

Politecnico di Torino

**Master's Degree in
Chemical and Sustainable Process Engineering**

Optimization of the Haber-Bosch process using membrane technologies

Towards more sustainable and efficient ammonia production



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List of Acronyms

ACM — Aspen Custom Modeler
Ar — Argon
CAPEX — Capital Expenditure
CCS — Carbon Capture and Storage
CH₄ — Methane
CMR — Catalytic Membrane Reactor
CO — Carbon Monoxide
CO₂ — Carbon Dioxide
EEA — European Environmental Agency
EJ — Exajoule
FAU — Faujasite
GHG — Greenhouse Gas
GPU — Gas Permeation Unit
HB — Haber–Bosch
HFCs — Hydrofluorocarbons
H₂ — Hydrogen
IEA — International Energy Agency
IL — Ionic Liquid
IMS — Immobilized Molten Salt
KAAP — Kellogg Advanced Ammonia Process
LTA — Linde Type A
MMMs — Mixed-Matrix Membranes
MOF — Metal–Organic Framework
N₂ — Nitrogen
N₂O — Nitrous Oxide
NH₃ — Ammonia
OPEX — Operating Expenditure
PDMS — Polydimethylsiloxane
PFCs — Perfluorocarbons
PFR — Plug Flow Reactor
SMR — Steam Methane Reforming
SF₆ — Sulfur Hexafluoride
TPS — 3-(Trihydroxysilyl)-1-propanesulfonic acid
ZIF — Zeolitic Imidazolate Framework

Introduction

Ammonia has become the basis of modern society, playing an important role not only in agriculture but also in the larger chemical and energy sectors. With its large production scale supports global food security, as nitrogen-based fertilizers that derive from ammonia and are responsible for sustaining a significant portion of the world's population [1], [2]. At the same time, ammonia is becoming recognized as a potential energy carrier thanks to its high hydrogen content and good storage and transport properties, making it a promising component that could be used in the future for low-carbon energy systems [1], [2].

Despite its importance, ammonia production is also associated to an important energy consumption and environmental impact. Currently industrial processes rely heavily on fossil-based feedstocks, in particular for hydrogen production, leading to significant greenhouse gas emissions. In fact, ammonia synthesis holds a significant part of global energy demand and CO₂ emissions, highlighting an urgent need of more sustainable production pathways [3].

In the last years, an increasing attention has been directed toward the decarbonization of ammonia production through the utilization of renewable energy sources, innovative hydrogen production routes, and alternative process designs. However, despite the development of new technologies, the conventional Haber–Bosch process remains the principal industrial route due to its solidity, scalability, and technological maturity [1].

In this context, a complete understanding of the current global demand, production distribution, and industrial applications of ammonia is essential to highlight both the challenges and opportunities associated with its future development. For this reason, the following chapter provides an overview of the global ammonia market, including production trends, regional distribution, and main areas of application, that will be useful for the subsequent analysis of production technologies and process improvements.

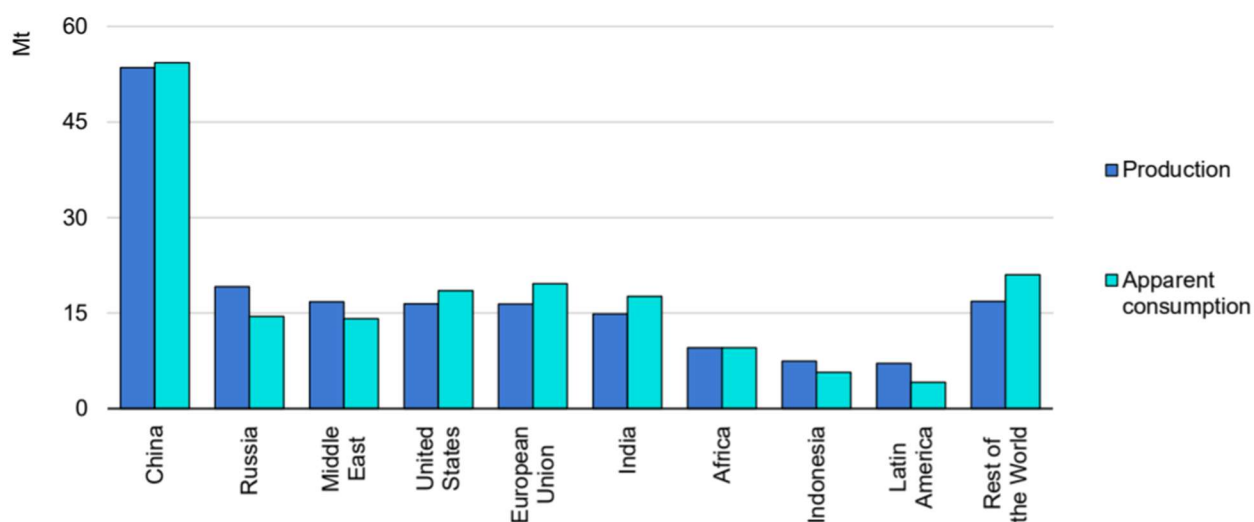
1. Global Demand and Production of Ammonia

Global demand of ammonia is primarily guided by the agricultural sector, with more than 80% of worldwide production used for fertilizer manufacturing, in particular for urea and ammonium-based products. Other applications include nitric acid production, which accounts for roughly 5% of ammonia consumption and is used, for example, in explosives manufacturing, as well as polyamide production, with also around 5% of usage, mainly for textile applications. Other smaller shares are used for pharmaceuticals and various cleaning products [4].

To simplify the discussion of environmental performance, the ammonia sector commonly adopts a color-based classification system in order to distinguish different production pathways basing to their associated carbon intensity (Figure 3). Brown and grey ammonia are produced from fossil fuel feedstocks, namely coal and natural gas, and as a consequence they are linked to high CO₂ emissions. Blue ammonia is also derived from fossil resources but include carbon capture and storage (CCS) technologies to limits CO₂ release to the atmosphere. Current CCS-based facilities produce around 1 Mt of blue ammonia annually, mainly in the United States, Canada, and China, with planned projects that could increase this value to around 4 Mt per year by 2030. On the other hand, green ammonia is based on hydrogen obtained through water electrolysis powered by renewable electricity, thus avoiding direct CO₂ emissions. Existing and planned electrolysis projects could enable global green ammonia production to exceed 3 Mt per year by 2030 [5], [6].

1.1 Global Ammonia Consumption, Production, and Applications

Ammonia (NH₃) is one of the highest-volume chemical produced worldwide, with global production reaching around 185 million metric tons in 2020. In the same year, ammonia manufacturing amounts roughly 2% of global energy consumption, that corresponds to about 8.6 EJ, and contributed roughly 1.3% of total energy-related CO₂ emissions, equivalent to around 450 million tonnes of CO₂[5].



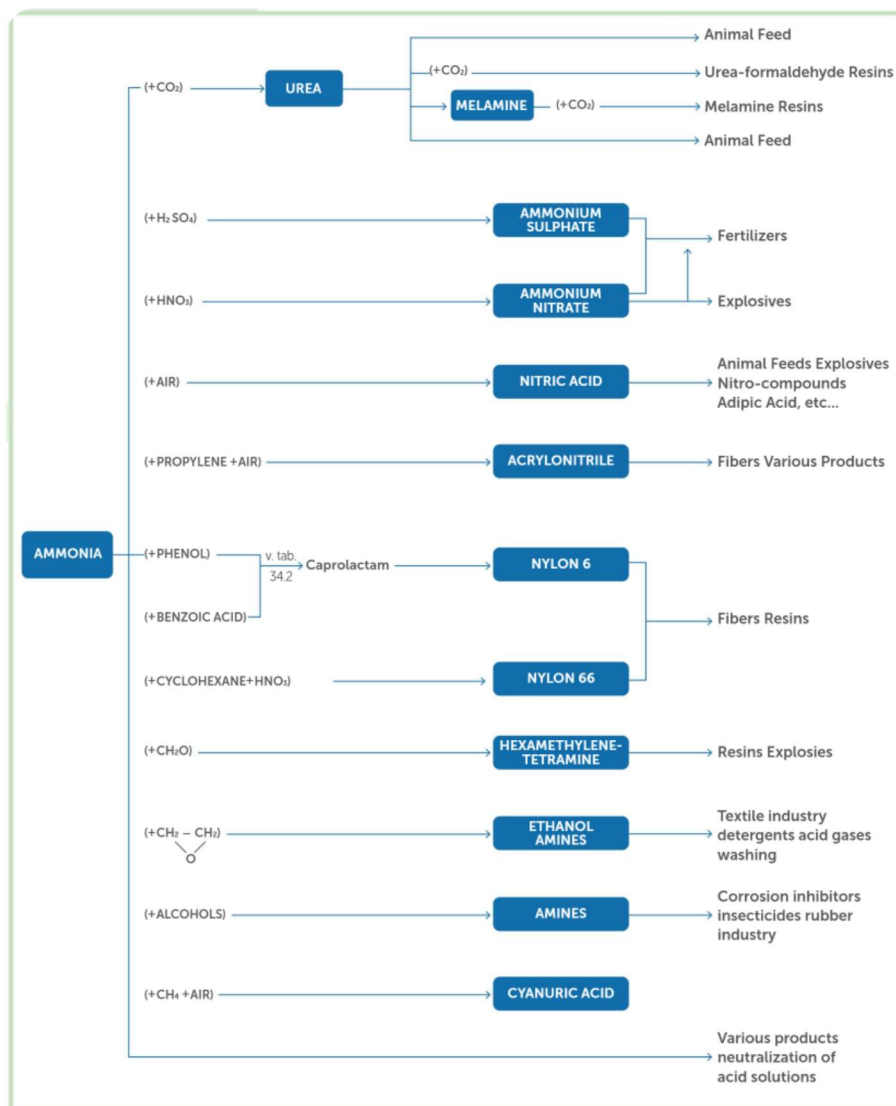
IEA, 2021.

Notes: The apparent consumption of a region is equal to its production plus imports minus exports.
Source: Data from [IFA](#).

Figure 1. Apparent consumption and production of ammonia in 2019

Its production is geographically concentrated in regions with strong agricultural demand or good access to competitive energy resources. China currently represents the largest producer, accounting for approximately 29% of global output in 2019, followed by Russia (10%), the United States (9%), the Middle East (9%), the European Union (8%), and India (8%). Despite market shares have shifted over time, the same regions have largely dominated production over the past decades. For example, in 1990 China contributed 19% of global output, while current EU countries accounted for 17%, the United States for 13%, Russia for 10%, and India for 7%, whereas the Middle East represented only 3% of global production. Over the last twenty years, the strongest increases in apparent ammonia consumption have been observed in the Middle East, Africa, and Russia, with an increase of roughly 140%, 110%, and 80%, respectively, while demand in the European Union, the United States, and South America has remained more or less stable [4].

Ammonia is also acknowledged as one of the seven major basic chemicals, together with ethylene, propylene, butadiene, aromatics, methanol, and carbon black, and it place in second position in the most produced chemical globally by mass ranking after sulfuric acid [7].



Source: Pasquon, I; G. F. Pregaglia: "Prodotti e processi dell'industria chimica", Città Studi (1998), p. 119.

Figure 2. Main uses of Ammonia

As shown in Figure 2. Ammonia has several uses. Its main application remains fertilizer production, but is used also as an important intermediate in several chemical value chains. Industrial uses include textile processing, in which ammonia is employed to treat and produce synthetic fiber, pharmaceutical manufacturing, and nitric acid production, which consequently reacts with ammonia to form ammonium nitrate fertilizers. Moreover, ammonia has also attracted recently interest as a potential carbon-free energy carrier and fuel for maritime transport, power generation, and energy storage applications [8].

Despite its wide industrial relevance, the environmental impact of ammonia production remains strongly dependent from the hydrogen sources. Currently, more than 96% of hydrogen used for ammonia synthesis comes from fossil fuels. More or less 70% is produced via steam methane reforming (SMR) of natural gas, leading to emissions of around 2.5–2.9 kg CO₂-equivalent per kilogram of ammonia produced. Coal gasification, predominantly used in China, contributes with about 26% of hydrogen demand but results in even higher emissions, reaching approximately 5.2 kg CO₂-equivalent per kilogram of ammonia[9].

