

INDIAN INSTITUTE OF TECHNOLOGY TIRUPATI

APE-I FINAL REPORT

भारतीय प्रौद्योगिकी संस्थान तिरुपति



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[2] Smith A.R. (2001), “A review of air separation technologies and their integration with energy conversion processes,” Fuel Processing Technology 70 (2001) 115–134	25
[3] National Institute of Standards and Technology NIST	25
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Abstract

Ammonia production is a critical industrial challenge, accounting for 1–3% of global energy usage and nearly 3% of global greenhouse gas emissions due to the energy-intensive nature of the Haber–Bosch process. Given that 85% of ammonia is utilized in fertilizers and its high toxicity complicates transport, localized production has become a vital strategic objective. This study explores the conceptual design of a 50 metric-ton/day plant capable of producing 99.5% purity commercial-grade anhydrous ammonia based on established Linde process guidelines. The design utilizes on-site nitrogen generation via air separation and hydrogen production through steam methane reforming (SMR) of natural gas, followed by water–gas shift conversion and purification to eliminate CO₂ and trace by-products. By integrating material-balance calculations, energy-requirement estimations, and detailed process flow charts, this work provides a comprehensive framework for plant design while explicitly addressing the underlying calculation methods, assumptions, and limitations.

1. Introduction

1.1 Background and Motivation

Ammonia is one of the most widely produced industrial chemicals, primarily due to its central role in fertilizers. Global ammonia production contributes significantly to resource consumption, accounting for 1–3% of world energy use, 5% of natural gas consumption, and nearly 3% of global greenhouse gas emissions. The dominant manufacturing route, the Haber–Bosch process, has historically depended on inexpensive natural gas and remains energy-intensive despite technological advancements.

Beyond its industrial relevance, ammonia is hazardous and toxic at ambient conditions, resulting in high transportation costs, strict regulations, and elevated insurance burdens. Consequently, decentralized or smaller-scale ammonia production facilities can reduce logistics risks and improve accessibility in regions where transport is unsafe or costly.

1.2 Problem Statement

The goal of this project is to design a 50 metric-ton/day ammonia production plant capable of supplying commercial-grade anhydrous ammonia ($\approx 99.5\%$ purity). The design must incorporate safe, reliable, and efficient production of nitrogen and hydrogen feedstocks on-site and achieve the required throughput while minimizing impurities.

1.3 Process Overview

Ammonia synthesis follows the established Haber–Bosch process, and this study takes guidance from Linde’s ammonia process, known for its industrial reliability. Key process blocks include:

- Feed purification: Removal of sulfur compounds (e.g., H_2S) from natural gas
- Hydrogen generation: Steam methane reforming (SMR) followed by water–gas shift
- CO_2 removal and gas cleanup
- Nitrogen production: Using cryogenic distillation, membrane separation, or PSA depending on scale
- Ammonia synthesis loop with recycle and condensation

