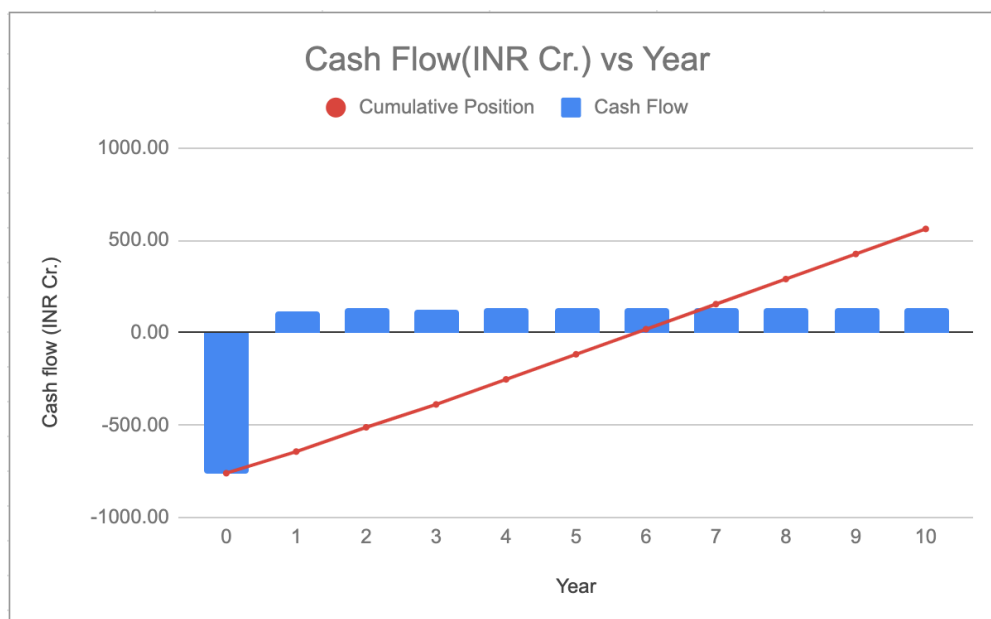


FIGURE 10.1: Estimated Cash flow from Plant Operation

Hence, Payback Period = **5.8 Years**

The usual payback period for a nitric acid plant is anywhere between 4-6 years [13]. The following comparison with economics of a 500 TPD Dual Pressure Plant set up in Donaldsonville, Louisiana, United States by Uhde in collaboration with CF Industries in 2016, shows that our plant economics are in accordance with actual industry economics.

	Our Plant	Uhde Plant
Location	Hazira, Gujarat, India	Donaldsonville, Louisiana, US
Capacity (TPD) (100% NA)	942	500
Total FCI (INR)	761 Crores	450 Crores
Payback Period (yrs)	5.8	5

TABLE 10.7: Plant Economics Comparison with recently setup plant

Chapter 11

Detailed Design - Absorption Column

The dual pressure process, requires an absorption column to absorb NO_x gases from the gaseous reactor into water and produce the desired concentration of nitric acid. The column handles three streams - (1) gas stream at 1,76,573 kg/hr, containing 13.35% by weight of nitrogen oxides at 50°C and 12 bar abs, (2) deionised make up water at 11,987 kg/hr, 10°C and 12 bar abs and (3) 37.8% nitric acid condensate from cooler condensers, at 25770 kg/hr, 50°C and 12 bar abs. The column is required to produce 62,673 kg/hr of 62% HNO_3 solution, excluding the dissolved NO_x gases.

A sieve tray absorption column is proposed, with a column diameter of 4 m, height of 44.6 m, 36 cross-flow type trays with spacings of 1 m between trays 1-13 and 1.2 m between trays 13-36. A larger tray spacing is used in the upper section of the column to ensure maximum NO to NO_2 oxidation. The operating pressure is approximately 12 bar abs, with an operating temperature range of 10°C - 50°C.

A rigorous mathematical model was also produced for this column, to determine the exact number of trays for the entire column, using correlations and data from Ray et. al. [8] and Thiemann et. al. [6]. The model was run using MATLAB and Google Spreadsheets.

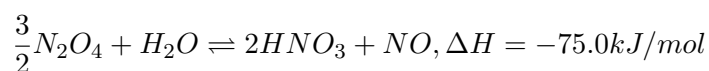
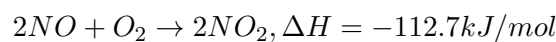
11.1 Mathematical Model

A rigorous mathematical model was used in sizing the column and determining the exact number of trays required for our column. The model is summarised below:

- Tray by tray approach based on the given feed compositions, temperatures and pressure is implemented
- First, NO oxidation conversion is calculated using correlations from Ray et. al. [8] and gas composition is recalculated - Step 1
- Next, NO₂ dimerisation equilibrium with N₂O₄ is calculated by solving a quadratic equation provided by Ray et. al. [8], giving us the required partial pressure of NO₂, and the gas composition is calculated again - Step 2
- Next, the amount of nitric acid formed in each plate is calculated using tray efficiency and related terms, available in Ray et. al. [8] and derived from Thiemann et. al. [6], and both liquid and gas phase compositions are recalculated - Step 3
- NO₂ - N₂O₄ equilibrium is recalculated, leading to another recalculation of the gas composition - Step 4
- Method is repeated until a tray achieves an almost zero concentration nitric acid. Tail Gas composition and the required amount of make up water are calculated at the end. Energy balances are also performed during each iteration.

The model was solved using an iterative method, implemented by solving 3 functions iteratively on MATLAB R2015b, using the fsolve function. Solutions from MATLAB were iteratively fed to Google Spreadsheets for the gas composition recalculation, as MATLAB R2015b didnt allow for the functions to defined within its for loops. The code can be found in the [Appendix B](#).

Reactions occurring in the Absorption column -



The results of the mathematical model are tabulated below:

Tray Number	Tray Spacing(m)	Nitric Acid Conc.(wt%)	X	F _a	Energy (kJ/s)	Cooling Water(kg/s)
1	1.5	0.6200	0.8786	0.0145	-2369.3334	28.3413
2	1	0.5939	0.8077	0.0126	-2184.3813	26.1290
3	1	0.5691	0.7909	0.0114	-2062.5688	24.6719
4	1	0.5448	0.7730	0.0103	-1901.1506	22.7410
5	1	0.5210	0.7547	0.0092	-1713.0681	20.4912
6	1	0.4982	0.7363	0.0082	-1537.1034	18.3864
7	1	0.4764	0.7183	0.0072	-1373.5775	16.4304
8	1	0.4561	0.7099	0.0065	-1236.6114	14.7920
9	1	0.4368	0.6839	0.0058	-1101.8346	13.1798
10	1	0.4186	0.6678	0.0052	-997.0431	11.9264
11	1	0.4015	0.6524	0.0046	-890.6925	10.6542
12	1	0.3857	0.6379	0.0041	-799.0663	9.5582
13	1.2	0.3710	0.6727	0.0038	-1546.1511	14.2266
14	1.2	0.3224	0.8300	0.0028	-729.7235	6.7144
15	1.2	0.2927	0.8227	0.0026	-481.0421	4.4262
16	1.2	0.2632	0.8164	0.0023	-412.6295	3.7967
17	1.2	0.2353	0.8107	0.0021	-369.9972	3.4045
18	1.2	0.2083	0.8053	0.0019	-336.2951	3.0944
19	1.2	0.1826	0.8002	0.0017	-304.1869	2.7989
20	1.2	0.1583	0.7955	0.0016	-279.8806	2.5753
21	1.2	0.1343	0.7910	0.0015	-262.3342	2.4138
22	1.2	0.1108	0.7867	0.0014	-246.1110	2.2645
23	1.2	0.0878	0.7825	0.0009	-191.3266	1.7605
24	1.2	0.0732	0.7794	0.0007	-144.0108	1.3251
25	1.2	0.0605	0.7770	0.0007	-124.7951	1.1483
26	1.2	0.0481	0.7748	0.0006	-143.4206	1.3197
27	1.2	0.0366	0.7729	0.0006	-99.8074	0.9184
28	1.2	0.0256	0.7843	0.0004	-89.8746	0.8270
29	1.2	0.0176	0.7828	0.0002	-54.5939	0.5023
30	1.2	0.0138	0.7819	0.0001	-30.9432	0.2847
31	1.2	0.0115	0.7815	0.0001	-11.4580	0.1054
32	1.2	0.0094	0.7811	0.0001	-8.7970	0.0809
33	1.2	0.0073	0.7808	0.0001	-8.2174	0.0756
34	1.2	0.0052	0.7804	0.0001	-8.2106	0.0755
35	1.2	0.0032	0.7800	0.0001	-7.5166	0.0692
36	1.5	0.0013	0.8212	0.0001	-8.1250	0.0744

TABLE 11.1: Mathematical Model Results

X - NO Conversion between trays; F_a - Nitric Acid formed on each tray (kmol/hr);
 Energy - Energy to be removed from each tray (kJ/s); Water Flowrate - Amount of
 Cooling/Chilled Water Required for each tray (kg/s)

Temp. for section below Tray 13 - 50°C - Cooled using cooling water

Temp. for section above Tray 13 - 10°C - Cooled using chilled water

Equations solved in each step:

Step 1 -

$$k_1 t P^2 = (b - a)^{-2} [X(b - a)/(1 - X)b] - \ln[(1 - X) - (aX/k_1)]$$

X - NO conversion

k_1 - NO Oxidation reaction rate constant

t - Residence time of gas between trays

P - Operating Pressure

b - Mole fraction of oxygen in gas

2a - Mole fraction of NO in gas

Step 2 -

$$p_{NO_2}^2[(2 - \mu)^2 + AB\mu] + p_{NO_2}[A(2 - \mu) - ABP\mu] + AP\mu[2BP\mu - (2 - \mu)] = 0$$

p_{NO_2} - NO₂ Partial Pressure

μ - Ratio of moles of nitrogen peroxide to total moles of gas

P - Operating Pressure

A, B - Reaction constants for NO₂-N₂O₄ equilibrium, given by $k_2 = A(1 - B^*p_{NO_X})$

Step 3 -

$$F_a = [P_{NO} + P_{NO_X} - (k_3 E^3 + 2E^2)/(k_2 + E)](G_{NO} + G_{NO_X})C(P_{NO} + P_{NO_X})^{-1}$$

F_a - Moles of nitric acid formed

P_{NO} - Partial Pressure of NO

P_{NO_X} - Partial Pressure of NO_X

E - Equilibrium partial pressure of NO₂

k_4 - Equilibrium relation between NO and N₂O₄ - Thiemann et. al. [6]

k_2 - Equilibrium relation between NO₂ and N₂O₄

$k_3 = k_4/k_2$; G_{NO} - Flow rate of NO; G_{NO_X} - Flow rate of NO_X; C - Tray Efficiency

11.2 Tray Selection and Specifications

The following parameters were considered while selecting the type of tray for the column:

Tray Type	Bubble cap	Dual Flow	Sieve	Valve
Capacity	Moderate	Very High	High	High
Pressure Drop	High	Low to Moderate	Low to Moderate	Moderate
Turndown	Very High	Low	Approx 2:1	Approx 3-5:1
Efficiency	0.6-0.8	0.5-0.7	0.7-0.9	0.7-0.9
Maintenance	Relatively High	Low	Low	Low to Moderate
Fouling Tendency	High	Extremely low	Low	Low to Moderate
Cost	High	Low	Low	Marginally higher than sieve trays

TABLE 11.2: Tray Selection Parameters

Sieve Trays were finally selected because of their versatile properties, making them feasible for almost every condition.

Plate Design Procedure provided in Sinnott et. al. [18] is used for our design. Sieve Trays of the following specifications are used in the absorption column:

Column Diameter, $D_c = 4\text{m}$

Area, $A_c = 12.57 \text{ m}^2$

Downcomer Area, $A_d = 0.12 A_c = 1.51 \text{ m}^2$

Net Area, $A_n = A_c - A_d = 11.06 \text{ m}^2$

Active Area, $A_a = A_c - 2A_d = 9.55 \text{ m}^2$

Hole Area, $A_h = 0.1A_a = 0.955 \text{ m}^2$

Referring to Sinnott et. al. [18], we get $l_w/D_c = 0.77$ for given hole area, hence

Weir Length, $l_w = 0.77D_c = 3.08 \text{ m}$

Weir height = 50 mm

Hole Diameter = 5mm

Plate Thickness = 5mm

11.2.1 Weeping Check

Maximum liquid flow rate = 17.83 kg/s

Minimum liquid flow rate, at 70% turn down = 12.48 kg/s

$h_w = 50$ mm liquid

Maximum $h_{ow} = 750(17.83/(1325*3.08))^{2/3} = 20.05$ mm liquid

Minimum $h_{ow} = 750(12.48/(1325*3.08))^{2/3} = 15.80$ mm liquid

Hence, at minimum rate, $h_w + h_{ow} = 65.80$ mm liquid

Referring to Sinnott et. al. [18], we get $K_2 = 30.2$ for given $h_w + h_{ow}$, hence

$U_{h,min} = (30.5 - 0.9(25.4 - 5))/(13.27)^{0.5} = 3.25$ m/s

Actual minimum vapour velocity = 3.333 m/s

So, the minimum operating rate will be above the weep point.

11.2.2 Plate Pressure Drop

Maximum vapour velocity, $U_{h,max} = 3.87$ m/s

Referring to Sinnott et. al. [18], we get $C_o = 0.84$ for given hole area and plate thickness, hence

Dry plate drop, $h_d = 51*(3.87/0.84)^2*(13.27/1325) = 10.84$ mm liquid

Residual head, $h_r = 12500/1325 = 9.43$ mm liquid

So, total plate pressure drop, $h_t = 10.84 + 9.43 + 50 + 20.05 = 90.32$ mm liquid =

1.174 kPa

11.2.3 Perforated Area and Hole Pitch

Referring to Sinnott et. al. [18], we get $\theta_c = 102^\circ$ for given hole area and plate thickness, hence,

Angle subtended at plate edge by unperforated strip = $180 - 102 = 78^\circ$

Mean length, unperforated edge strips = $(4 - 0.05) \cdot \pi \cdot 78 / 180 = 5.38 \text{ m}$

Area of unperforated edge strips = $0.05 \cdot 5.38 = 0.269 \text{ m}^2$

Mean length of calming zone = $(4 - 0.05) \cdot \sin(102/2) = 3.07 \text{ m}$

Area of calming zone = $2(3.07 \cdot 0.05) = 0.307 \text{ m}^2$

Total area of perforations, $A_p = 9.55 - 0.269 - 0.307 = 8.974 \text{ m}^2$

$A_h/A_p = 0.106$, hence, referring to Sinnott et. al. [18], we get,

$l_p/d_h = 3$ for given hole area and perforated area, hence,

Hole pitch, $l_p = 15 \text{ mm}$, equilateral triangular.