These figures highlight that, despite ammonia plays a crucial role in global food production and industrial supply chains, with its current production pathway is still associated with significant energy consumption and emissions. For this reason, improving synthesis efficiency and integrating lower-carbon hydrogen sources have become central goals in ongoing technological developments, which will be examined in the following sections.

1.2 Main Ammonia Production Processes

Industrial ammonia production generally are subdivided in two main stages: hydrogen generation and ammonia synthesis. In modern plants, hydrogen is first produced from primary energy sources, after that it reacts with nitrogen derived from air separation in the Haber–Bosch synthesis loop to form ammonia [5]. In the past, several production routes have been explored before the widespread adoption of current technologies. One of the earliest industrial techniques was the Birkeland–Eyde process, developed in 1903, which used an electric arc to oxidize atmospheric nitrogen and afterwards produce nitric acid. Although original at the time, this method required extremely high energy inputs, on the order of 400 GJ per tonne of ammonia equivalent, making it economically unsustainable and leading to its eventual abandonment.

Advance to nearly a decade later, when the Haber–Bosch process was first used in industry, and it quickly became the most common method for ammonia synthesis. During initial deployment with this technology, the energy requirements are lower than past methods at approximately 100 GJ per tonne of ammonia. As the process was utilized in explosives production over World War I, it acquired strategic significance and by the 1930s it had already become the standard industrial technique [5] , which is not changed until present days.

Ammonia production could be generally separated in three main sections as follows show Figure 3 [10].

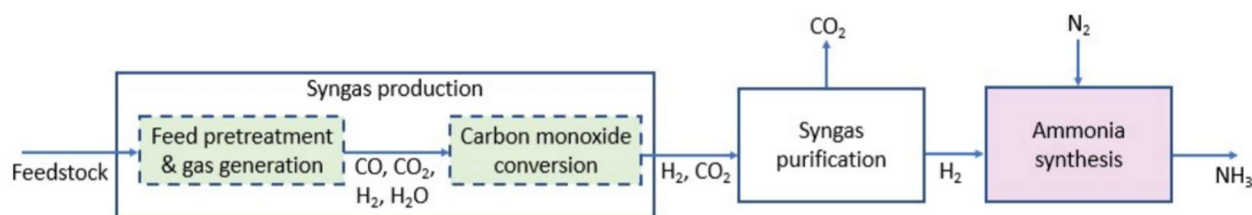


Figure 3. Main ammonia production steps

Stage-1: It is for producing synthesis gas, where they produce hydrogen-rich gas from natural gas, coal or other hydrocarbons followed by doing carbon monoxide conversion reactions to get more hydrogen. The second step is gas purification, filtering out carbon dioxide and other impurities to achieve a hydrogen stream suitable for synthesis. Finally, in the synthesis loop, pure hydrogen and nitrogen are combined using high temperature and pressure to produce ammonia, unreacted gases are recycled for improved conversion of reactant gases.

Ammonia (NH_3) synthesis is still one of the foundation reactions in chemical industry, providing an important building block for fertilizers, explosives and many nitrogen-containing chemicals. There are several synthesis methods available, each with specific strengths and technical challenges that may determine the economical, environmental, and operational limitations of process choice.

The Haber–Bosch process, originally developed by Fritz Haber and later industrialized by Carl Bosch, continues to dominate large-scale production. It relies on the catalytic reaction of nitrogen and hydrogen in a high temperature and pressure environment, allowing ammonia to be continuously produced at an industrial level. Although the process is extremely robust yielding an operationally efficient process, it remains energy intensive requiring complicated infrastructure resulting in its potential place as a research target for improvements [11].

The alternative production concepts are currently being explored to decrease environmental impact and increase the flexibility of processing. For example, **electrochemical synthesis** lets you apply electricity to split water into hydrogen and oxygen, so in a sense, ammonia production could be carbon zero if we use renewable electricity for it. While still at an early stage of development and not commercially widely deployed, this enables the potential for decentralized and more sustainable ammonia production [12].

Plasma-assisted synthesis may also be used, which activates the nitrogen and hydrogen molecules before they undergo recombination to ammonia under plasma conditions. This technology can work at lower temperature and pressure conditions compared to the traditional process, potentially

reducing energy needs. However, the relatively high equipment costs and process control challenges currently inhibit large-scale implementation.

At the same time, extensive research efforts are directed towards creating novel catalysts that can drive reaction rates and selectivity. However, conventional iron-based catalysts and ruthenium-based systems currently employed in industrial practice remain limited from the performance perspective. Thus, recent developments have been focused on exploring a range of new catalytic materials such as metal nitrides and carbides that exhibit significantly improved catalytic activity [13].

While these alternative approaches are emerging, nearly all industrial ammonia production still takes place with the Haber–Bosch process, which is subject to both intrinsic thermodynamic and kinetic limits that impose challenging reaction-condition requirements. With this in mind, there is consequently greater focus on process intensification strategies for enhancing synthesis efficiency while maintaining the same existing industrial infrastructure (e.g., utilization of membrane-based separation units that will also be discussed in subsequent chapters).

1.3 Ammonia Classification by Colour

Currently, the major industrial pathway for hydrogen production is through ammonia from nitrogen and hydrogen in a thermo-catalytic system via the Haber–Bosch process under high-temperature pressure. In our global ammonia production pathway, this results in over 400 Mt of CO₂-equivalent emission each year, averaging approximately 2.4 tonnes of CO₂ emissions per tonne of actual ammonia produced. A significant portion of these emissions comes from hydrogen production, which still largely depends on fossil fuels.

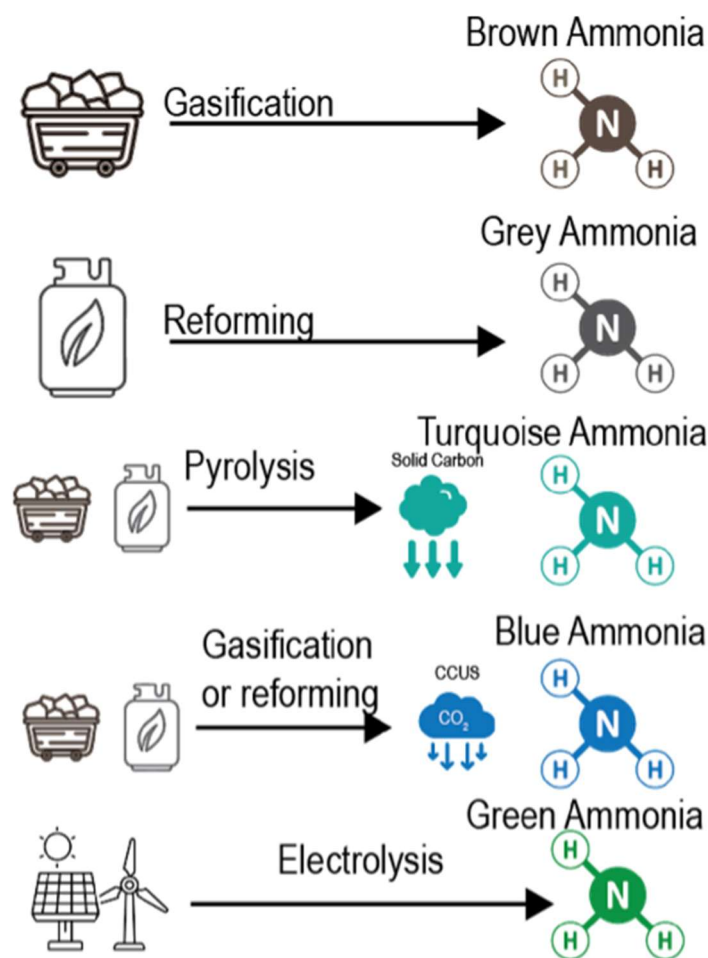


Figure 4. Various colors of ammonia.

In order to differentiate production routes with respect to their environmental impact, ammonia is largely classified (Figure 4.) according to the source of hydrogen used throughout synthesis. Brown ammonia is defined as ammonia produced using the hydrogen from coal gasification, a route that currently represents around 30% of global production and entirely located in China. This process is linked to a certain span of emission intensities between 2.4 and 3.2 ton CO₂ per production ton ammonia. Grey ammonia, by contrast, is made using hydrogen derived from steam methane reforming of natural gas—the source for around 70% of global ammonia production today.

Depending on plant efficiencies and natural gas characteristics, emissions in this route are usually 1.6 - 1.8 tonnes CO₂/tonne ammonia produced.

In turquoise ammonia the production is based on hydrogen generated through methane pyrolysis. In this process, methane is thermally decomposed into hydrogen and solid carbon, avoiding the direct formation of CO₂ emissions.

Blue ammonia refers to production pathways using fossil-derived hydrogen in conjunction with carbon capture and storage (CCS) technologies, avoiding atmospheric emissions. CCS implementation, while adding to the plant energy consumption (typically around 0.7GJ per tonne of ammonia) is likely to result in a much lower emission intensity, e.g, such that carbon intensity reduces to 0.1–0.2 tonnes CO₂ /tonne ammonia. At last, green ammonia is created from hydrogen based on renewable electricity matching every molecule through water electrolysis, so there are no direct fossil-based CO₂ emissions. Although this pathway is the most promising and sustainable, it needs plenty of renewable electricity input (36 GJ per ton ammonia generation) [14].

This categorization illustrates the large range of energy input and carbon emissions across ammonia production technologies. Thus, there is still a need to improve the efficiency of processes and reduce the energy share of existing synthesis technologies for lower ammonia environmental footprint which motivates us to analyze process improvements in chapters as follows

2. The Haber–Bosch Process: State of the Art and Challenges

In this chapter, an overview on the traditional Haber–Bosch (HB) process that continues to set the standard for ammonia production everywhere over the globe is provided. This chapter begins with a brief description of the historical evolution of ammonia synthesis, followed by an overview of the key aspects that govern ammonia synthesis and operational issues facing current industrial practices.

This latter aspect emphasizes the thermodynamic and kinetic limitations of reactor performance, where reaction rates, conversion and yield are affected by temperature, pressure and catalyst properties. Moreover, the energy consumption and CO₂ emissions of a modern HB plant with high product rate are analyzed. The analysis incorporates both the economic aspects, such as capital and operating costs associated with high-pressure operation and gas recycling components in an integrated fashion to gain insight on the constraints influencing conventional ammonia plants. Application of any process improvement strategy requires an understanding of these limitations. Thus, the analysis in this chapter establishes the technical foundation needed to compare various

potential solutions and process intensification strategies detailed in successive chapters, culminating on the configuration incorporating membranes investigated herein.

2.1 Historical Development of the Haber–Bosch Process

The process of industrial-level ammonia synthesis has undergone changes over time to meet the growing global demand for nitrogen-based chemicals and fertilizers. The first methods of nitrogen fixation included: the Birkeland–Eyde process (from the early 20th century) using electric arc to produce nitric acid from atmospheric nitrogen. This method, while clever, devoured so much energy that it was never going to make economic sense at scale [3].

In a major technological revolution in this direction, the Haber–Bosch process was developed for direct synthesis of ammonia from nitrogen and hydrogen via an industrially scalable catalytic reaction. It contributed to a substantial enhancement of energy efficiency in relation to methods available at that time, and it also permitted continuous production on an industrial scale, thereby laying the foundations for today's ammonia industry [1], [3].

The Haber–Bosch process has been progressively optimized in the 20th century, primarily concerning catalyst development, reactor design and heat integration. Ammonia production was particularly important in World War I for explosives manufacture, which led to the rapid development of an industrial-scale process. The process had grown into the dominant worldwide technology for ammonia synthesis by the 1930s [1].

Later development efforts have remained around the broader efficiencies of operation and integrations, including better heat recoveries systems and catalyst performance. Nevertheless, even accompanied with those developments the basic framework of Haber–Bosch process has not been changed significantly. Most modern plants continue to operate at high temp & pressure conditions to overcome thermodynamic and kinetic barriers associated with nitrogen activation [1], [15].