1.4 Schematic Flow charts

1.4.1 Hydrogen

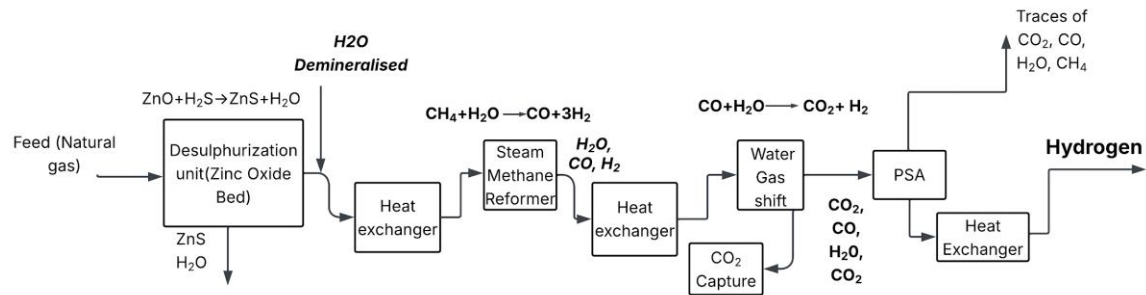


Fig. 1.1. Hydrogen Production Schematic Flow Chart

1.4.2 Nitrogen

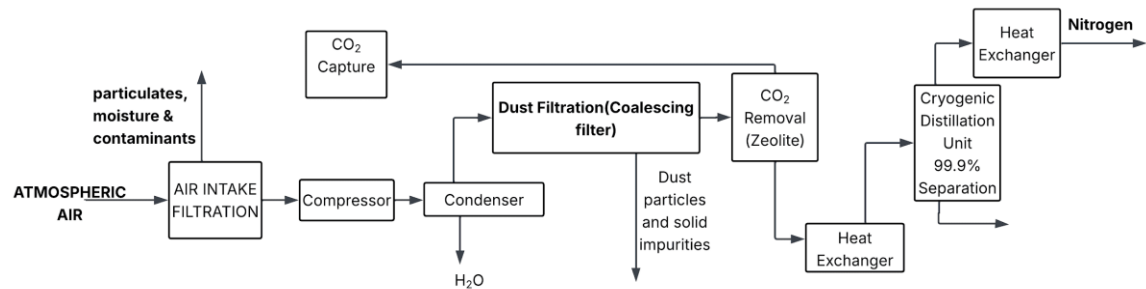


Fig. 1.2. Nitrogen Production Schematic Flow Chart

1.4.3 Ammonia

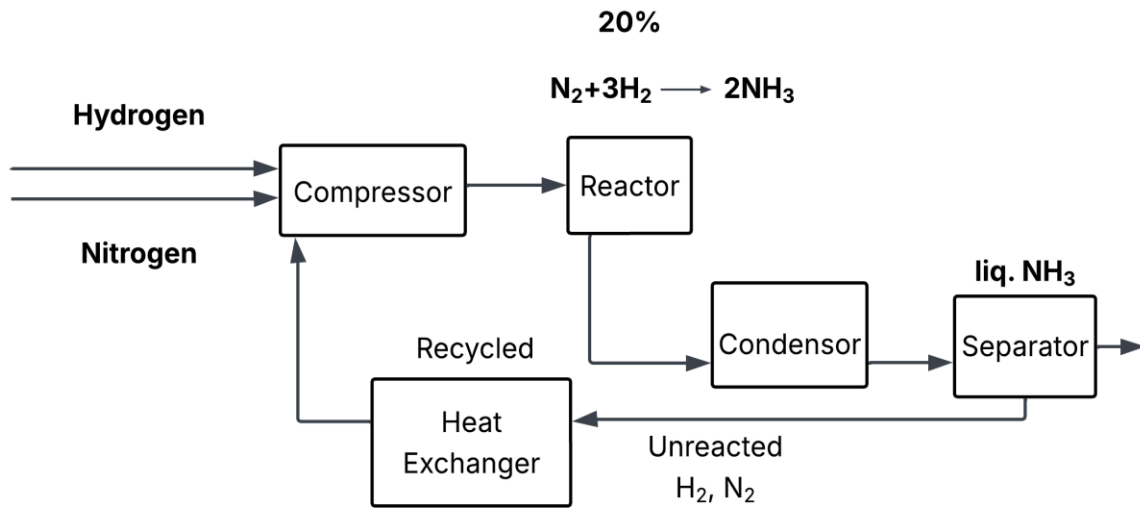


Fig. 1.3. Ammonia (Haber Bosch) Synthesis Schematic Flow Chart

1.5 Scope

This study includes:

- Material-balance calculations for all major units
- Energy-requirement estimation for SMR, air separation, and synthesis.
- Detailed process flow charts with pressures and temperatures at critical locations.
- Integration of nitrogen and hydrogen production into the overall process.

1.6 Discussion

1.6.1 Why Linde's ASU is chosen

1. LAC is a modern modular ammonia production route (Haber-Bosch with optimized front-end).
2. High Purity & Flexibility
3. Scalability
4. PSA (Pressure Swing Adsorption) and membranes are more economical for small plants.

But for medium - mega scale, cryogenic (especially Linde's) wins both economically and technically.

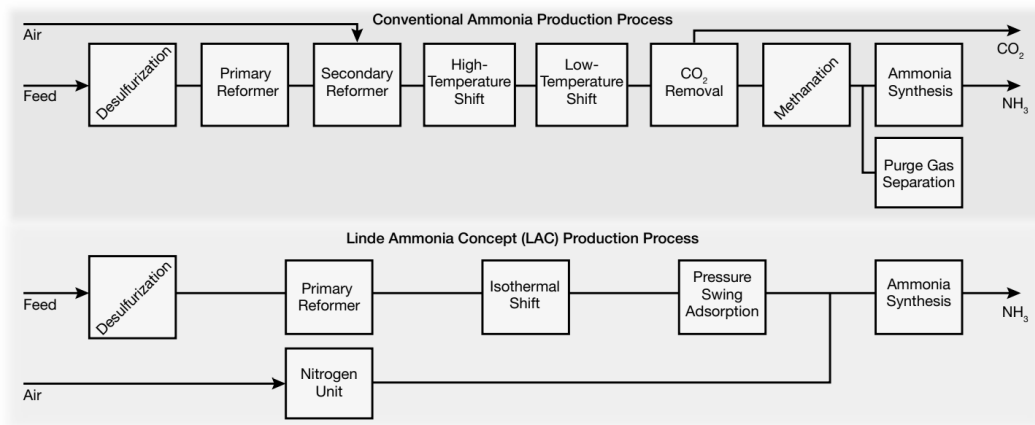


Fig. 1.4 Comparison of LAC and conventional Ammonia Production Processes [\[5.4\]](#)

1.6.2 Justification for Cryogenic Separation

Table 1.1. Technology comparison table ^[5.3]

Process	Status	Economic Range (sTPD)	Byproduct capability	Purity Limit (vol.%)	Start-up time
Adsorption	semi-mature	<150	poor	95	minutes
Chemical	developing	undetermined	poor	99+	hours
Cryogenic	mature	>20	excellent	99+	hours
Membrane	semi-mature	<20	poor	40	minutes
ITM	developing	undetermined	poor	99+	hours

Since cryogenic separation is a mature technology with high purity we chose it for separation of nitrogen from air.