11.2.4 Number of Holes

Area of one hole = $1.964 \cdot 10^{-5} \text{ m}^2$

Hence, number of holes = $0.955 / (1.964 \cdot 10^{-5}) = \mathbf{48,650}$

Type of Tray	Sieve Tray
Flow type	Cross Flow
Diameter (D_c)	4 m
Area (A_c)	12.57 m ²
Downcomer Area (A_d)	1.51 m ²
Net Area (A_n)	11.06 m ²
Active Area (A_a)	9.55 m ²
Hole Area (A_h)	0.955 m ²
Hole diameter	5 mm
Active Holes	48600
Weir Height	50 mm
Weir Length (= $0.77D_c$)	3.08 m
MoC	SS 304L (Nitric Acid Grade)
Plate thickness	5 mm
Plate Pressure Drop	1.175 kPa
Hole pitch	Equilateral Triangular - $l_p = 15 \text{ mm}$
Turn Down	70% of Max Liquid Flow Rate
Liquid Hold up on tray	50 mm

TABLE 11.3: Final Tray Specifications

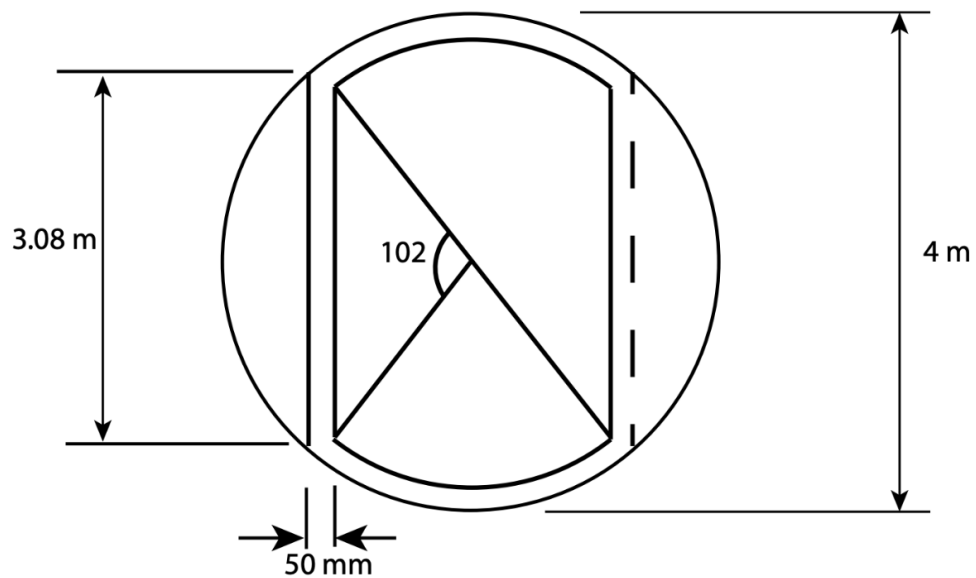


FIGURE 11.1: Sieve Tray Perforated Area with Downcomer



FIGURE 11.2: Sieve Tray Cooling Coils, Image provided by Krupp Uhde [13]

Pipe Diameter - 2 - 4 inches

Pipe Length on each tray - 10m

Process fluid - Cooling and Chilled water

Instead of the staggered arrangement, a packed single layer arrangement is used in the Dual Pressure Nitric Acid Absorption Column, with each layer of cooling coils, instead of being stacked over each other are packed in one layer, one after the other horizontally.

11.3 Head Selection

Head type	Pressure range
Torispherical	Upto 150 psig
Ellipsoidal	150 - 500 psig
Hemispherical	Greater than 500 psig

11.4 Tower Thickness

The column is an internal pressure vessel, with cylindrical body and ellipsoidal heads.

Design Pressure, $P = 12.1$ bar

Internal Diameter, $D_i = 4$ m

S_a , for SS304L = 180 MPa

Weld joint efficiency, $E = 0.9$

Corrosion allowance, $c = 1$ mm

Milling tolerance, $m = 12.5\%$

Cylindrical Body -

$$t = \frac{PD_i}{2[S_a E - 0.6P]}$$

Hence, we get, $t = 15$ mm and subsequently, $t_{\text{rec}} = 18.29$ mm

Volume of MoC used = $\pi * D_i * \text{height} * t_{\text{rec}} = 10.013$ m³

Density = 8000 kg/m³

Hence, Weight of Shell = **80,103.2 kg**

Ellipsoidal Heads -

$$t = \frac{PD_i}{2[S_a E - 0.1P]}$$

Hence, we get $t = 14.95$ mm and subsequently, $t_{\text{rec}} = 18.23$ mm

Volume of MoC used = Ellipsoid Surface Area * $t_{\text{rec}} = 0.393$ m³

Weight of Head = **3141.04 kg**

Skirt and Wind Considerations - MoC - CS

Column height = 44.6 m

Skirt height = 3.4 m

Insulation diameter = 5 m

Area = 240 m²

Wind velocity = 70.4 mph¹

$P_w = 0.002 \times 70.4^2 = 9.905 \text{ psf} = 474.25 \text{ Pa}$

Force = $P_w \times G \times \text{Area} = 474.25 \times 1.9 \times 240 = 216.3 \text{ kN}$

$M = 216.3 \times 1000 \times (48/2) = 5190.2 \text{ kNm}$

Thickness, $t = 2.296 \text{ mm}$ and subsequently, $t_{\text{rec}} = 3.767 \text{ mm}$

Column Height	44.6 m
Column Diameter	4 m
Tray Type	Sieve Tray
Number of trays	36
Tray Spacing	Trays 0 - 12: 1m, Trays 13 - 35: 1.2 m
Inlets	Tray 0 - NO Gas Tray 35 - Process Water Tray 12 - Acid Condensate Trays 0-12 - Cooling Water Trays 13-35 - Chilled Water
Body Thickness	18.29 mm
Head Type	Ellipsoidal - Axis Ratio = 1.56:2
Head Thickness	18.23 mm
MoC	SS 304L (Nitric Acid Grade)
Operating Pressure	11 barg
Operating Temperature	10-50°C
Design Pressure	12.1 barg
Design Temperature	65°C
Bottom and Top Disengaging spaces	1.5 m each

TABLE 11.4: Final Column Specifications

A Detailed Mechanical Drawing of the Absorption Column, with all design specifications is available in [Appendix C](#)

¹<https://www.weatheronline.in/weather/maps/city?WMO=42840&CONT=inin&LAND=IGJ&ART=WST&LEVEL=162&MOD=tab>

Chapter 12

Environmental Impact

Only one waste stream exits our plant - Tail Gas containing pollutants NO and NO₂, widely known to be precursors to acid rain and smog, and greenhouse gas N₂O, having a global warming potential 280 times that of CO₂. Though there is no statutory limit on N₂O emissions in India, United Nation's Clean Development Mechanism provides monetary benefits for reducing N₂O emissions. NO_x have a strict limit to be followed for Nitric Acid Plants in India, and we require an abatement unit to take care of reducing these emissions.