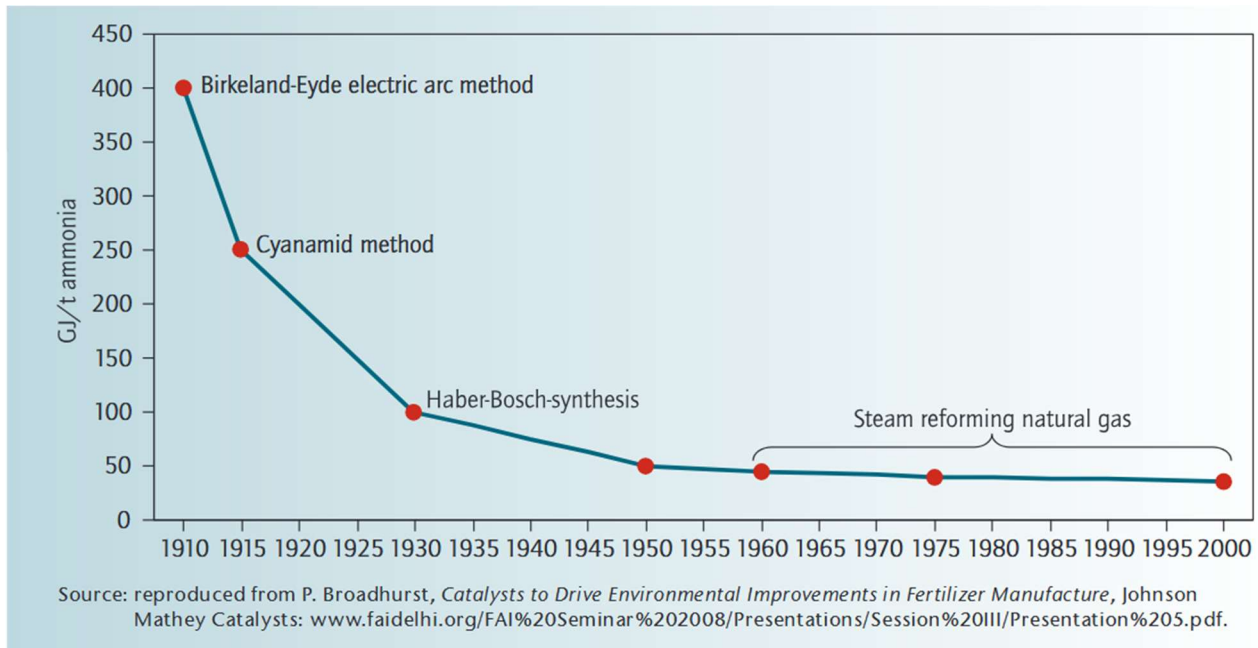


Figure 5. Ammonia synthesis breakthrough and energy efficiency

Today, the Haber–Bosch process still remains the main vector for ammonia production that supports global yields of hundreds of millions of tonnes per year. However, its highly fossil-dependent hydrogen supply chain and catastrophic high energy demand have been identified as two of the main contributors to global CO₂ emissions ranking ammonia synthesis in one of the most high-energy consuming processes among large-scale industrial manufacturing in chemical process [2], [3].

This has inspired significant research on alternative synthesis pathways and process intensification strategies like membrane-based systems and novel catalytic strategies to increase energy efficiency and mitigate environmental impact while remaining compatible with existing industrial infrastructure [15].

2.2 Thermodynamic and Kinetic Limitations

Ammonia synthesis proceeds according to the following reaction:



Usually, a system having an exothermic heat of reaction under operating conditions should react spontaneously. However, to form ammonia from hydrogen and nitrogen molecules, significant energy input is required for the nitrogen molecule to achieve the activated state. This is because of its high dissociation energy of 941 kJ/mol, which is considerably higher than that of hydrogen. The

Gibbs free energy for the dissociation reaction was determined as $N_2 \rightleftharpoons 2N$ $\Delta G_{298}^0 = 977 \text{ kJ/mol}$.

The distance between the triply bonded nitrogen atoms of 1.098 Å is rather short. The first ionization energy is 1503 kJ/mol.

$t, ^\circ\text{C}$	$p_{\text{abs}}, \text{ MPa}$										
	5	10	20	30	40	50	60	70	80	90	100
300	32.11	43.10	54.27	60.62	64.95	68.12	70.56	72.49	74.03	75.28	76.31
310	29.52	40.51	51.98	58.63	63.20	66.59	69.22	71.31	72.99	74.37	75.51
320	27.05	37.96	49.66	56.57	61.38	64.98	67.79	70.04	71.87	73.38	74.63
330	24.71	35.46	47.32	54.45	59.48	63.29	66.28	68.70	70.67	72.31	73.68
340	22.51	33.03	44.96	52.30	57.52	61.52	64.69	67.27	69.39	71.16	72.65
350	20.46	30.68	42.62	50.11	55.51	59.68	63.02	65.76	68.03	69.93	71.54
360	18.56	28.42	40.30	47.90	53.46	57.79	61.29	64.18	66.59	68.63	70.36
370	16.80	26.27	38.01	45.69	51.37	55.85	59.49	62.52	65.08	67.24	69.10
380	15.19	24.33	35.77	43.48	49.26	53.86	57.64	60.81	63.49	65.79	67.77
390	13.72	22.31	33.59	41.29	47.14	51.85	55.74	59.03	61.84	64.27	66.36
400	12.39	20.50	31.48	39.13	45.02	49.81	53.81	57.21	60.14	62.68	64.89
410	11.18	18.81	29.44	37.01	42.91	47.76	51.84	55.34	58.38	61.03	63.35
420	10.08	17.24	27.49	34.93	40.83	45.71	49.86	53.44	56.57	59.32	61.75
430	9.10	15.79	25.62	32.92	38.77	43.67	47.86	51.52	54.73	57.57	60.09
440	8.21	14.45	23.85	30.97	36.75	41.64	45.87	49.58	52.86	55.78	58.39
450	7.41	13.22	22.17	29.09	34.78	39.65	43.88	47.63	50.97	53.96	56.65
460	6.70	12.09	20.59	27.29	32.87	37.68	41.92	45.68	49.06	52.11	54.87
470	6.06	11.05	19.10	25.56	31.02	35.77	39.97	43.75	47.16	50.25	53.06
480	5.49	10.11	17.71	23.92	29.23	33.90	38.06	41.83	45.25	48.38	51.24
490	4.97	9.24	16.41	22.36	27.51	32.08	36.20	39.94	43.36	46.51	49.40
500	4.51	8.46	15.19	20.89	25.87	30.33	34.37	38.08	41.49	44.64	47.56
510	4.10	7.74	14.07	19.50	24.30	28.64	32.61	36.26	39.65	42.79	45.72
520	3.73	7.09	13.02	18.19	22.81	27.02	30.89	34.49	37.84	40.97	43.90
530	3.40	6.50	12.05	16.96	21.39	25.46	29.24	32.76	36.07	39.17	42.09
540	3.10	5.97	11.16	15.81	20.05	23.98	27.65	31.09	34.34	37.41	40.31
550	2.83	5.48	10.33	14.73	18.79	22.57	26.12	29.48	32.66	35.68	38.56
560	2.59	5.04	9.57	13.73	17.60	21.23	24.67	27.93	31.04	34.01	36.84
570	2.38	4.64	8.87	12.79	16.48	19.96	23.28	26.44	29.47	32.38	35.17
580	2.18	4.27	8.22	11.92	15.43	18.76	21.95	25.01	27.96	30.80	33.54
590	2.01	3.94	7.63	11.12	14.44	17.63	20.69	23.65	26.51	29.28	31.96
600	1.85	3.64	7.08	10.37	13.52	16.56	19.50	22.35	25.12	27.81	30.43

Table 1. Equilibrium ammonia content (in mol%) in the presence of inert gases (2.5 mol% Ar; 7.5 mol% CH₄);
N₂:H₂=1:3

In this case, the activation energy necessary for the homogenous reaction of nitrogen and hydrogen to form ammonia gas is in a range of 230 - 420 kJ/mol. This activation barrier requires temperatures far above 800 - 1200 K to reach observable reaction rates for purely thermal energy supply with a good yield of collisional excitation. But at these high temperatures and industrially realistic pressures, the maximum feasible gas-phase ammonia yield approaches zero due to its unfavorable position on the thermodynamic equilibrium. In fact, all previous attempts at thermal combination of molecular nitrogen with atomic or molecular hydrogen failed. From pressures greater than 200 MPa (2000 bar), the manufacture of ammonia take place also without precise catalysts. The vessel walls also seem to catalyze creation of the ammonia at such high pressures.

In the thermodynamically advantageous temperature range determined for homogeneous phase, ammonia formation processes are put in effect by other types of energies inputs which can originate from electrochemical reaction activity or be generated at the result of ionizing radiation.

Thermodynamics suggest a low temperature would favour the reaction, though kinetic reasons dictate that higher operating temperatures are required for an acceptable productivity. Without a catalyst the reaction is impossible, but even in presence of it very high pressures ($\sim 10\text{--}30$ MP) have to be used to achieve a practically non-negligible conversion at normal temperature ~ 670 K. The commercial catalysts utilized for the same are either derived from Fe on magnetite oxide (Fe_3O_4)/wustite (Fe_{1-x}O) or Fe–Co catalysts. Kellogg advanced ammonia process (KAAP) has employed different materials based on Ru/C as an alternative processes and became feasible due to lowering the operating pressure below 100 bar in the 1990s with huge energy and economic savings. [16]

The equilibrium constant of the reaction depends upon the temperature according to the following equation [17]:

$$\log_{10} K_{eq} = -\frac{59.9024}{R} + \frac{37656}{RT} - 2.691122 \log_{10} T - 5.519265 * 10^{-5}T + 1.848863 * 10^{-7}T^2$$

which leads to a decreasing maximum ammonia concentration when raising the temperature, while increasing pressure boosts the conversion.

2.3 Energy Consumption and CO₂ Emissions

One important issue in ammonium synthesis comes from the equilibrium constraints of reaction. Since the Haber–Bosch reaction is exothermic, a more elevated temperature drives equilibria towards the reactants and results in lower achievable ammonia concentrations even if higher temperatures raise reaction kinetics. As such the need to obtain reasonably high yields in an industrial setting requires a balance between fast enough reaction rates and equilibrium conversion. Even elevating pressure is relevant too, as inciting ammonia equilibrium products consistent with Le Chatelier's principle weighted favors formation. However, even if high pressure operation is not required due to gas being compressed at some stage, it will mean a lot of energy consumed and extra investment in the plant. Thus, selecting appropriate operating pressure and temperature conditions is crucial to develop a cost-effective and high efficiency synthesis process [13]. The actual energy requirements for ammonia production are thus a direct consequence of these operating conditions.

Ammonia synthesis technologies are being developed further with potential new production routes, catalyst systems and alternative feedstocks to improve performance in industry. Enabling a wider scope of manufacturing methods can optimize process efficiency while simultaneously minimizing

energy use and environmental impact. As a result, continued research activity is vital for improving ammonia production processes and assisting the chemical sector in becoming more sustainable. However, ammonia production technology has become increasingly energy efficient over the past century, with consumption decreasing from approximately 100 GJ per tonne NH_3 in the early industrial era to around 27 GJ per tonne of product in modern units. It reflects advances such as the move from coal and lignite gasification to steam methane reforming in the mid-20th century, use of centrifugal rather than reciprocating compressors, and continuous improvements in heat recovery and process integration at large single-train plants. Moreover, the synthesis of more stable and reactive catalysts allows for operation at milder conditions, which reduces energy consumption even more. Nevertheless, theoretical gains could still be made: the energy requirement (theoretical minimum) for ammonia synthesis assuming a natural gas feedstock is estimated to approximately 20.9 GJ per tonne of NH_3 . [18]. As summarized in Table 2, the energy demand of the process remains substantial despite technological improvements.

Energy Requirement and CO ₂ Footprint of Brown Ammonia, Blue Ammonia, and Green Ammonia Based on the Conventional High Pressure Ammonia Synthesis Loop. The Best Available Technology (BAT) Represents the BAT in the Year 2020, Whilst the Potential Represents the Year 2050.					
	ENERGY REQUIREMENT (GJ/t _{NH₃})		CO ₂ FOOTPRINT (t _{CO₂} /t _{NH₃})		Relative Investment
	BAT	Potential	BAT	Potential	
Brown ammonia	26	26	1.6	1.6	1.0
SMR	26	26	1.6	1.6	1.0
Naphtha	35	—	2.5	—	1.1–1.2
Heavy fuel oil	38	—	3.0	—	1.5
Coal	42	—	3.6	—	1.8–2.1
Blue ammonia	33	26	0.4	0.2	1.5
Byproduct hydrogen	—	—	1.5–1.6	0.6	—
SMR with CCS	33	27	0.4	0.2	1.5
Coal with CCS	57	—	1.0–2.0	0.5	2.5–3.0
eSMR	—	26	—	1.1	1.0
Green ammonia	33	26	0.1	0.0	1.2–1.5
Low temperature electrolysis	33	31	0.1	0.0	1.2–1.5
High-temperature electrolysis	—	26	—	0.0	1.5–2.0
Biomass (with CCS)	—	33	1.1–1.2 ^a	0.5 ^a	1.2–3.0
Global average	35	27	2.0	1.4	

Table 2. Energy Requirement and CO₂ Footprints on the Conventional High Pressure Ammonia Synthesis Loop [18].