1.6.3 Rationale for Continued Use of Natural Gas

- Natural gas is used because technology is already mature and widely available.
- Green hydrogen is not fully commercial yet due to limited electrolyzer capacity and renewable power
- Carbon capture allows continued natural-gas use while reducing emissions.

2. Methods and Theory

2.1 Assumptions and Analysis

1. Enthalpy Calculations

Enthalpy changes for all reactions and streams are calculated using the expression ^[4]:

$$Cp^{ig}/R = A + BT + CT^2 + D/T^2 \quad \dots (1)$$

These values are assumed to operate at higher pressures (such as 125 bar) as well.

2. Compressor Work

The work required for compression is calculated using standard thermodynamic relations, with the following isentropic efficiencies:

- PSA Compressor: 75%
- ASU Compressor: 78%
- Haber–Bosch Feed Compressor: 75%

$$w = \gamma/(\gamma - 1) RT_1 [(P_2/P_1)^{((\gamma-1)/\gamma)} - 1] \quad \dots (2)$$

$$w_{Actual} = w/\eta_{isentropic} \quad \dots (3)$$

$$W_{comp} = w_{Actual} \cdot \dot{m} \text{ (kJ/s = kW)} \quad \dots (4)$$

$$W_{comp_day} = W_{comp} \cdot 86400$$

3. Reactor Assumptions

- Haber–Bosch Reactor: Assumed to have a 20% single-pass conversion of reactants.

- Steam Methane Reformation (SMR) and Water Gas Shift (WGS): Assumed to achieve 100% single-pass conversion.

4. Separator Assumptions

Separators of nitrogen and hydrogen from liquid ammonia are assumed to have 95% efficiency, cryogenic unit for nitrogen & oxygen separation is assumed to have 99.9% efficiency.

5. Cooling duties

Heat removed from systems by cooling is re-used to heat other parts of the system.

2.2 Hydrogen

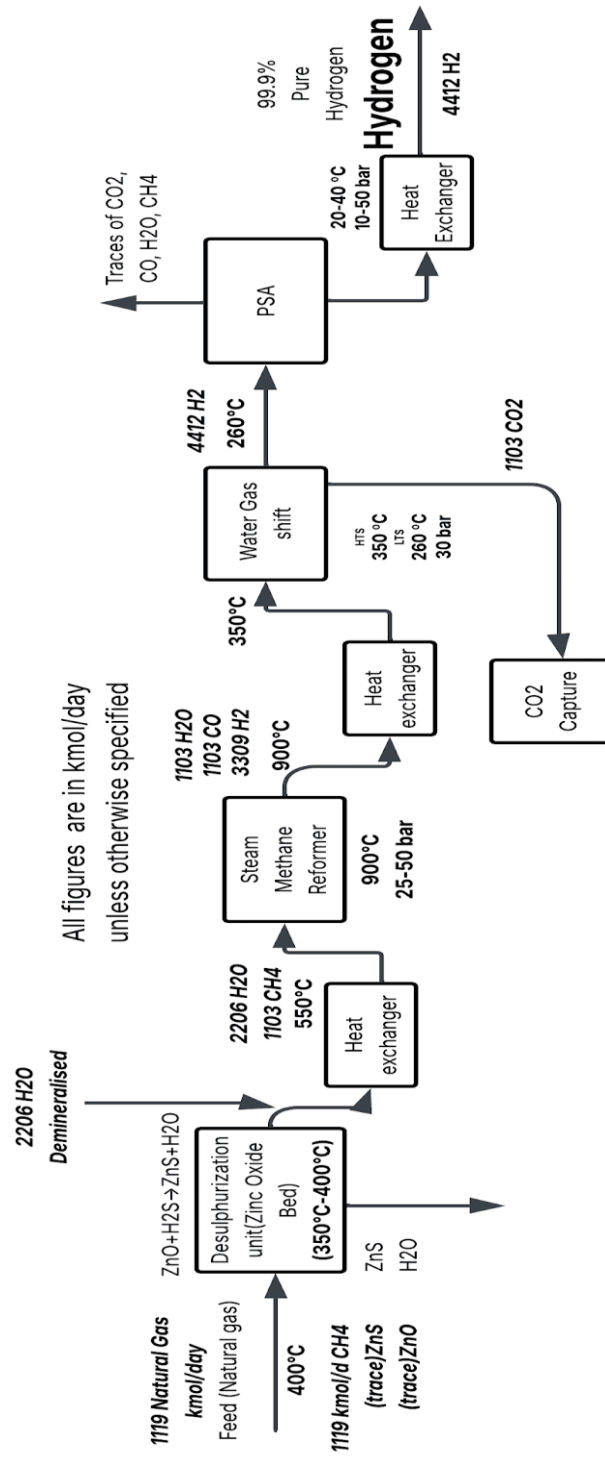


Figure 2.1. Hydrogen Production Material Balance

2.2.1 Material Balance

As illustrated in the Fig. 2.1, Natural gas at a flow rate of 1119 kmol/day is first subjected to desulfurization in a ZnO bed operating at 350–400 °C to remove H₂S and trace ZnS. The purified gas is then mixed with steam at 2206 kmol/day, preheated, and introduced into the Steam Methane Reformer (SMR) at 550 °C and 25–50 bar, where methane reacts with steam to form synthesis gas according to the reaction $\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2$. The resulting syngas is subsequently processed through high-temperature shift (HTS) reactors at 350 °C and low-temperature shift (LTS) reactors at 260 °C, converting carbon monoxide into carbon dioxide while generating additional hydrogen. Following the water–gas shift reactions, carbon dioxide is separated from the gas stream. The remaining gas is then purified using Pressure Swing Adsorption (PSA) operating at 20–40 °C and 10–50 bar, which removes residual CO₂, CO, H₂O, and CH₄. This final purification stage produces hydrogen at a rate of **4412 kmol/day with a purity of 99.9%**.