12.1 Tail Gas Composition and Emission Limits

The table below shows the composition of the Tail Gas leaving the Absorption Column:

Component	Flow rate (kg/hr)	Concentration
O ₂	3307	2.21 wt%
N ₂	145812	97.71 wt%
N ₂ O	142	1194.8 ppmv
NO ₂	18	637.8 ppmv
NO	58	
Flow Rate	149337 kg/hr	118846 Nm³/hr

TABLE 12.1: Composition of Tail Gas leaving Absorption Column

According to the data from the Ministry of Environment, Forest and Climate Change of the Central Government of India [19], the permissible emission levels of NO_x for Nitric Acid Plants is 400 mg/m³ or 400ppmv. Since our NO_x emissions are over the limit, we will require an abatement unit to reduce the NO_x levels.

12.2 Abatement Technology

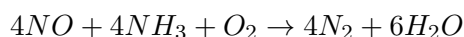
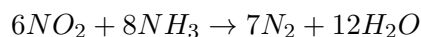
EnviNO_x[®] by Uhde GmbH is world's best abatement technology for Nitric Acid Plants. The EnviNO_x[®] Unit provides >97% NO_x and >98% N₂O removal, ensuring minimal pressure drop (<40 mbar), for an average period of more than 10 years.

Referring Groves et. al. [20], many process variants of this technology are available, but we will be using the EnviNO_x[®] process variant-2 for our nitric acid plant. The reasons for choosing this is the lower reducing agent costs and lower reaction temperature requirements for achieving very high emission reductions. Catalysts used in this technology, EnviCat[®]-NO_x and EnviCat[®]-N₂O, are both Iron Zeolites, used individually in the DeNO_x and DeN₂O[®] stages.

Being a proprietary technology, Uhde has given exclusive rights to Clariant and Süd Chemie for production of these catalysts for the vast nitric acid process market.

EnviNO_x[®] process variant-2 involves preheating the tail gas using the secondary air and the reactor outlet gas stream to a temperature of 350°C at 12 bar abs. Stoichiometric amounts of gaseous ammonia are mixed with the tail gas before entering the reactor unit containing the catalyst pellets in an annular porous cylindrical setup. Ammonia reduces NO_x in the DeNO_x stage of the reactor unit, ensuring that the DeN₂O[®] process downstream doesn't get hampered by the presence of NO_x in the tail gas. Propane is added to this mixture, which acts as a reducing agent for N₂O in the DeN₂O[®] stage, removing >98% N₂O from the tail gas, giving us vastly reduced emissions for our plant. The tail gas can is then expanded in the tail gas turbine. The tail gas turbine provides around 65% of the power required to run the compressors.

DeNO_x Reactions:



DeN₂O[®] Reactions:

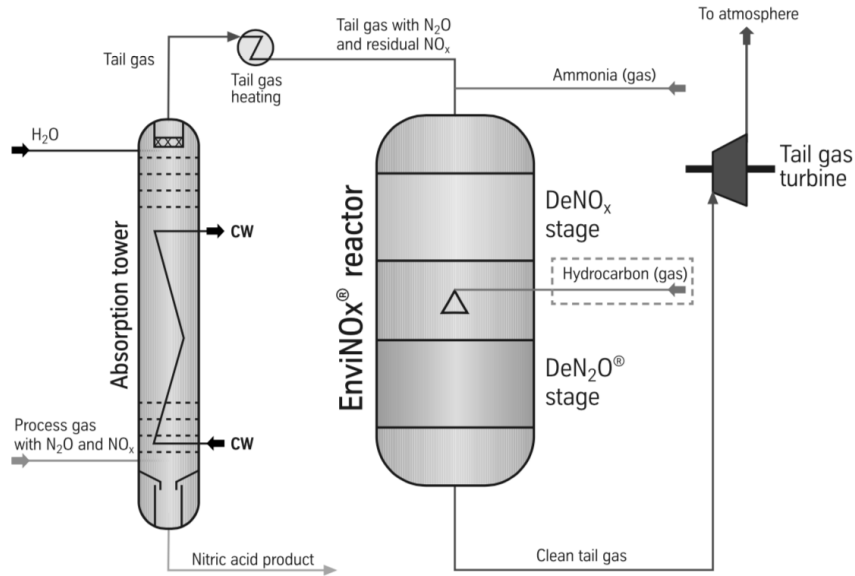
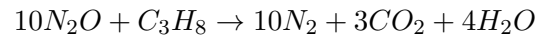


FIGURE 12.1: EnviNO_x[®] Process Variant - 2, recreated from [20]

12.3 Tail Gas Post Abatement

A catalyst volume of 7m³ is used, as suggested Krupp Uhde [13]. This volume of catalyst gives us a N₂O removal of 98.5% and NO_x removal of 97%. The final tail gas composition is shown in the table below:

Component	Flow rate (kg/hr)	Concentration
O ₂	3292	2.2 wt%
N ₂	145966	97.7 wt%
N ₂ O	2.13	18 ppm
NO ₂	0.54	5 ppmv
NO	1.74	15 ppmv
CO ₂	42	339 ppmv
H ₂ O	87	730 ppmv
Total	149392 kg/hr	119144 Nm³/hr

12.4 Revised Plant Economics

Addition of the EnviNO_x[®] Unit in the plant will incur increased fixed and working capital investments, mainly involving the catalyst, additional ammonia and propane costs.

12.4.1 Reactor Unit Cost

According to the data provided by Krupp Uhde [13],

Catalyst cost = **€100,000 per m³** of catalyst

Since the catalyst is has an average life of 10 years, only one batch of catalyst is capitalised and the amount catalyst used is 7 m³, hence, using €1 = INR 78,

Total Catalyst Cost = €100,000 * 7 = €700,000 = **INR 5.46 Crores**

The reactor is an annular cylindrical fixed bed reactor, with two catalyst bed of around 3.5 m³ each, filled inside a perforated cylinder, to allow gas flow from outside the cylinder to the inner annular region. The beds are housed inside a cylindrical shell of 5 m internal diameter, with ellipsoidal heads, operating at 12 bar abs. The MoC used is SS 321. According to the data provided by Krupp Uhde [13], the reactor setup is designed by Uhde GmbH and will cost around **INR 1 Crore** for the given catalyst volume. Hence,

Additional Fixed Capital Investment = **INR 6.46 Crore**

12.4.2 Additional Raw Material Costs

Additional Ammonia costs were included in the [Raw Material Cost Estimation done in Chapter 10](#)

Additional Ammonia Required = 40 kg/hr

Propane Required = 15 kg/hr = 8.09 gallon/hr = 64,073 gallon/year Propane Cost = INR 50/gal

Total Propane costs per year = **INR 32,03,690 / year = \$ 45,767 / year**

Using the method outlined in Chapter 10, calculation were again done, giving us,

New Total Capital Investment = **INR 921.29 Crores**

New Raw Material Cost = **\$ 42.28 Million / year**

New Total Product Cost = **\$ 118.09 Million / year = INR 826.65 Crores / year**

12.4.3 Additional Revenue Calculation

Addition of a N₂O abatement technology can be registered under the United Nation's Clean Development Mechanism as a Large Scale Emission Reducing Project. Under the CDM, in developing countries, efforts taken to reduce potential global warming causing emissions are rewarded with Certified Emission Reduction units, or Carbon Credits, that can be purchased by Annex I countries¹ to comply with their emission limitation targets as set by the Kyoto Protocol².