^a The CO₂ emitted is part of a short carbon cycle, as opposed to the CO₂ emitted for natural gas, naphtha, heavy fuel oil, and coal feedstocks.

The Haber–Bosch processes ammonia production through a thermochemical, energy-intensive process which on its own is mostly powered by fossil-fuels both as feedstock and energy source to

drive the reaction — resulting in massive CO₂ emissions. As the majority of this energy is still generated from fossil fuels, ammonia production is also linked to significant CO₂ emissions. Lately, there has been a growing interest in environmental control legislation and climate change to shift toward greener production pathways. A significant portion of the industrial energy demand across the globe still essentially depends on fossil fuel consumption, which drive major ambient problems (e.g., global warming, atmospheric pollution, acid rain).

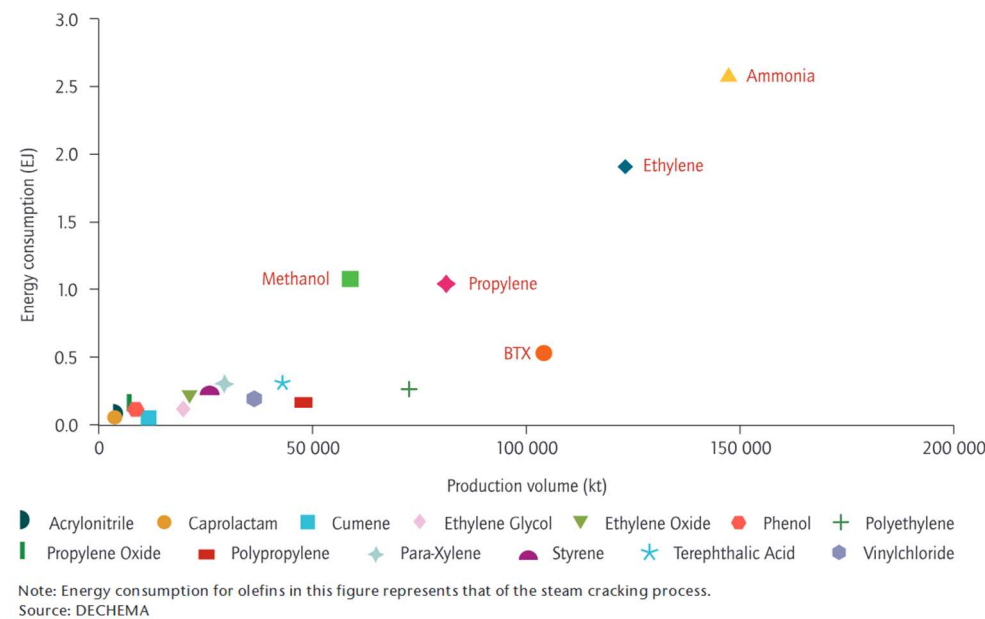


Figure 6. Global energy consumption versus production volumes of top 18 large-volume chemicals, 2010

The distribution of greenhouse gas emissions in the chemical sector shows that CO₂ represents the dominant contribution.

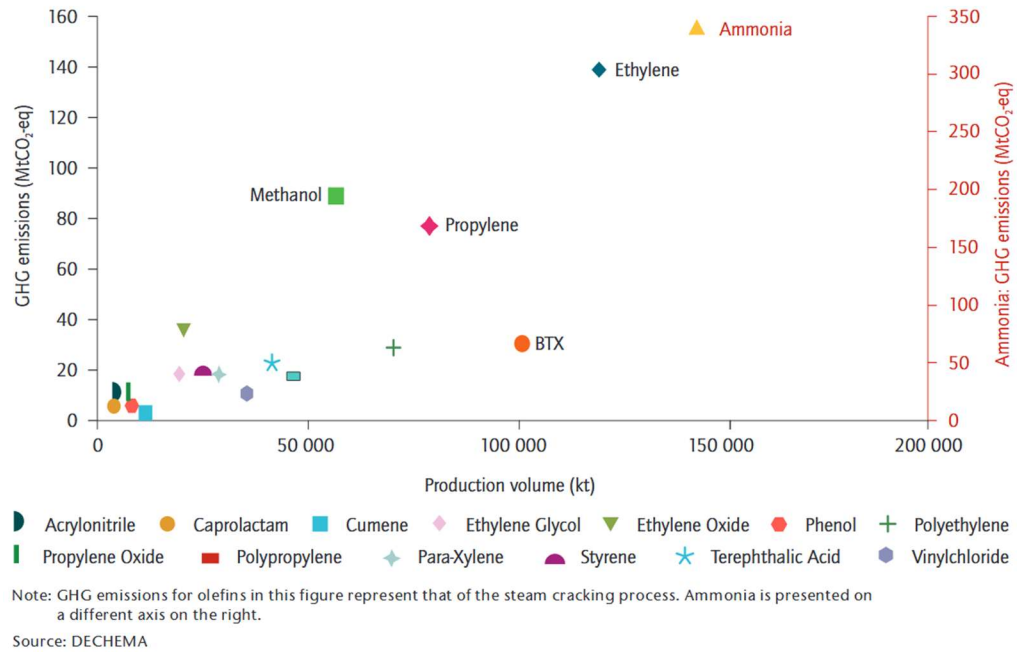
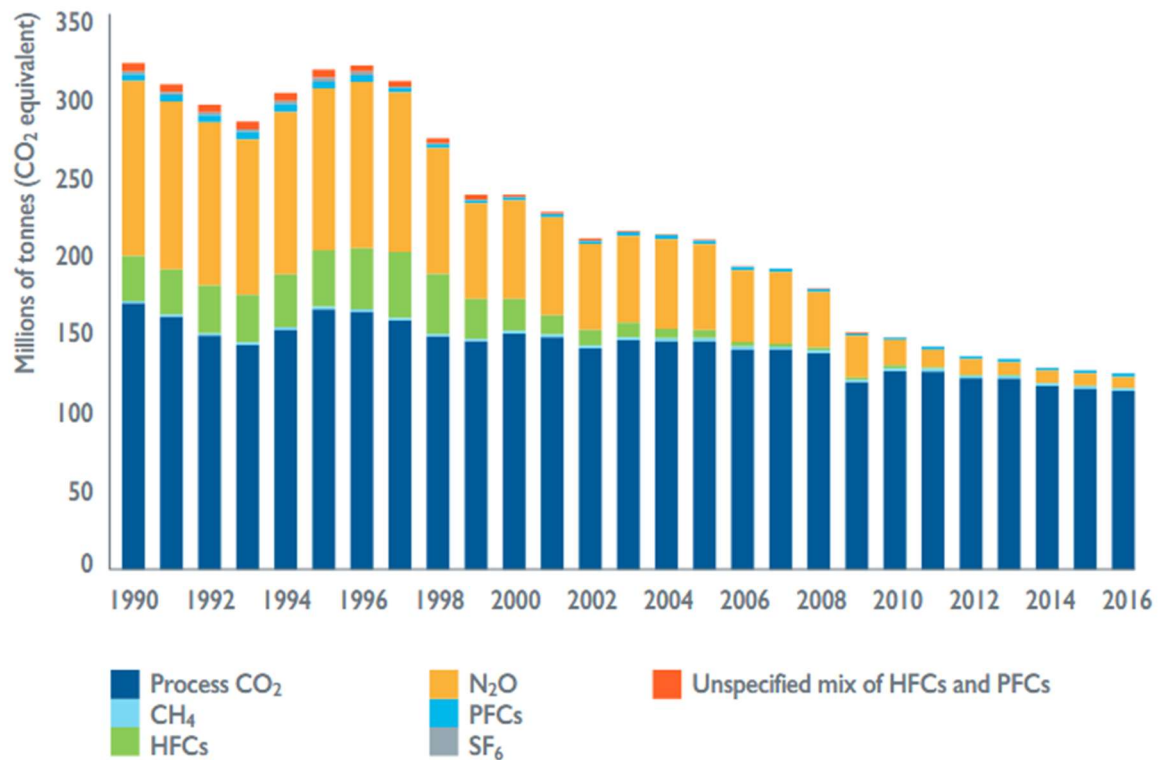


Figure 7. Global GHG emissions versus production volumes of top 18 large-volume chemicals, 2010



Source: European Environment Agency (EEA) and Cefic analysis 2018
 * Energy (Fuel and Power CO₂) included

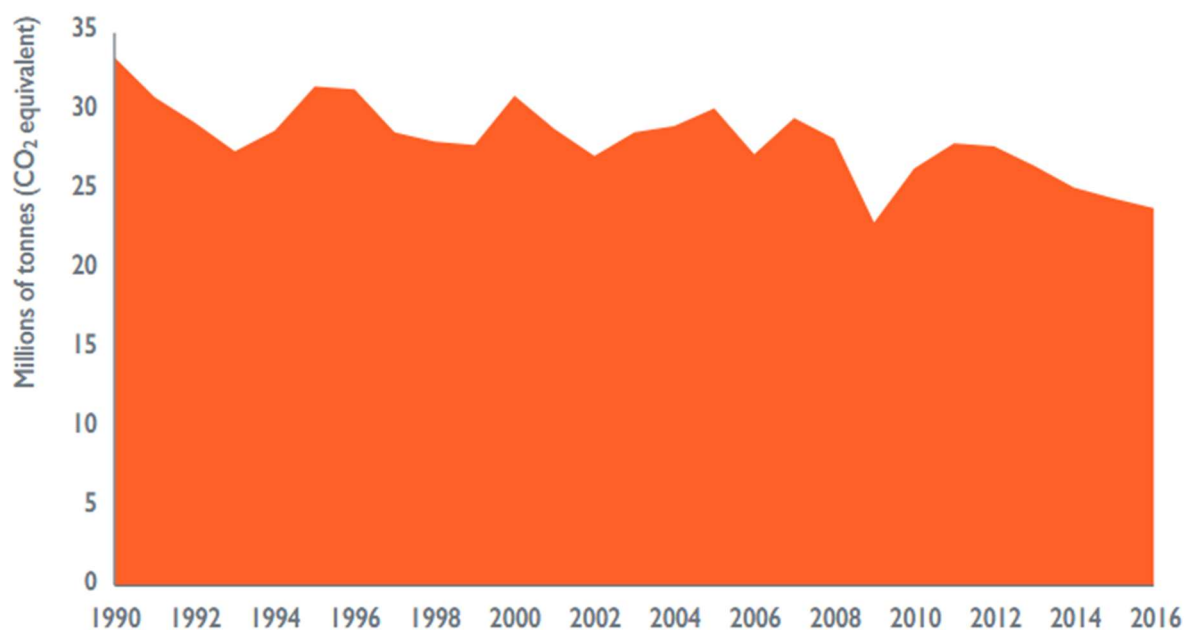
Unless specified, chemical industry excludes pharmaceuticals
 Unless specified, EU refers to EU 28

Figure 8. Evolution of greenhouse gas emissions

This is especially for ammonia production because emissions are highly related to the fossil-based hydrogen generation like methane. Data reported by the European Environmental Agency (EEA) show that CO₂ is by far the main GHG emitted from the EU chemical industry, including its other sectors (mainly pharmaceuticals), with emissions in 2016 corresponding to around 91% of total sectoral GHG emissions. CO₂ emissions peaked at 114.6 Mt in that year which was about 33% lower than the level emitted in 1990, and a further decrease of -1.2% since 2015.

In total, this has reduced greenhouse gas emissions by roughly 199.1 million tonnes of CO₂ equivalent since 1990. Methane emissions (CH₄) did rise slightly during this time, but the other GHGs — CO₂, HFCs, N₂O, SF₆ and PFCs — tended to follow the general downward trend [19].

This trend is illustrated in Figure 8.