2.2.2 Energy Balance

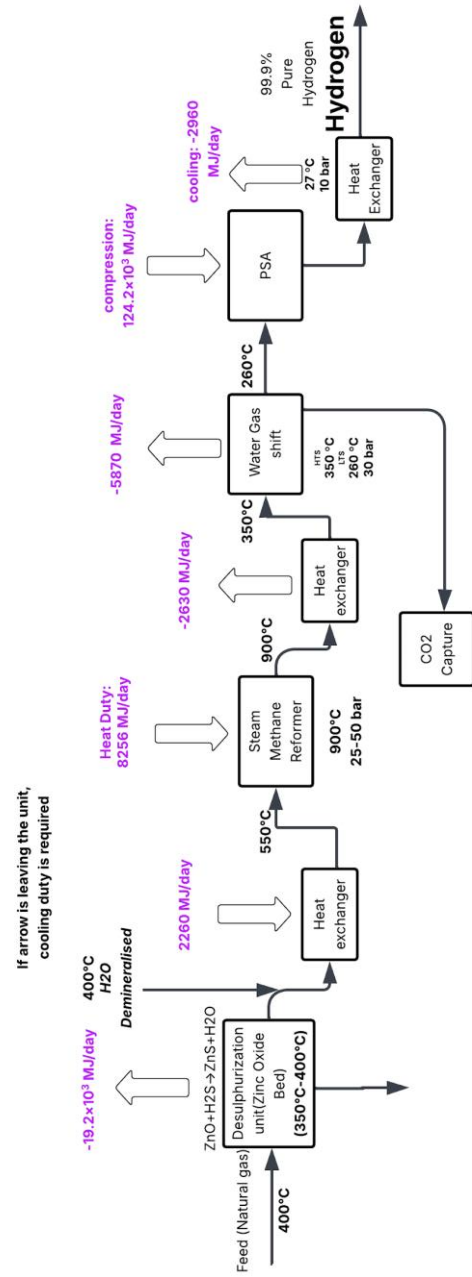
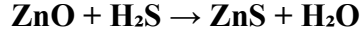


Figure 2.2. Hydrogen Production Energy Balance

With reference to the Fig.2.2, The desulfurization stage employs a ZnO bed in which hydrogen sulfide is removed according to the reaction:



The reaction enthalpy at approximately 400 °C is calculated using:

$$\Delta H_{\text{rxn}}(T) = \Delta H_{298} + \int \Delta C_p(T') dT' \quad \dots(5)$$

The enthalpy change for desulfurization is $\Delta H_{\text{des}} \approx -116.21$ kJ/mol, resulting in a heat release of 1859.35 MJ/day.

In the feed preheating stage, water (2206 kmol/day) and methane (1103 kmol/day) are heated from 400 °C to 900 °C. The enthalpy change for each component is determined from:

$$\Delta h_i = \int C_{p,i}(T) dT \quad \dots(6)$$

The total heat required is calculated as:

$$Q_{\text{preheat}} = \sum \dot{n}_i \Delta h_i \quad \dots(7)$$

This yields a total heat input of 22602.75 MJ/day.

The reformer effluent is cooled from 900 °C to 350 °C, allowing recovery of 26274.94 MJ/day of heat. In the water–gas shift (WGS) section, the exothermic reaction releases 58724.25 MJ/day.

The Pressure Swing Adsorption (PSA) unit requires compression from 1 bar to 20 bar with an efficiency of 0.75, corresponding to a compression work of 124606 MJ/day. Finally, the heat exchanger provides cooling from 260 °C to 27 °C, with a total cooling duty of 29606.28 MJ/day.