Since the prices of CERs fluctuate from year to year, two calculations were done for calculating the payback period, (1) without the CER Revenue, and (2) with the CER Revenue.

12.4.3.1 No CER Revenue

Total Revenue remains the same, hence we have,

Total Capital Investment = **INR 921.29 Crores**

Total Depreciable FCI = **INR 697.80 Crores**

Total Depreciation per year = **INR 69.780 Crores / year**

Taxation Rate, including surcharge and education cess = 28.3% = 0.283

Total Product Cost = \$ 118.09 Million = **INR 826.65 Crores / year**

Revenue = \$ 141.82 Million = **INR 992.74 Crores / year**

Bank Interest Rate = 6%

Gross Profit = Revenue - Total Product Cost - Depreciation per year
= **INR 96.308 Crores**

¹Annex I countries - https://en.wikipedia.org/wiki/United_Nations_Framework_Convention_on_Climate_Change#Annex_I_countries

²Kyoto Protocol - https://en.wikipedia.org/wiki/Kyoto_Protocol

Net Profit = Gross Profit * (1 - Taxation Rate) = **INR 69.053 Crores**

Interest on TCI = Bank Interest Rate * TCI = **INR 55.278 Crores**

Hence, Payback Period = **6 Years**

12.4.3.2 With CER Revenue

According to the UN's Clean Development Mechanism, project registered under it will be rewarded with 1 CER / tonne CO₂eq. reduced below the baseline for the entirety of the crediting period. The baseline model was selected to be the emission from the plant, as India doesn't have any limits on N₂O emissions. The baseline model was selected after referring to Methodology AM0028 [21], accessible from the CDM portal of UN.

Crediting Period = 10 years

Global Warming Potential(GWP) of N₂O = 280 * GWP of CO₂

Emission Reduction = (142 - 2.13)*8000 = 1119 tonnes N₂O = 3,12,973 tonnes CO₂eq.

Trading value of CER = €0.26 / CER³ (Assuming trading value to remain constant)

Revenue Earned per year = €81,373 = **INR 63.48 Lakhs / year**

Hence, Revenue earned during Crediting Period = **INR 6.348 Crores**

Hence, the revenue earned from CER trading, will help us recover the fixed capital investment required for setting up the abatement unit.

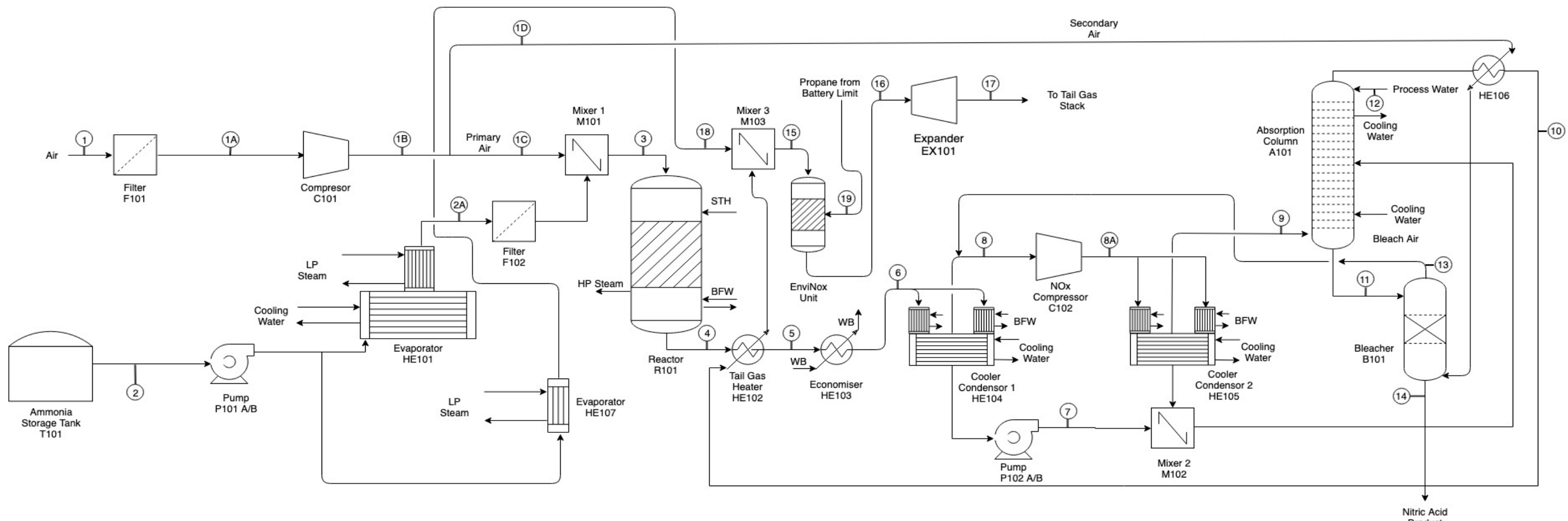
Payback Period = **6 years**

³<https://www.moneycontrol.com/commodity/cer-price.html>

Appendix A

Final Process Flow Diagram

The Final Process Flow Diagram with the Stream Table is shown below. The collective image was taken using Google Spreadsheets. The PFD was made using draw.io.