Source: European Environment Agency (EEA) and Cefic analysis 2018

* Energy (Fuel and Power CO₂) included

Unless specified, chemical industry excludes pharmaceuticals

Unless specified, EU refers to EU 28

Figure 9. Ammonia production: total greenhouse gas emissions, million of tonnes (CO₂ equivalent)*

The data that takes you through October 2023 of the European Environmental Agency (EEA) states that the production of ammonia by the EU chemical industry was responsible for a total CO₂ equivalent for a released volume of 23.9 million tonnes in 2016, down from a total CO₂ equivalent release of 33.4 million tonnes back 1990. Ammonia production-related GHG emissions fell by 1.3% per annum on average from 1990 to 2016. More than a fifth of the original emission values from 1990 are decreased (28%). As a result, for 2016 ammonia represents more than one third (38%) of total GHG emissions (23.9 versus 62.5, million tonnes) and this figure is significantly above the relative contribution established in 1990 (15.7% -33.4 versus 212.5, million tonnes) [19]. Note that the reported emission figures refer to different system boundaries and geo-spatial contexts. Global ammonia production emits millions of tonnes of CO₂ per year, but regional figures (e.g. for the EU) are very low since production is limited in scale in these regions. Figure 9. exemplifies this trend well. These recent improvements notwithstanding, ammonia production continues to account for a major portion of overall emissions from the chemical sector.

The above arguments indicate that these vigorous or harsh conditions certainly need to be avoided, and hence there is an increasing urge for the process efficiency improvement during ammonia synthesis while aligning towards sustainable development. The average carbon intensity from ammonia synthesis technologies is around 2.0 tCO₂/tNH₃ (Table 2.3.1). Within the EU, total CO₂ equivalent emissions fell from ~33.4 million tCO₂ in 1990 to 23.9 million tCO₂ in 2016. Hands-on exploration of advanced technologies and process intensification strategies inspires the discussion of process development in the following chapters.

2.4 Economic Constraints in Conventional Plants

Ammonia production by the conventional Haber–Bosch process has a high energy requirement, which is significantly affected by the associated process units (economics). Ammonia synthesis must be performed at high temperature and pressure, as we discussed in previous sections, which naturally incurs a large amount of energy consumption. Because energy is the largest operating cost in ammonia and its consumption directly affects the overall process economics.

The largest portion of the total cost comes from hydrogen production, which for now is mostly performed via fossil routes using steam methane reforming or coal gasification. Such routes have been energy and cost intensive to a great extent governed by the availability and price of fossil fuels. Thus, the ammonia process is inherently economically sensitive to variations in natural gas (or coal) prices.

In addition to energetic costs, high capital expenditures are driven from the extreme operation conditions applied in the Haber–Bosch process. The operation at high pressure, therefore requires substantial design of the reactors with much more robust designs often needed and provides cost-effective rheology within thick-walled vessels, in addition to this needs compression systems that can handle large gas volumes. These prices substantially raise both the first installation and upkeep costs throughout the service life of your plant. Additionally, gas compression accounts for a significant portion of the energy use and therefore OPEX.

The other major economic limitation is the one-pass conversions of nitrogen and hydrogen in synthesis reactor which are relatively low. To permit overall acceptable yields the gases not reacting should be continuously recycled within the process loop. This recycling complicates the process and adds to energy usage through multiple compressions and recirculations of gasses. In addition, the

separation of ammonia from the reaction mixture (which is usually conducted by condensation at high pressure) also necessitates extra energy input and limits operational flexibility.

Cumulatively, the economic drawbacks of conventional Haber-Bosch process stem from its high energy and fossil-based feedstock requirement together with operation under harsh conditions. This has rendered ammonia production both energy and capital-intensive with limited process flexibility making it very sensitive to changes in energy prices as well as environmental regulation.

All these constraints show the importance and necessity of developing more efficient and greener technologies for their production. This will be particularly achieved through the reduction of energy consumption, simplification of process design and improvement in overall economic performance via process intensification strategies as well as innovative solution integration. More on these is to come in the next chapter.

3. Technologies for Ammonia Synthesis

The common Haber–Bosch process has numerous downsides, as outlined in our previous chapter leading to significant research activity searching for new ammonia synthesis technologies. This heavy energy use, plus reliance on fossil-based hydrogen and the resultant greenhouse gas emissions, has emphasised the need for more sustainable and efficient production pathways [2], [3]. This has elicited a plethora of innovative approaches to these challenges. This consists of alternative routes for the synthesis which can work under milder conditions, and intricate catalytic systems that are designed to offer improved implementation of nitrogen activation and reaction. Moreover, new approaches towards overcoming the intrinsic thermodynamic restrictions of ammonia synthesis and improving the overall process performance have been provided using process intensification strategies [15].

Another major area of research is combining ammonia production with renewable energy sources. Specifically, alternative hydrogen production routes are being developed that rely on electrolysis of water or the use of renewable electricity as a green substitute for conventional fossil-based routes. These strategies focus on drastically cutting carbon emissions and facilitating the construction of more modular, localized ammonia production systems [3], [5].

In addition, the recent studies indicate that efforts have to be placed into developing technologies suitable for scaling up this investigation to industry by which they are compatible with the current industrial framework. Hybrid systems with other reactor configurations are being investigated to increase the use of reactants, minimize energy consumption, and simplify the design while maximizing the potentials for industrial scalability [15].

In this chapter, the key technologies that have been researched for ammonia synthesis are summarized with consideration of their operation mechanism, possible advantages and current challenges. The focus will be on novel methods that can allow both process intensification and increased efficiency which are promising approaches to more sustainable ammonia production platforms. The next section describes each of the key alternative pathways, which are currently being examined.

3.1 Alternative Pathways for Ammonia Synthesis

A significant share of the total energy consumption in ammonia production is associated with hydrogen generation, as summarized in Table 3.

Stages	Technology		Technology readiness level	Feedstock	Driving force (type of energy used)	Approximate energy consumption			
						MJ/kg	kWh/kg		
Hydrogen production ^a	Reforming	Steam	<u>Commercially used</u>	Hydrocarbons	Fossil fuels	165–180	45.8–50		
		Autothermal	To-be-developed in short term	n/a					
		Plasma	To-be-developed in long term	<u>29–31.8</u>		<u>8.05–8.83</u>			
		Aqueous phase	To-be-developed in medium term	Carbohydrates	Fossil fuels-to-electricity/ nuclear/ renewables	n/a			
	Gasification		<u>Commercially used</u>	Biomass		<=151.2	<=42		
	Photolysis		To-be-developed in long term	Water and sunlight		n/a			
	Partial oxidation		<u>Commercially used</u>	Hydrocarbons	Fossil fuels	~120	~33.3		
	Electrolysis	Atmospheric alkaline	<u>Commercially used</u>	Water and electricity	Fossil fuels-to-electricity/ nuclear/ renewables	188.96–192.24	52.5–53.4		
		High pressure alkaline				224.28–252.36	62.3–70.1		
		Proton exchange membrane							
	Thermochemical water splitting		To-be-developed in long term	Water and heat	n/a				
Nitrogen production	Air separation	Adsorption	To-be-developed in short term	Air, electricity, heat	Fossil fuels/ fossil fuels-to-electricity/ nuclear/ renewables	0.86–1.98	0.24–0.55		
		Chemical	To-be-developed in long term						
		Cryogenic	<u>Commercially used</u>	Air and electricity	Fossil fuels-to-electricity/ nuclear/ renewables			n/a	
		Polymeric membrane	To-be-developed in short term						
		Ion transport membrane	To-be-developed in long term	Air, electricity, heat	Fossil fuels/ fossil fuels-to-electricity/ nuclear/ renewables				
	Pressure swing adsorption		<u>Commercially used</u>	Air/biogas (landfill gas) and electricity		<u>0.4–1.04</u>	<u>0.11–0.29</u>		
Ammonia synthesis	Haber-Bosch	Fe catalyst	<u>Commercially used</u>	Air, electricity, heat	Fossil fuels-to-electricity/ nuclear/ renewables	14.4–28.44	4–7.9		
		Ru catalyst							
		Co ₃ Mo ₃ N catalyst							
	Electrolytic (electrochemical) synthesis	Liquid electrolyte	To-be-developed in long term	Electricity	Fossil fuels-to-electricity/ nuclear/ renewables	35.64–41.4	9.9–11.5		
		Molten salts							
		Composite membrane	To-be-developed in medium term			<=35,64	<=9.9		
		Solid state electrolyte							

Table 3. Main ammonia production technologies: Summary by stage [20]

In the past decades, a few alternative pathways for ammonia synthesis have been investigated to crack the main barriers of conventional Haber–Bosch process as intolerable energy consuming and harsh operation conditions. The hope of these methods is to create greater efficiency whilst also lowering environmental impact and utilising more sustainable production. Certain strategies involve changes to the reaction environment, such as absorbent-enhanced processes, while others take

advantage of biological systems in biocatalytic synthesis. Electrochemical and electrocatalytic approaches deploy electricity to convert nitrogen, while photocatalytic and photoelectrocatalytic strategies activate nitrogen molecules using light. Membrane-based technologies (membrane separation, and membrane reactors) also give opportunities for intensified processes by better reactant utilization and continuous product removal. The next sections elaborate on those methods in more detail.

Absorption-enhanced Haber–Bosch process: the conventional synthesis loop in the Haber-Bosch process is adjusted with respect to ammonia condensation replaced by an absorption unit (generally using water as an absorber) operated downstream of the reactor. By continuously removing ammonia, the reaction equilibrium is pushed down towards more production and can be run at lower pressure than conventional systems. It is a compelling method to produce decentralized and renewable ammonia as well. While better energy performance has been shown at moderate pressures, additional techno-economic assessment is needed to determine industrial feasibility and the higher process complexity before widespread commercialization [21].

Biocatalytic ammonia synthesis: utilizes microorganisms or enzymes capable of reducing nitrogen compounds to ammonia through biological pathways. Electroactive microorganisms can acquire electrons directly from an electrode and use them to reduce nitrogen species with high selectivity, such as nitrite or nitrate in bioelectrochemical systems. Such a process allows for ammonia production and potentially treatment of nitrogen-containing waste streams. Prospects for its main application areas in sustainable and distributed production scenarios include but are limited to improvements in microbial stability, process reaction rates, and reactor scalability before practical implementation [22].

Electrochemical and electrocatalytic ammonia synthesis: ammonia is synthesized in electrochemical cells by using electrical energy to power the reduction of nitrogen (N_2) gas at a cathode with water acting as the proton source. Electrochemical synthesis indicates the entire process from nitrogen or nitrogen-based species to ammonia, whereas electrocatalytic synthesis specifies the catalyst for nitrogen activation and the ability to modify reaction selectivity on the electrode surface. Both aspects are closely related in practice since catalyst performance is what ultimately defines the efficiency of a process. [23], [24].

Such routes are appealing because they can be directly integrated with renewable electricity and may help decentralize ammonia production. Nonetheless, practical implementation is still hampered

by low productivity, catalyst degradation and the competing hydrogen evolution reaction suppressing ammonia selectivity and necessitating greater energy input. Thus, further development of catalyst design and reactor operation is needed before real-life industrial implementation can be possible [24].

Photocatalytic and photoelectrocatalytic ammonia synthesis: use light activated semiconductor systems to motive this nitrogen reduction. Photocatalytic configurations utilize light irradiation to generate electron–hole pairs, as electrons take part in ammonia formation while the holes are consumed over oxidation reaction pathways. In photochemical systems, the photoinduced charge separation and reaction control at an accessible electrode. Upon deposition of a thin layer surrounding semiconductor particles, significant improvement in utilization of photogenerated charges in photoelectrocatalytic systems is led by an externally applied electrical bias [25], [26], [27].

Given that these approaches enable direct solar use, they are very attractive for renewable-powered ammonia production. However, the current performance is still limited by improper light utilization, charge recombination and catalyst stability which define the ammonia production rates below industrial applications. Therefore, developments on photocatalyst materials and reactor configurations are necessary for increasing the overall efficiency.

Membrane-based technologies, such as membrane separation and membrane reactors have a great potential for process intensification to achieve sustainable ammonia production with enhanced efficiency. Membrane separation systems, where selective diffusion processes utilise selectively permeable materials to separate ammonia from reaction mixtures or gas streams in order to facilitate continuous product removal and optimise reactant usage. Various classes of membranes have been studied, such as polymeric, inorganic, hybrid and new materials that can function under conditions suitable for ammonia synthesis processes.