2.3 Nitrogen

2.3.1 Material Balance

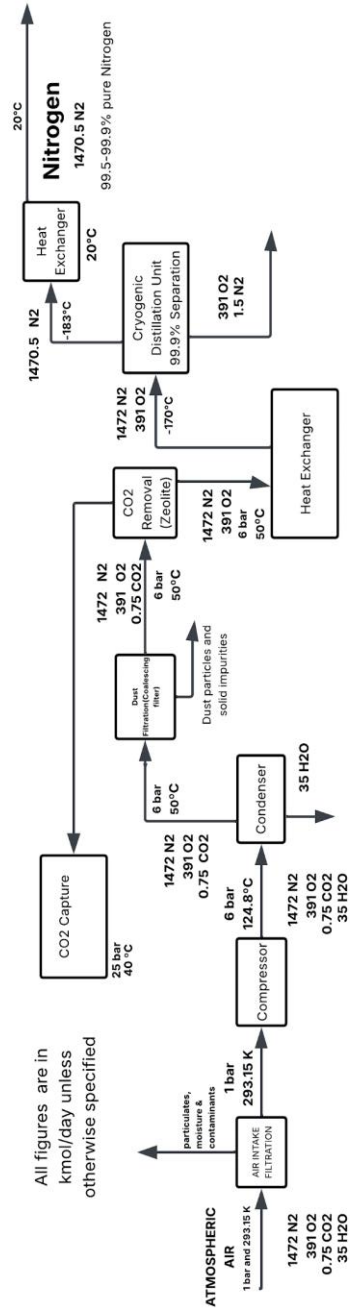


Fig. 2.3. Nitrogen Production Material Balance

As illustrated in detail in Fig. 2.3., atmospheric air consisting of nitrogen, oxygen, and trace amounts of carbon dioxide and water vapor enters the system at 1 bar and 293.15 K. The air first passes through filtration units that remove particulates, moisture, and contaminants. It is then compressed to 6 bar, causing the temperature to rise to approximately 125 °C. The compressed air is subsequently cooled to 50 °C in a condenser, where water vapor condenses and is removed. Further purification is achieved using a coalescing filter to eliminate residual dust and solid impurities. Carbon dioxide is then removed by adsorption in a zeolite bed, producing a cleaned air stream composed mainly of nitrogen and oxygen at 6 bar and 50 °C.

The purified air is cooled to approximately $-170\text{ }^{\circ}\text{C}$ in a heat exchanger for cryogenic preparation and is fed into a cryogenic distillation unit, where nitrogen and oxygen are separated to 99.9% purity. This unit produces a nitrogen-rich stream of 1470.5 kmol/day and an oxygen-rich stream of 391 kmol/day containing 1.5 kmol of nitrogen. The cold nitrogen product is passed through a heat exchanger and warmed to 20 °C, yielding a final nitrogen output of **1470.5 kmol/day at 20 °C**.

2.3.1 Energy Balance

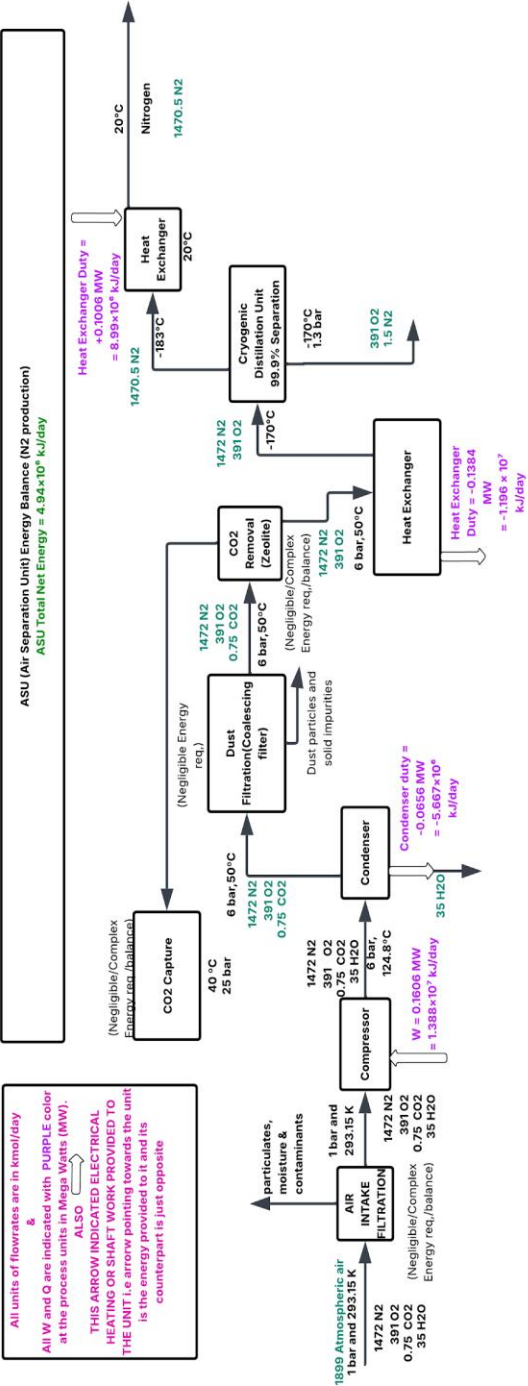


Fig. 2.4. Nitrogen Production Energy Balance

As illustrated in the Fig. 2.4., the air compression stage involves raising the pressure from 1.00 bar and 293.15 K to 6.00 bar under the assumption of isentropic compression with an efficiency of 0.78. For an ideal diatomic gas with $\gamma = 1.4$, the compressor work is calculated using:

$$W = (\gamma / (\gamma - 1)) \cdot R \cdot T_1 \cdot [(P_2 / P_1)^{(\gamma - 1)/\gamma} - 1] \quad (\text{From Eq. 2})$$

For a feed flow rate of 21.99 mol/s (1899.05 kmol/day), the required power input is 0.1606 MW, corresponding to 13,875,840 kJ/day. In the condenser, both sensible and latent heat are removed. The sensible heat is calculated as:

$$Q_s = n C_p \Delta T = 21.99 \text{ mol/s} \times 29.24 \text{ J/mol} \cdot \text{K} \times 74.85 \text{ K} \approx 48.1 \text{ kW}$$

The latent heat for water condensation is: $Q_l = n \Delta H_{\text{vap}} = 0.4087 \text{ mol/s} \times 42,900 \text{ J/mol} \approx 17.5 \text{ kW}$

Thus, the total condenser duty is:

$$Q_t = Q_s + Q_l \approx 65.6 \text{ kW} = -0.0656 \text{ MW} = -5,667,840 \text{ kJ/day}$$

The negative sign indicates heat rejection.