Line No	1	1C	1D	2	2A	3	4	5	6	7	8	8A	9	10	11	12	13	14	15	16	17	18	19
Stream Comp.	Air feed	Primary Air	Secondary Air	Ammonia Feed	Evaporated NH3	Reactor Inlet	Reactor Outlet	HE102 Outlet	HE103 Outlet	Acid Condensate	NOx Comp. inlet	NOx Comp. Outlet	Absorption Inlet	Tail Gas	Absorption Outlet	Process Water	Bleaching Air	Nitric Acid Pdt	Mixed Tail Gas	Reduced Tail Gas	Tail Gas Out	Reducing Ammonia	Propane
Phase	g	g	g	l	g	g	g	g	g	l	g	g	g	g	l	l	g	l	g	g	g	g	g
NH3	0.00	0.00	0.00	11003.30	10963.30	10963.30	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	40.00	0.00	0.00	40.48	0.00
O2	43518.85	39004.55	4514.30	0.00	0.00	39004.55	13569.84	12125.47	9855.66	0.00	8590.66	8590.66	7042.89	3306.59	0.00	0.00	4514.30	0.00	3306.59	3291.59	3291.59	0.00	0.00
N2	145541.03	128386.69	17154.34	0.00	0.00	128386.69	128657.55	128657.84	128657.84	0.00	145812.18	145812.18	145812.18	145812.18	0.00	0.00	17154.34	0.00	145812.18	145966.09	145966.09	0.00	0.00
H2O	0.00	0.00	0.00	0.00	0.00	0.00	17412.30	17412.30	17412.30	16019.32	0.00	0.00	0.00	0.00	23815.84	11986.72	0.00	23815.84	0.00	87.18	87.18	0.00	0.00
N2O	0.00	0.00	0.00	0.00	0.00	0.00	141.88	141.88	141.88	0.00	141.88	141.88	141.88	141.88	0.00	0.00	0.00	0.00	141.88	2.13	2.13	0.00	0.00
NO2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	4153.16	10679.54	0.00	18932.46	18932.46	23382.28	17.75	2319.83	0.00	2319.83	0.00	17.75	0.54	0.54	0.00	0.00
NO	0.00	0.00	0.00	0.00	0.00	0.00	18573.12	15864.54	11608.20	0.00	3095.52	3095.52	193.47	58.05	0.00	0.00	0.00	0.00	58.05	1.74	1.74	0.00	0.00
HNO3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	9750.89	0.00	0.00	0.00	0.00	38857.50	0.00	0.00	38857.50	0.00	0.00	0.00	0.00	0.00
CO2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	41.96	41.96	0.00	0.00
C3H8	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	15.00
Total	189059.88	167391.24	21668.64	11003.30	10963.30	178354.54	178354.69	178355.18	178355.42	25770.20	176572.69	176572.69	176572.69	149336.44	64993.17	11986.72	23988.47	62673.34	149376.44	149391.23	149391.23	40.48	15.00
Pressure (bar)	1.00	5.00	5.00	1.00	5.00	5.00	5.00	5.00	5.00	12.00	5.00	12.00	12.00	12.00	12.00	12.00	5.00	5.00	12.00	12.00	1.00	12.00	12.00
Temperature (C)	35.00	240.00	240.00	-33.00	70.00	230.00	427.00	300.00	185.00	50.00	50.00	260.00	50.00	130.00	50.00	10.00	80.00	50.00	350.00	350.00	35.00	350.00	350.00

Appendix B

MATLAB Code for the Mathematical Model for NO_x Absorption

AbsorptionColumn.m File

```
1 clear all;
2 clc;
3 X1 = fsolve(@myfunc, 0.5);
4 Gno2 = fsolve(@myfunc3, 0.5)*1.487391841/12;
5 F = fsolve(@myfunc2, 0.5);
6 %Gno2 = fsolve(@myfunc3, 0.5)*1.587702888/12;
7 % [p1, p2, p3] = myfunc4();
8 % p = [p1, p2, p3];
9 % roots(p)*1.552573202/12
```

Solving Step - 1

```
1 function [ y ] = myfunc( x )
2
3     Vw = 176576.4/3600;
4     G = 1.614361111;
5     b = 0.06158333333/G; % O2 molfrac
6     a = 0.0018055555556/(2*G); % NO molfrac
7
8     T = 283;
9     P = 12;
10    rhov = P*100*(Vw/G)/(8.314*T);
11    k1 = (10^((635/T) - 1.0261))/(8.206*T*10^-3);
```

```

12 %    k1 = exp((530/T) + 7.78)
13    ar = pi*(4^2)/4;
14    vel = Vw/(rhov*ar);
15    t = 1.5/vel;
16
17    y = ((x*(b-a)/(b*(1-x))) - log(1-x-(a*x/k1)))/((b-a)^2) - k1*t*P*P;
18
19 end

```

Solving Step - 3

```

1 function [ y ] = myfunc2( f )
2
3    X = 0.7804;
4    P = 12;
5    T = 307.68;
6
7    V = 152108.312/3600;
8    Gno = 0.00001418700968;
9    Gno2 = 0.0041;
10   Gn2o4 = 0.006510581495;
11   Gnox = Gno2 + Gn2o4;
12   G = 1.487318477;
13   Ghno3 = 0.00028495318;
14   Gh2o = 0.1785554731;
15
16   Pno = P*Gno/G;
17   Pno2 = P*Gno2/G;
18   Pn2o4 = P*Gn2o4/G;
19   Pnox = Pno2 + Pn2o4;
20
21   A = 10^(8.756 - (2838/T));
22   B = (T/210.3) + (790/T) - (3.8794);
23   k2 = A*(1-B*Pnox);
24   w = (Ghno3*63)/(Ghno3*63 + Gh2o*18);
25   rho1 = (Ghno3*63 + Gh2o*18)/((Ghno3*63/1513) + (Gh2o*18/1000));
26   nHNO3 = (Ghno3*63)/((Ghno3*63 + Gh2o*18)*10/rho1);
27   k4 = 10^(7.412 - 20.28921*w + 32.47322*w*w - 30.87*w*w*w);
28   k3 = k4/k2;
29   function [f] = myfunc5(x)
30       f = 3*k3*x*x*x + (2*x*x/k2) + x - 3*Pno - Pnox;
31   end
32   E = fsolve(@myfunc5, 0.5);
33   rhov = P*100*(V/G)/(8.314*T);
34   H = 0.04;
35   nNONOx = (Gno*30 + Gno2*46 + Gn2o4*92)/(10*V/(rhov));
36   R = (Pno + Pnox)/P;
37   if R < 0.01

```

```

38     A = 10.86 - 1.65*(R^970000) + 37.59*exp(-28.8*R);
39     else
40         A = 8.73;
41     end
42     ar = pi*(4^2)/4;
43     vel = V/(rhov*ar);
44     Dh = 0.003;
45     s = 0.9;
46     C = (A*(P^0.15)*(nNON0x^0.1)*(X^0.4)*(H^0.15)*((nHNO3)^0.1))/((vel^0.26)*(Dh
    ^0.15)*(T^0.87)*(s^0.13));
47     y = ((Pno + Pnox - ((k3*E*E*E + 2*E*E)/(k2 + E)))*(Gno + Gnox)*C/(Pno + Pnox)
    ) - f;
48
49 end