Compared with those reactors which carry out chemical reaction and selective separation separately, **membrane reactors** integrate these two processes in the same unit. These systems thus continuously remove ammonia from the reaction zone, which results in an equilibrium shift toward additional product formation, facilitating milder operating conditions and a more efficient overall process.

Such technologies are being pursued for their potential to couple with existing Haber–Bosch plants and next-generation green ammonia production schemes. Below are sections with further

elaboration on discussion of membrane materials, separation mechanisms and reactor configurations relevant to the synthesis and recovery of ammonia [28].

3.2 Fundamentals of Membrane Separation

Among the numerous process intensification strategies described previously, membrane-based separation is an important topic to enhance ammonia synthesis performance.

Membrane separation relies on the differential transport of chemical species through a semi-permeable barrier, where some molecules diffuse faster than others, allowing for continuous and gentle separations without phase change at lower energy costs compared to traditional methods. The performance of a membrane in separation relies on its structural properties as well as interactions between gas molecules and the membrane mats, where surface adsorption, solubility effects and diffusion govern facilitated transport [30].

In Figure 10, it is possible to observe the different NH_3 separation mechanisms adopted in ammonia-selective membranes. In particular, section (a) shows the solution–diffusion mechanism typical of organic membranes, while section (b) represents the chain-transfer facilitated diffusion occurring in polymeric and ionic liquid membranes. Section (c) illustrates the mobile-carrier facilitated diffusion mechanism characteristic of IMS membranes, whereas section (d) shows the selective adsorption and surface diffusion mechanism typical of microporous inorganic membranes.

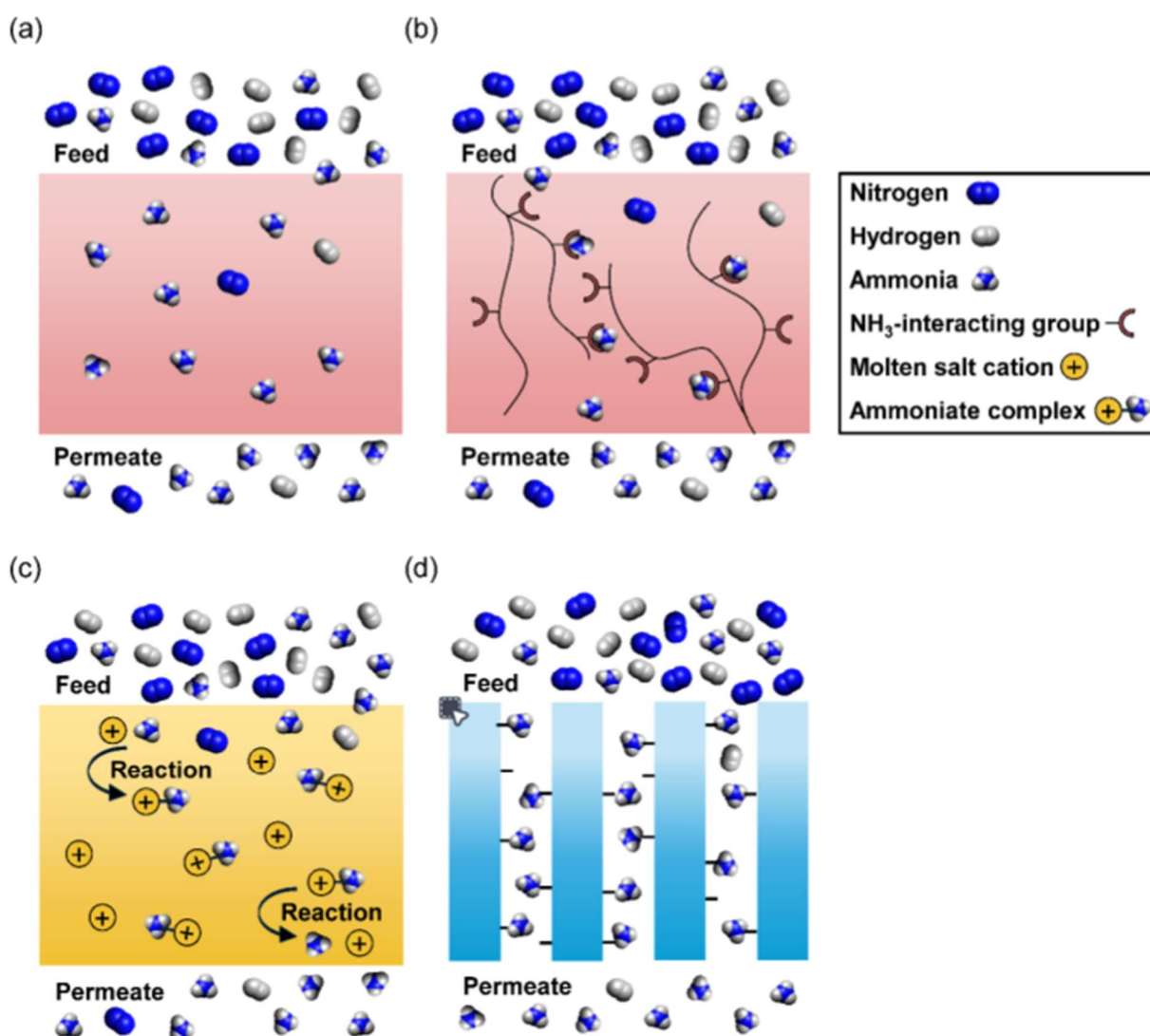


Figure 10. Schematic illustration of NH₃ separation mechanisms in NH₃-separative membranes

Gas transport mechanisms differ between **dense and porous membranes**. In **dense (nonporous) membranes**, solution–diffusion is the most common case for gas permeation: the molecules must first dissolve into the membrane and diffuse through it. Since each gas behaves differently in solubility and diffusivity through the membrane matrix, this leads to separation. In ammonia containing mixtures, this mechanism can be heavily affected by the greater polar and adsorption characteristics of NH₃ in comparison with H₂ and N₂ which when membranes contain polar or reactive functional groups can improve ammonia transport [28], [30].

Transport in **porous membranes** occurs through networking pores, where beneficial consequences of many mechanisms may simultaneously contribute. Molecular sieving happens at pore sizes comparable to the molecular dimension; therefore, smaller molecules can preferentially pass through. But selective size exclusion is still insufficient because the kinetic diameter of NH₃ falls in

between those of hydrogen and nitrogen, hence a pure size exclusion mechanism cannot solely be used. In contrast, separation often occurs through selective adsorption and surface diffusion, where ammonia preferentially adsorbs to pores — a phenomenon that is particularly evident under conditions favoring in pores of micron-wide size ranges. These interactions can facilitate the permeation of NH_3 and simultaneously blockade H_2 and N_2 transport [28], [30].

The second major type of mechanism include **facilitated transport** where ammonia in the form of complex binds to carrier species contained within the membrane after which they migrates through the membrane and finally releases NH_3 on the permeate side. The carrier then goes back to the feed side, and goes through the cycle again. This transport mode takes place by immobilized carriers being localized to the membrane matrix or via mobile carrier species and can enhance ammonia selectivity compared purely to physical transport mechanisms. Very similar concepts are also applied in immobilized molten salt membranes, where the formation of these complexes allows for ammonia transport even when working at elevated temperatures [30], [31].

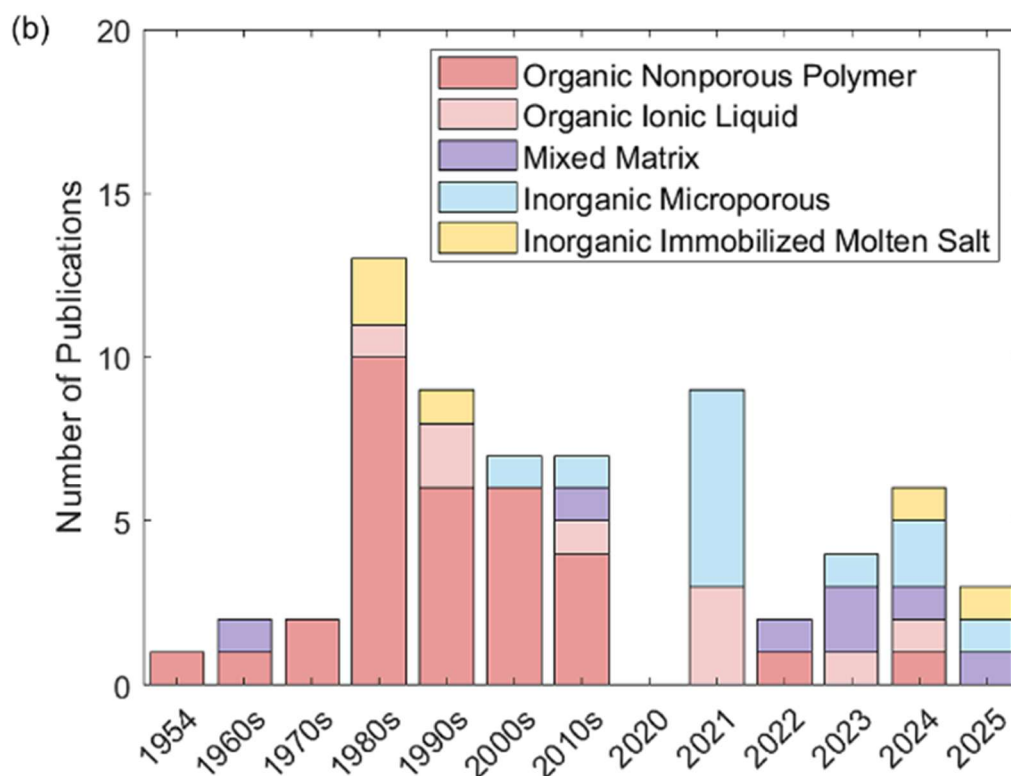
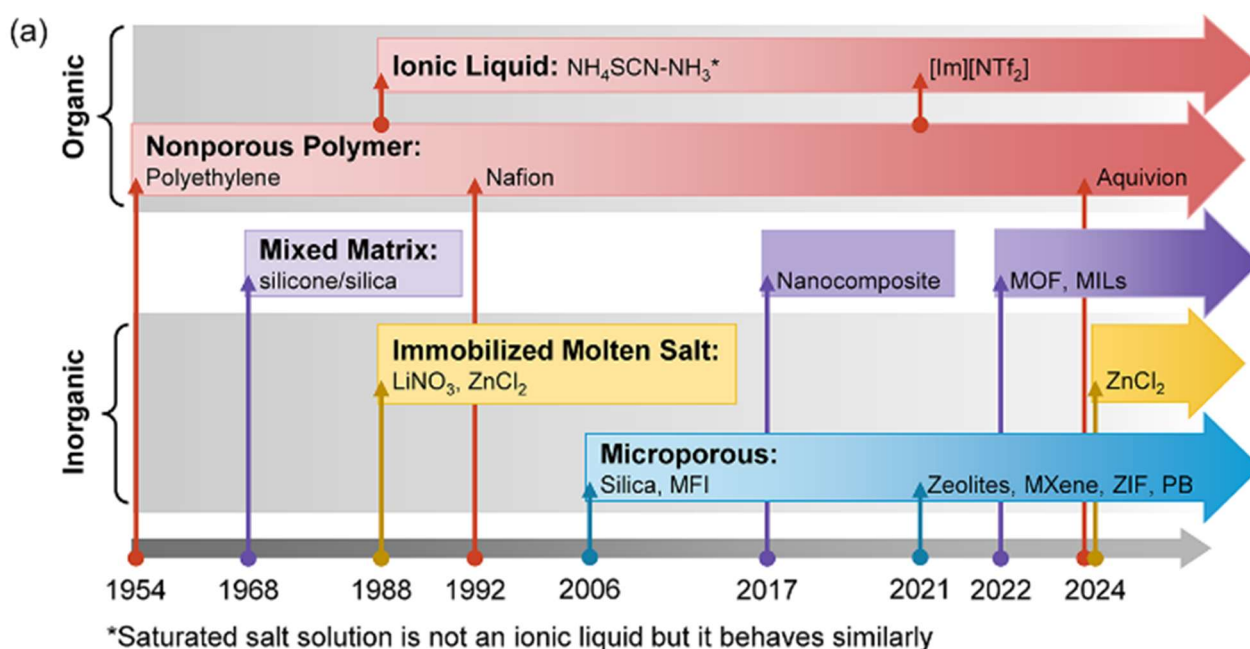


Figure 11. Historical development of NH_3 -separative membranes [30]

Membrane materials for ammonia separation have been well developed over the past years. Polymers were salient in early research since they were relatively easy to fabricate and scale, but the effects of solvent swelling, chemical instability or performance loss at either elevated temperature or pressure was detrimental. Later on, efforts were extended to the point that inorganic microporous membranes (consisting of silica-, alumina-, zeolite- and framework-based materials)

are now a very popular material due to their improved thermal and chemical stability. More recently, hybrid and advanced membrane systems associated with mixed-matrix membranes composed of polymer and inorganic phases, ionic-liquid-based systems or hybrid carrier-assisted membranes for stronger ammonia selectivity using an appropriate chemical interaction have been considered. Increasing membrane research efforts tend to focus on developing membranes that maintain stability and separation efficacy using gases under reactive conditions in proximity to ammonia synthesis [28], [30].