After condensation and CO₂ removal, the cleaned gas stream (N₂ + O₂) is cooled in the main heat exchanger from 50 °C to -170 °C before entering the cryogenic distillation unit. The total flow rate is 1863.05 kmol/day (21.56 mol/s), with molar fractions of 0.7902 for N₂ and 0.2098 for O₂.

Using weighted averaging, the mixture heat capacity is:

$$C_{p, \text{mix}} = 0.7902(29.12) + 0.2098(29.36) \approx 29.16 \text{ J/mol} \cdot \text{K}$$

(Note: Used Cp values taken at ~300 K) $C_{p, \text{N}_2} = 29.12 \text{ J/mol} \cdot \text{K}$ $C_{p, \text{O}_2} = 29.36 \text{ J/mol} \cdot \text{K}$ [\[3\]](#)

With a temperature change of $\Delta T = 220 \text{ K}$, the sensible heat per mole is:

$$\Delta h = C_{p, \text{ mix}} \Delta T = 29.16 \times 220 \approx 6415.2 \text{ J/mol}$$

The exchanger duty is therefore:

$$Q = \dot{n} \Delta h = 21.56 \times 6415.2 \approx 138,380 \text{ W} \approx 0.1384 \text{ MW}$$

Using the adopted sign convention, this corresponds to:

$$Q = -11,957,760 \text{ kJ/day}$$

The cold nitrogen product is subsequently warmed from -183°C (90.15 K) to 20°C (293.15 K).

For a nitrogen flow rate of 1470.59 kmol/day (17.02 mol/s) and $C_p = 29.12 \text{ J/mol}\cdot\text{K}$, the heat duty is calculated as:

$$Q = \dot{n} C_p \Delta T = 17.02 \times 29.12 \times 203.0 \approx 100,600 \text{ W} = 0.1006 \text{ MW} = 8,691.84 \text{ MJ/day}$$

The energy requirement of the cryogenic distillation unit cannot be accurately estimated without detailed phase-equilibrium data, column design parameters, and refrigeration cycle performance.

Therefore, it is beyond the scope of this analysis.

The heat capacity values used are close approximations at relevant temperatures and were verified using MATLAB by integrating C_p with respect to temperature and comparing with standard enthalpy data. The detailed calculations are provided separately in the attached MATLAB script.