```

Solving Step - 2 and 4

```

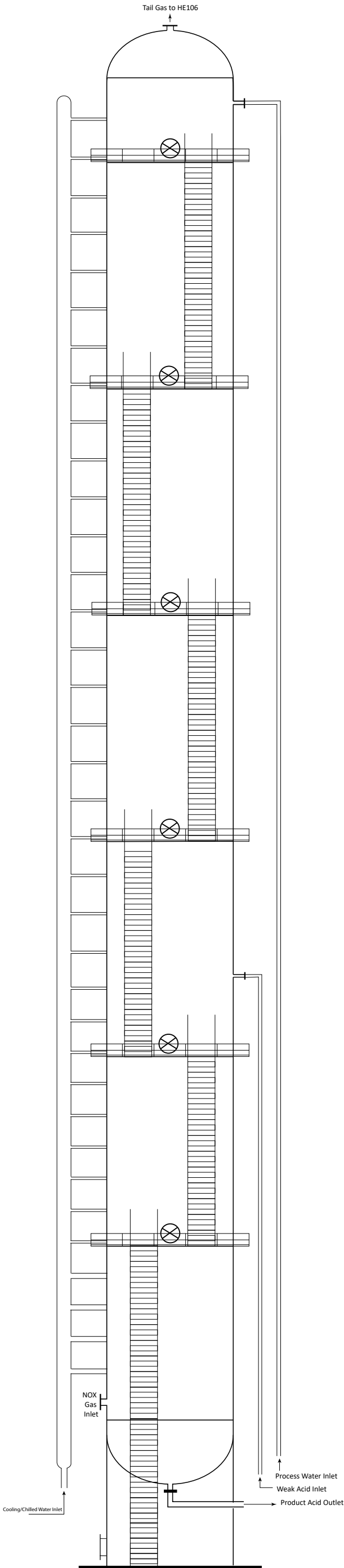
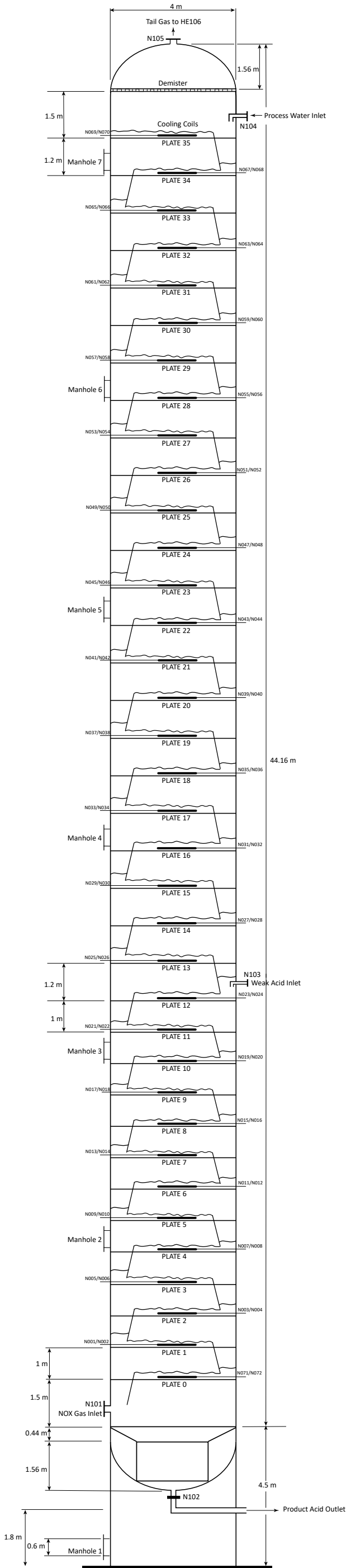
1 function [ y ] = myfunc3( x )
2
3     T = 280;
4     A = 10^(8.756 - (2838/T));
5     B = (T/210.3) + (790/T) - (3.8794);
6
7     Gno2 = 0.004150791582;
8     Gn2o4 = 0.006550149653;
9     G = 1.487441445;
10
11     u = (Gno2 + Gn2o4)/G;
12     P = 12;
13
14     %y = (((((Gno2-2*x)^2) * P)/((Gn2o4+x) * (G-x))) - A*(1 - B*((Gno2 + Gn2o4 - x
    )*P/(G - x)))));
15     y = x*x*(((2-u)^2) + A*B*u) + x*(A*(2-u) - A*B*P*u*(2-u)) + (A*P*u*(2*B*P*u -
    (2-u)));
16
17 end

```

Appendix C

Detailed Drawing of Absorption Column

The detailed drawing for the Absorption Column was made using Adobe Illustrator.
The detailed calculations to arrive at the dimensions have been shown in Chapter 11.



Material of Construction

For the column : SS304L (Nitric Acid Grade)
For the skirt : CS

Operating Parameters

Operating Pressure - 11 barg
Operating Temperature - 283-323 K
Weak Acid Feed (Plate 12) - 25770 kg/hr
Process Water Feed (Plate 35) - 11580 kg/hr
NO Gas feed (Column Bottom) - 176577 kg/hr

Design Parameters

Design Pressure - 12.1 barg
Design Temperature - 338 K
Weld Joint Efficiency - 90%
Shell Thickness - 18.3 mm
Head Thickness - 18.3 mm
Skirt Thickness - 3.8 mm

Nozzle Details

- Cooling Coils
- 1) N001-N024, N071-N072 - Cooling Water Cooled coils
- Diameter : 2-4 inches
 - 2) N025-N070 - Chilled Water Cooled coils
- Diameter : 2 inches

- Main Process Streams
- 3) N101 - NO Gas Inlet
- Diameter : 8 inches
 - 4) N102 - Product acid outlet
- Diameter : 6 inches
 - 5) N103 - Weak Acid Inlet
- Diameter : 4 inches
 - 6) N104 - Process Water Inlet
- Diameter : 4 inches
 - 7) N105 - Tail Gas Outlet
- Diameter : 8 inches