3.3 Types of Membranes for Ammonia Separation

Membrane–reactor process design is a challenge centered on the selective membrane separation of ammonia from hydrogen and nitrogen in conditions relevant to the Haber–Bosch synthesis loop. As introduced in the previous section, multiple transport mechanisms can be exploited based on membrane class and operating conditions. Thus, research in this discipline has utilized tremendous variation of material families, with individual processes specific to their fabrication methodology and separation performance, but also practical limitations.

membrane category	permeance & permeability	selectivity	operating temperature & pressure	performance trends	ease of manufacturing & cost
IMS	high very high	very high	250–350 °C 1 bar	selectivity ↑ as T ↑ permeance ↓ as NH_3 in feed ↑ stability ↓ as ΔP ↑	low mechanical stability low cost
microporous	high high	low	<400 °C 1–35 bar	selectivity ↓ as T ↑ selectivity ↑ as P ↑	rigid and fragile moderate cost
polymer	depends on geometry low	moderate	<200 °C 1–10 bar (maximum = 115 bar)	selectivity ↓ as T ↑ stability ↓ as T ↑	easy fabrication variable design low cost
ionic liquid	low moderate	high	25 °C 1 bar	separation better than polymer alone	low mechanical and thermal stability high cost
mixed matrix	depends on materials	depends on materials	<200 °C 1–3 bar	separation better than polymer alone thermal stability better than polymer alone	depends on materials

Table 4. Summary of Membrane Performance, Operating Conditions, and Manufacturability

Today, the focus of most research has been conducted on four main classes of membranes: polymeric membranes, inorganic microporous membranes, metal–organic framework–based membranes and superior hybrid systems, while new materials maintaining high ammonia selectivity during a high-temperature operation gradually gain more importance [28], [30].

Of all the classes, **polymeric membranes** are the most researched due to them being easy to manufacture at a large scale, low cost to make. Published work indicated that dense polymers including polydimethylsiloxane (PDMS), polyimide and block copolymers consisting of polyethylene oxide and a polyamide segment (commercially named as Pebax) have appreciable NH_3 permeability at near-ambient conditions, mainly due to the preferential solubility of polar ammonia molecules in polymer matrices containing either ether or amide functional groups [28]. For extra selectivity, **ionic liquids (ILs)** have been integrated directly into polymeric matrices with an emphasis on the solid acid–base interactions between IL functional groups and NH_3 . Research into Pebax/IL composites has showed NH_3/N_2 ideal selectivities of over 1800, and NH_3/H_2 selectivities above 200 at ambient conditions, indicating that solubility driven selectivity can be significantly enhanced via chemical functionalization [32]. On the contrary, polymeric membranes experience swelling under high ammonia partial pressures, plasticization and strong performance loss with temperature above $\sim 100\text{--}150\text{ }^\circ\text{C}$ which renders their direct use at synthesis loop conditions technically challenging [28], [30].

Inorganic microporous membranes (such as zeolite-based and silica-based systems) are more thermally and chemically stable than their polymeric equivalents. This is an advantage in terms of compatibility to the production environment for ammonia via the Haber–Bosch process. Faujasite (FAU) zeolite membranes with low Si/Al ratios have been found to produce significant NH_3/N_2 separation factors due to the preferential adsorption of polar ammonia molecules on aluminium rich acid sites present in the micropore channels. [28]. Studies of metal–organic zeolite analogues, such as LTA-type zeolitic imidazolate framework (ZIF-21) membranes have shown NH_3 permeances as high as 1727 GPU with NH_3/N_2 and NH_3/H_2 ideal selectivities of 35 and 12, respectively, with the separations driven by differences in adsorption affinity due to polar–polar interactions between ammonia and the linker channels in ZIFs [33].

However, these optimistic results are combined with moderate zeolite membrane selectivities towards the ternary $\text{NH}_3/\text{H}_2/\text{N}_2$ mixture and relatively unexplored behavior under high-pressure reactive conditions.

Silica and organosilica membranes represent a compelling alternative in this inorganic class due to their tunability of the microporous network and good hydrothermal stability. Silica precursors with polar or acidic functionalities improve NH_3 loading inside the membrane structure. The strong affinity of certain functional groups, such as the Brønsted-acid sulphonic group from membranes prepared from 3-(trihydroxysilyl)-1-propanesulfonic acid (TPS), is clearly important in enhancing ammonia uptake through integration of an acid–base interaction between the basic NH_3 molecule.

Membranes made from TPS have achieved NH_3 permeances of $2.6 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ with NH_3/N_2 selectivities approaching 266 at 300 °C, and are stable under conditions far more representative to the ones used in integrations with membrane reactors [28], [31].

Metal–organic framework (MOF) membranes and mixed-matrix membranes (MMMs)

represent an emerging field with rapid research growth. Pure MOF membranes leverage both the ordered crystalline pore structure and tunable surface chemistry of frameworks like ZIF-8 and UiO-66 to achieve selective transport. This approach is to mix mixed-matrix membranes with MOF particles embedded in a steady polymer membrane aiming at high permeability and selectivity mixing the great classic performance of polymers experienced in industrial applications with well-defined separation characteristics of inorganic fillers [30].

Employing Lewis-acid metal centres or amine-functionalized linkers in the MOF phase can strongly enhance the binding of NH_3 . However, the most serious and common limitation found in almost all the systems based on MOFs is that chemical degradation occurs with ammonia over long time scales especially at relatively high pressures and temperatures, understandably limiting their use for extended periods of operation [28].

Immobilized molten salt (IMS) membranes and nanochannel membranes constitute the latest generation, and represent the most advanced membrane class for high-temperature ammonia separation. In IMS membranes, a molten salt (usually zinc chloride (ZnCl_2)) is trapped in an inorganic support that has high pore volume. The molten salt creates reversible coordination complexes with NH_3 molecules, which allows for facilitated transport across the membrane with exceptional selectivity. At 300 °C, ZnCl_2 -derived IMS membranes have been made to show NH_3 permeance of $6.1 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$, NH_3/N_2 ideal selectivity of 11,375 and NH_3/H_2 selectivity exceeding 10^7 and >99.9% NH_3 purity in the permeate stream along with stable operation for more than 180 hours [31]. Likewise, Na^+ -gated nanochannel membranes gave NH_3/H_2 selectivities as high as 4280 and NH_3/N_2 selectivities over 10,000 at much moderate conditions (250 °C, 35 bar) that is close to the lower bound of industrial synthesis loop operation [34].

These results suggest that IMS and nanochannel membranes are the most promising candidates for successfully integrating into membrane-assisted Haber–Bosch configurations, if long-term stability under cycling pressure and reactive gas environments can be established at pilot scale.

In summary, the status of NH_3 -separative membranes performance reveals an evident trade-off behavior for operating-temperature compatibility vs. separation performances. Polymeric and MOF-based systems are highly selective at room temperature but less so at high temperatures, while

advanced inorganic and IMS-type membranes come close to the loop implementation targets. The current membrane development efforts are motivated by the requirements of co-optimising permeability and selectivity at mid to high temperature (≥ 200 °C), whilst maintaining stability under relevant industrial pressures and gas compositions [28], [30].

3.4 Membrane-Based Concepts for Ammonia Synthesis

The analysis of membrane types presented in the previous section highlights that, among all the classes investigated, two systems stand out as the most technically promising for integration into the Haber–Bosch synthesis loop: immobilized molten salt (IMS) membranes based on ZnCl_2 and Na^+ -gated nanochannel membranes. Although both exhibit exceptional selectivity and thermal compatibility at temperatures relevant to ammonia synthesis, their respective operating pressure ranges lead to fundamentally different integration strategies, making them suitable for distinct process configurations within the synthesis loop.

IMS membranes integrated into membrane reactors. The ZnCl_2 IMS membrane operates primarily at atmospheric or near-atmospheric pressure, a constraint that arises from the liquid nature of the immobilized salt phase: exposure to significant transmembrane pressure differentials risks mechanical displacement of the molten salt from the support pores, compromising both membrane integrity and long-term stability [28], [31]. This pressure limitation, while restrictive from the standpoint of direct loop integration at industrial pressures of 100–300 bar, makes the IMS membrane well suited for application inside a catalytic membrane reactor (CMR) operating at reduced synthesis pressure. In this configuration, the membrane is incorporated directly within the reactor volume, where it continuously removes ammonia from the reaction zone as it is produced. By doing so, the membrane shifts the equilibrium of the exothermic synthesis reaction toward further ammonia formation, in accordance with Le Chatelier's principle, allowing operation at pressures substantially lower than those required in the conventional Haber–Bosch process while maintaining or exceeding the overall nitrogen conversion [30].

Simulation studies of microstructured membrane reactors incorporating ZnCl_2 IMS membranes have confirmed the viability of this approach. At inlet conditions of 613 K and 50 bar with a stoichiometric H_2/N_2 feed, continuous in-situ ammonia removal via the IMS membrane has been shown to yield N_2 conversions of approximately 47%, significantly exceeding the thermodynamic equilibrium conversion of 13.5% achievable without membrane separation under the same conditions [35]. These results underscore the potential of IMS-based membrane reactors to operate as intensified synthesis units, capable of delivering high per-pass conversion at milder pressures,

with direct implications for energy consumption and capital cost reduction relative to conventional high-pressure plants.

Na⁺-gated nanochannel membranes as external separation units. In contrast to the IMS membrane, Na⁺-gated nanochannel membranes are composed of a dense, crystalline NaA-type zeolite layer deposited on an inorganic support, which confers solid-state mechanical robustness and the ability to maintain separation performance under substantially elevated pressures. Experimental demonstrations have confirmed stable NH₃/H₂ selectivities of up to 4,280 and NH₃/N₂ selectivities exceeding 10,000 at temperatures up to 250 °C and pressures up to 35 bar, with no measurable performance degradation observed over 100 hours of continuous operation in ternary NH₃/H₂/N₂ mixtures [33]. This combination of high selectivity, elevated temperature compatibility, and pressure robustness makes the Na⁺-gated membrane uniquely suited for a different integration role: replacement of the energy-intensive cryogenic condensation step currently used in the conventional Haber–Bosch separation loop.

In the conventional process, the reactor effluent gas mixture, which exits the synthesis reactor at 400–500 °C and 100–200 bar, must be cooled to temperatures between –18 and –24 °C to condense and separate ammonia from unreacted hydrogen and nitrogen, before the gases are reheated and recycled [18]. This thermal cycling constitutes a major source of energy loss within the synthesis loop. A membrane-based separation unit operating at high temperature and pressure could in principle intercept the reactor effluent directly, extracting ammonia selectively without the need for deep cooling. The techno-economic analysis conducted by Padinjarekutt et al. estimated that replacing the cryogenic condensation step with a Na⁺-gated nanochannel membrane separation unit could reduce the energy consumption of the ammonia separation section by more than 80%, with a corresponding reduction in production cost of approximately 20% [33]. This result positions the Na⁺-gated membrane as a drop-in replacement for the condensation unit within an otherwise conventional synthesis loop, offering a pathway to significant process intensification without requiring a complete redesign of the reactor system.