2.4 Ammonia

2.4.1 Material Balance

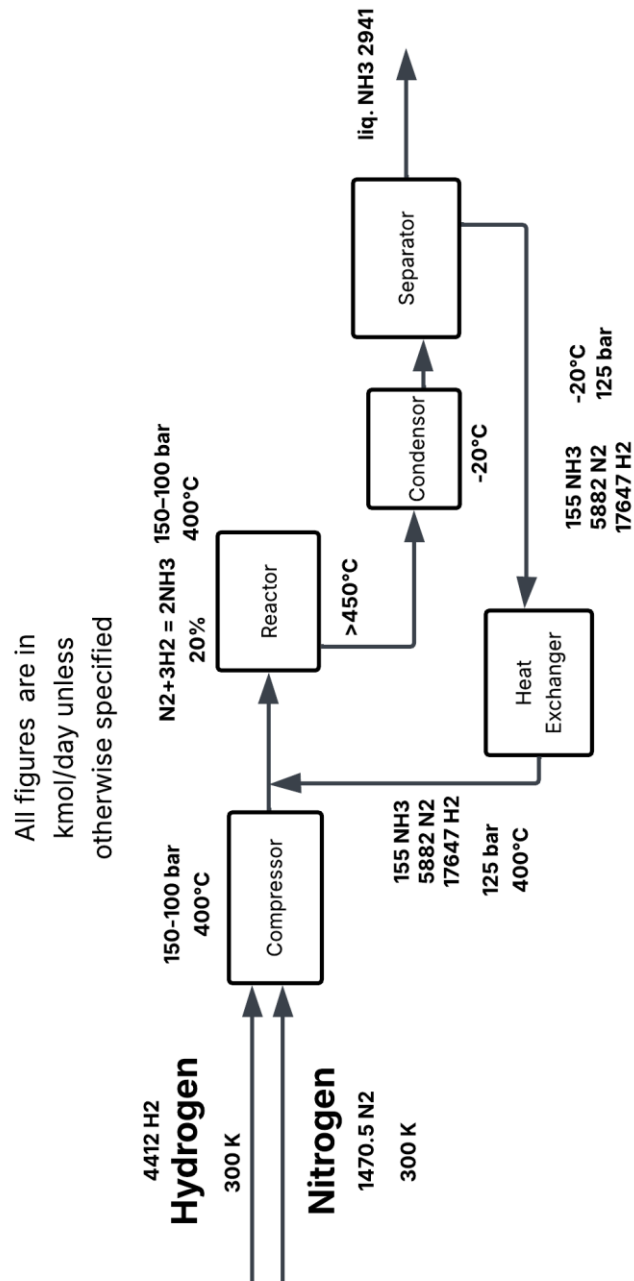


Fig. 2.5. Ammonia Synthesis Material Balance

As illustrated in the Fig. 2.4., Hydrogen and nitrogen are fed to the ammonia synthesis loop at flow rates of 4412 kmol/day and 1470.5 kmol/day, respectively, both at 300 K. The feed gases are compressed to a pressure range of 150–100 bar and heated to 400 °C before entering the reactor. Ammonia synthesis takes place according to the reaction $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$, with a single-pass conversion of 20% at 400 °C. The reactor effluent, leaving at temperatures above 450 °C, is cooled in a heat exchanger to recover heat.

After heat recovery, the gas mixture is further cooled to −20 °C to condense ammonia. The condensed liquid ammonia product is separated, yielding 2941 kmol/day. The remaining unreacted gases, consisting of 155 kmol/day NH_3 , 5882 kmol/day N_2 , and 17647 kmol/day H_2 , are recycled. This recycle stream, at −20 °C, is returned to the heat exchanger and compressor for recompression and reuse in the synthesis loop.

2.4.2 Energy Balance

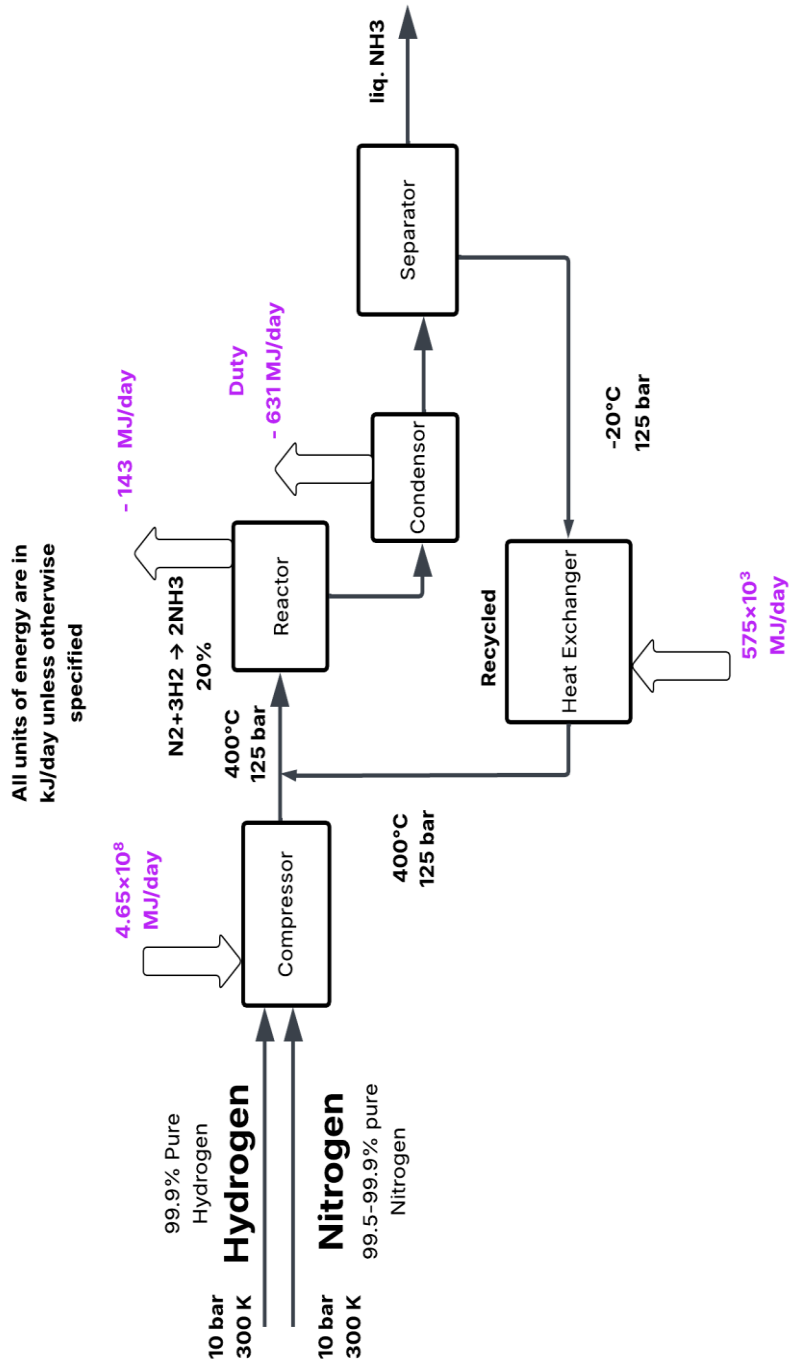


Fig. 2.6. Ammonia Synthesis Energy Balance

With reference to Fig. 2.4., in the ammonia synthesis loop, the recycle gas stream is heated in the heat exchanger from 253 K to 673 K. The energy required for this temperature rise is 5.75×10^5 MJ/day. The fresh feed stream is compressed and heated in the compressor section from 300 K to 673 K, while the pressure is increased from 10 bar to 125 bar. This process requires an energy input of 4.65×10^8 MJ/day.