- Manholes
- 8) Manhole 1-Manhole 7 - Diameter: 0.6 m

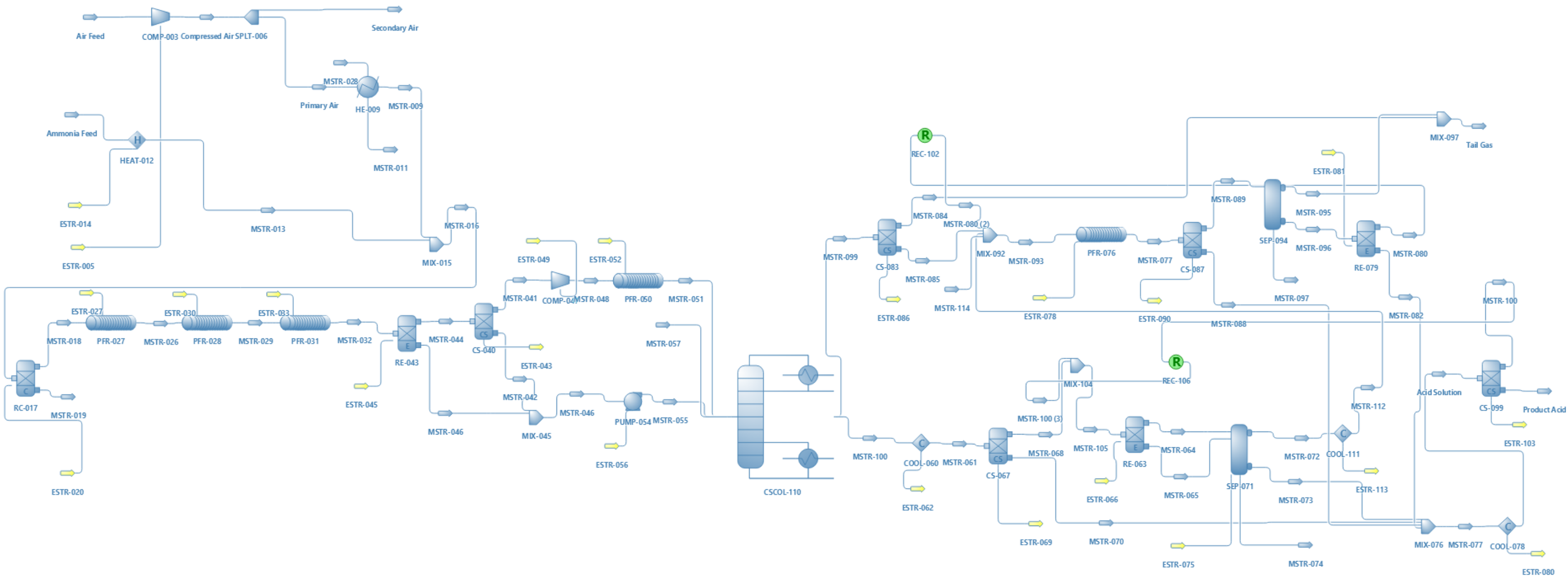
Design Notes

- 1) Distance between the plates : Plate 0 to Plate 12 - 1 m
Plate 12 to Plate 35 - 1.2 m
- 2) Fillet weld joining column cylinder to ellipsoidal heads
- 3) Stainless Steel plate is used to join the skirt and the column
- 4) Exact representation of manhole and pipe positions is as in figure 2
- 5) For figure 1, cooling coils are not diametrically opposite for consecutive trays, they are represented as such for ease of viewing.

Appendix D

DWSIM Flowsheet

The Process Flowsheet was developed using DWSIM simulations software. It is an Free and Open Source software. More info on DWSIM can be found [here](#)



References

- [1] Thyssenkrupp Industrial Solutions Nitric Acid Process Handbook -
https://d13qmi8c46i38w.cloudfront.net/media/UCPthyssenkruppBAIS/assets.files/products__services/fertilizer_plants/nitrate_plants/brochure-nitric-acid_scr.pdf
- [2] Global Nitric Acid Market By Plant Type, By Sales Channel, By Application, By Region, Competition Forecast and Opportunities, 2011-2025, Research and Markets Nitric Acid Sample Market Report -
https://www.researchandmarkets.com/research/qsn6h4/global_nitric
- [3] Nitric Acid Market Size, Share & Trends Analysis Report By Application (Fertilizers, Adipic Acid, Nitrobenzene, Toulene di-isocynate, Nitrochlorobenzene), By Region, Vendor Landscape, And Segment Forecasts, 2012-2022, Grand View Research Nitric Acid Sample Market Report -
www.grandviewresearch.com/industry-analysis/nitric-acid-market
- [4] Nitric Acid IHS Chemical Economics Handbook -
www.ihsmarket.com/products/nitric-acid-chemical-economics-handbook.html
- [5] Jacob A. Moulijn, Michiel Makkee, Annelies E. Van Diepen, *Chemical Process Technology*, p.260-267, 2nd ed., 2013, John Wiley & Sons Ltd., Great Britain
- [6] Thiemann M, Scheibler E, Wiegand KW, *Nitric acid, nitrous acid, and nitrogen oxides*, *Ullmann's Encyclopedia of Industrial Chemistry*, Vol. 23, Wiley-VCH Verlag GmbH & Co. KGaA, 2003. doi:10.1002/14356007.a17_293
- [7] Deepak Fertilisers and Petrochemicals Corporation Ltd., MIDC Road, Talaja, Navi Mumbai, Maharashtra - 410208, India

- [8] Martyn S. Ray (Curtin University of Technology, Western Australia), David W. Johnston (Shell Refining(Australia) Pvt. Ltd.), *Chemical Engineering Design Project: A Case Study Approach*, **Topics in Chemical Engineering**, ISSN: 0277-5883, Vol. 6, Gordon and Breach Science Publishers, 1989, United Kingdom
http://inspect.nigc.ir/Portal/Images/Images_Training/files/files/chemist%20book/Chemical%20Engineering%20Design%20Project%20-%20A%20Case%20Study%20Approach.PDF
- [9] Hirokazu Tsukahara, Takanobu Ishida, Mitsufumi Mayumi, *Gas-Phase Oxidation of Nitric Oxide: Chemical Kinetics and Rate Constant*, **Nitric Oxide**, Vol. 3 - Issue 3, Elsevier, 1999, Japan. doi:10.1006/niox.1999.0232
- [10] Max S. Peters, Klaus D. Timmerhaus, **Plant Design And Economics For Chemical Engineers**, 4th ed., ISBN - 0-07-100871-3, McGraw Hill Inc., International Edition, 1991, United States
- [11] Stanley M. Walas, **Chemical Process Equipment Selection and Design**, Butterworth - Heinemann Series in Chemical Engineering, ISBN - 0-7506-9385-1, Butterworth - Heinemann, Reed Publishing, 1990, United States
- [12] The Chemical Engineering Cost Index, Chemical Engineering Online - <https://www.chemengonline.com/pci>
- [13] Mr. Amrish Dholakia, Engineering Manager & General Manager-Process, Uhde House, Thyssenkrupp Industrial Solutions (formerly Uhde India), Vikhroli, Mumbai - 400083
- [14] Gold Price India Website - <https://www.goldpriceindia.com>
- [15] Infomine - <http://www.infomine.com/investment/metal-prices/rhodium/>
- [16] CL 407 - Process Equipment Design, Handouts and Reading Material by Prof. Arun S. Moharir, Prof. Yogendra Shastri, Indian Institute of Technology Bombay, Mumbai - 400076
- [17] United Nations Industrial Development Organisation (UNIDO), International Fertiliser Development Centre (IFDC), **Fertilizer Manual**, ISBN - 0-7923-5032-4, Kluwer Academic Publishers, 1998, Netherlands

- [18] R.K. Sinnott, J.M. Coulson, J.F. Richardson, *Chemical Engineering Design, Chemical Engineering*, p.564-586, Vol. 6 3rd ed., ISBN - 0-7506-4142-8, Butterworth - Heinemann, 1999, Great Britain
- [19] G.S.R. 1607(E), Ministry of Environment, Forest and Climate Change, Central Government of India, 29th December 2017
<https://drive.google.com/open?id=1xkQjup6FQcv8fdppsAhLQLrq0oE6upVp>
- [20] Groves, M.C.E., Sasonow, A., Hydrogen and Nitrates Division, Uhde GmbH, *Uhde EnviNO_X[®] technology for NO_X and N₂O abatement: a contribution to reducing emissions from nitric acid plants*, ***Journal of Integrative Environmental Sciences***, 7(sup1), p.211222, 2010, doi:10.1080/19438151003621334
- [21] AM0028: N₂O destruction in the tail gas of Caprolactam production plants - Ver. 06.0, United Nations Framework Convention on Climate Change
https://cdm.unfccc.int/filestorage/b/g/IV326LBA5XCTF04RUQ7MWDKG8SPNZ1.pdf/EB73_repan05_AM0028_ver06.0.pdf?t=a2d8cHBxcm1ifDCgYNMsIPmIXChVn94xNxCI