Within the reactor, the ammonia synthesis reaction is exothermic, and therefore cooling is required to maintain the operating temperature. The reactor cooling duty is 143.03 MJ/day. After reaction, ammonia is condensed from the product mixture, and the condenser provides a cooling duty of 631.32 MJ/day.

3. Results and Discussion

3.1 Numerical Data

The process (formation of 50 tonnes of ammonia per day) requires **1899 kmol/day of air**, **1118.6 kmol/day of natural gas**, and **2206 kmol/day of demineralised water** as feedstocks. The energy demand associated with each major unit operation varies significantly: hydrogen production via the **Linde–Ammonia–Converter (LAC)** requires approximately **1.128×10^5 MJ/day**, while nitrogen production through the **air separation unit (ASU)** consumes about **4.94×10^3 MJ/day**. In comparison, the **Haber–Bosch ammonia synthesis loop** dominates the overall energy consumption, with a requirement of roughly **4.65×10^8 MJ/day**, making it the most energy-intensive step in the process.

Calculations for Material Balances are presented in an Excel spreadsheet along with this document.

Calculations for Energy Balances are presented in MATLAB codes along with this document.

4. Conclusions

Numerical Data

The process requires **1899 kmol/day of air**, **1118.6 kmol/day of natural gas**, and **2206 kmol/day of demineralised water** as feedstocks. The energy demand associated with each major unit operation varies significantly: hydrogen production via the **Linde–Ammonia–Converter (LAC)** requires approximately **1.128×10^5 MJ/day**, while nitrogen production through the **air separation unit (ASU)** consumes about **4.94×10^3 MJ/day**. In comparison, the **Haber–Bosch ammonia synthesis loop** dominates the overall energy consumption, with a requirement of roughly **4.65×10^8 MJ/day**, making it the most energy-intensive step in the process.

Major Limitations of this work

1. Cooling of units also requires power for which an exact expression has not been given.
2. Reactors are assumed to operate isothermally, which does not often reflect reality.
3. Thermodynamic data is sometimes not available and so ideal gas data has been used with reasonable assumptions.
4. Losses in energy due between units and pump work have not been considered. Only enthalpies and shaft works have been considered in this work.
5. Energy considerations for carbon capture (due to complexity), dust filtration (negligible) and air compression (different available methods) have not been included in this work.

5. References

[1] Pritchard D., Feroz S. (2021), “*Mass and Energy Balancing, Calculations for Plant Design*”
CRC Press, 2021

[2] Smith A.R. (2001), “*A review of air separation technologies and their integration with energy conversion processes,*” *Fuel Processing Technology* 70 (2001) 115–134

[3] Nitrogen (CAS 7727-37-9), NIST Chemistry WebBook, Standard Reference Database 69, <https://webbook.nist.gov/cgi/cbook.cgi?ID=C7727379>

Oxygen (CAS 7782-44-7), NIST Chemistry WebBook, Standard Reference Database 69, <https://webbook.nist.gov/cgi/cbook.cgi?ID=7782-44-7>

Carbon dioxide (CAS 124389), NIST Chemistry WebBook, Standard Reference Database 69, <https://webbook.nist.gov/cgi/cbook.cgi?ID=C124389>

Water (CAS 7727379), NIST Chemistry WebBook, Standard Reference Database 69, <https://webbook.nist.gov/cgi/cbook.cgi?ID=C7727379>

Engineering Toolbox — *Specific heat capacity of air* (quick Cp and γ values used for approximate arithmetic). Engineering ToolBox+1
https://www.engineeringtoolbox.com/air-specific-heat-capacity-d_705.html

[4] Smith, J. M., Van Ness, H. C., Abbott M. M., Swihart M. T. (2018), “*Introduction to Chemical Engineering Thermodynamics*” (8th ed.). McGraw-Hill. (Appendix C)

[5] Study Material

[5.1]

<https://www.aiche.org/sites/default/files/cep/20160969.pdf>

[5.2]

https://assets.linde.com/-/media/global/engineering/engineering/home/products-and-services/process-plants/h2_1_1_e_12_150dpi_nb.pdf

[5.3]

<https://netl.doe.gov/sites/default/files/2023-08/Smith%202001%20Review%20of%20Air%20Separation%20Technologies.pdf>

[5.4]

<https://ammoniaknowhow.com/short-history-of-ammonia-process-past-present-and-future/>

6. Supplementary Data

Excel_Calculations

<https://drive.google.com/drive/folders/1LAggonU3Xx5ZpJqTWR61d8BhU-DzegjA?usp=sharing>

MATLAB_Codes

<https://drive.google.com/drive/folders/1dMC6oGHWUpCiNAUoyi241IKgV9EPwbTo?usp=sharing>