The complementarity of these two integration strategies is therefore clear: IMS-based membrane reactors address the conversion side of the process by enabling equilibrium-shifting operation at reduced synthesis pressure, while Na⁺-gated nanochannel membranes target the separation side, replacing the thermodynamically costly condensation step with a high-temperature, pressure-compatible membrane unit. Taken together, these two approaches represent the most technically

mature membrane-based concepts currently available for integration into next-generation Haber–Bosch processes, and they form the basis for the process configurations examined in the following chapter.

4. Membrane-Assisted Process Design and Methodology

The results presented in the previous chapters establish both the limitations of the conventional Haber–Bosch process and the technical potential of membrane-based separation technologies to address them. In particular, the analysis of available membrane types has identified IMS and Na⁺-gated nanochannel membranes as the most promising candidates for integration into the synthesis loop, each suited to a distinct process role. However, translating this potential into quantifiable process improvements requires a structured simulation-based methodology capable of evaluating energy and economic performance under consistent and comparable assumptions.

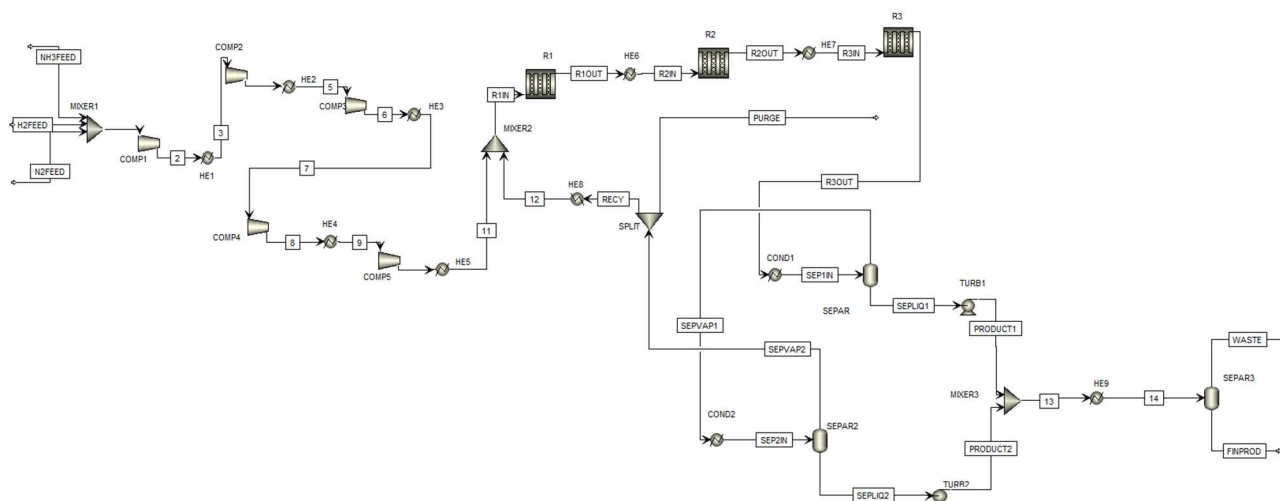
This chapter describes the modelling framework developed in this work to assess the membrane-assisted Haber–Bosch process. The starting point is the construction of a reference simulation model that faithfully reproduces the conventional synthesis loop and serves as the benchmark against which all proposed modifications are evaluated. Building on this reference, the conceptual design of the membrane-integrated process is then introduced, outlining the process modifications, integration logic, and underlying engineering assumptions that define the proposed configuration. Subsequently, the simulation tools and modelling approaches adopted to represent both the conventional units and the membrane separation module are described, together with the main simplifying assumptions that govern the model. Finally, the key performance indicators selected to quantify and compare the energy and economic performance of the two process configurations are defined, providing the evaluation framework used throughout Chapter 5.

4.1 Description of the Reference Haber–Bosch Process

The reference Haber–Bosch process considered in this work is based on a detailed Aspen Plus simulation of the ammonia synthesis loop, reproduced from a validated literature source using the Temkin–Pyzhev kinetic model .

The reaction is modeled assuming a conventional iron-based catalyst system, promoted with Al₂O₃ as a physical (structural) promoter and K₂O as a chemical (electronic) promoter. The presence of Al₂O₃ enhances the mechanical stability and surface area of the catalyst, while K₂O increases catalytic activity by facilitating nitrogen adsorption and weakening the N≡N bond.

Hydrogen and nitrogen are assumed to be available as purified feed streams and are directly introduced into the process, without including upstream production units within the system boundaries.



The process consists of four main sections:

The fresh feed is composed of hydrogen and nitrogen with flow rates of **1004.35 kmol/h and 344.9 kmol/h**, respectively. These values are selected to be close to the **stoichiometric ratio required for ammonia synthesis**, while also accounting for the presence of recycle streams and ensuring sufficient reactant availability throughout the process.

A negligible ammonia stream is also introduced at the inlet to ensure numerical stability in the Aspen Plus simulation, without affecting the overall process behaviour .

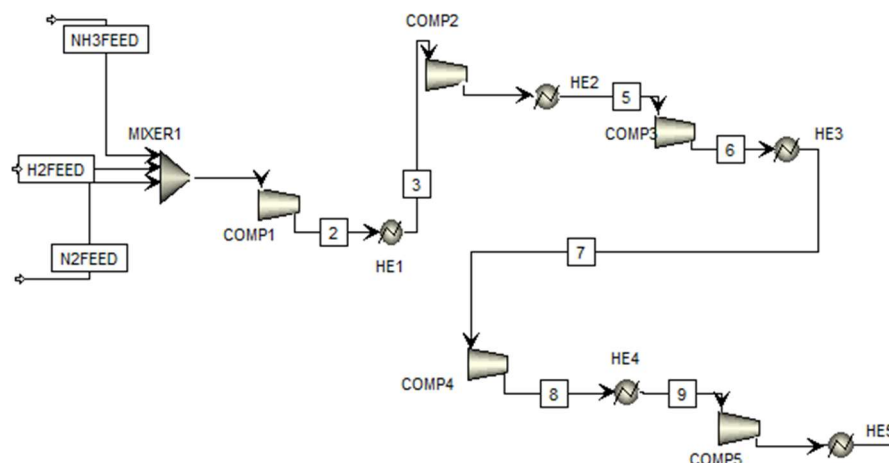


Figure 13. Reactant heating and compression section of the reference Haber–Bosch process

Feed compression and thermal conditioning

The reactants are brought to synthesis conditions through a **multi-stage compression system consisting of five compressors with interstage cooling**. The use of multiple stages is required both for thermodynamic efficiency and for mechanical constraints.

From a thermodynamic point of view, dividing the total pressure increase into several stages allows the compression process to approach an ideal isothermal transformation, thereby reducing the overall compression work. This is achieved by distributing the total compression ratio approximately equally among the stages.

From a mechanical perspective, multi-stage compression is necessary to limit the outlet temperature of each compressor, which must remain below approximately **200 °C**, ensuring safe operation and preventing material degradation .

The pressure is progressively increased from the inlet conditions to the reactor operating pressure of **250 bar** through five stages with nearly constant compression ratios (approximately equal to 2 per stage), following the sequence:

$7 \rightarrow 14 \rightarrow 28 \rightarrow 56 \rightarrow 112 \rightarrow 250$ bar

Between each compression stage, the gas is cooled back to approximately **30 °C**, reducing the work required in subsequent stages and preventing excessive temperature rise.

After compression, the stream is heated up to approximately **450 °C**. Although lower temperatures would thermodynamically favor ammonia formation, a higher operating temperature is selected to ensure sufficiently fast reaction kinetics and consistency with the reference model.

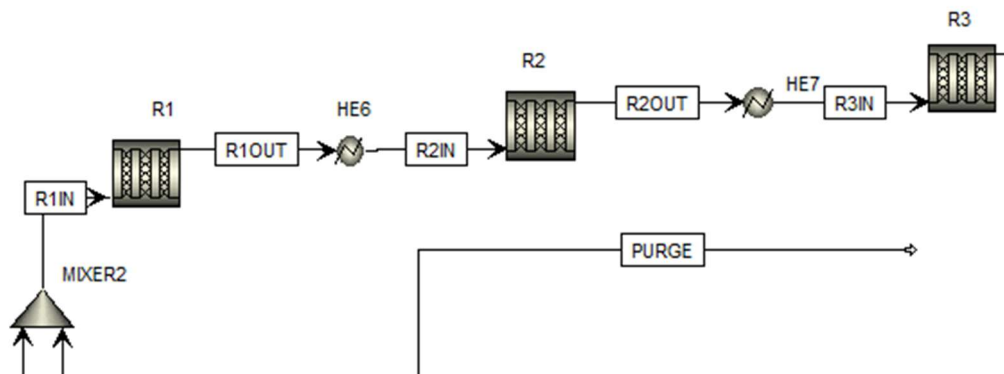
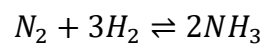


Figure 14. Reaction section of the reference Haber-Bosch process

Ammonia synthesis section

The synthesis section consists of **three plug flow reactors (PFRs) arranged in series**, with increasing dimensions along the reaction path .

The ammonia synthesis reaction is:



The process operates at approximately **450 °C and 250 bar**, conditions selected as a compromise between kinetic and thermodynamic requirements.

The reactors are characterized by the following dimensions:

- **Reactor 1:** length 1.30 m, diameter 0.65 m
- **Reactor 2:** length 2.04 m, diameter 1.02 m
- **Reactor 3:** length 2.64 m, diameter 1.32 m

The progressive increase in reactor size along the series is adopted to provide a longer residence time as the reaction proceeds, allowing the system to approach equilibrium more closely. As the ammonia concentration increases along the reactor sequence, the reaction rate decreases due to thermodynamic limitations. Therefore, larger reactor volumes are required in the downstream stages to sustain further conversion and maximize overall ammonia production.

With this configuration, the conversions are approximately:

11.24% in the first reactor

8.25% in the second reactor

6.01% in the third reactor

This behavior reflects the progressive approach to thermodynamic equilibrium.

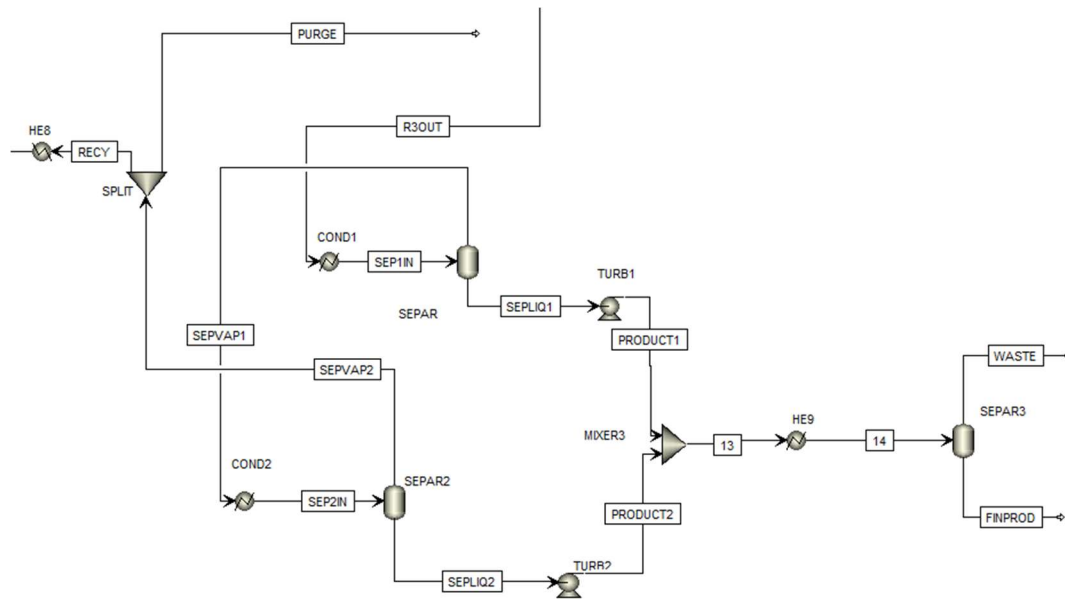


Figure 15. Separation section of the reference Haber–Bosch process.

Cooling and separation section

The reactor outlet stream, containing ammonia together with unreacted hydrogen and nitrogen, is sent to the separation section, where ammonia is recovered through two consecutive condensation stages.

In the first stage, the reactor effluent is cooled to approximately $-20\text{ }^{\circ}\text{C}$ while maintaining the synthesis pressure at 250 bar. Under these conditions, part of the ammonia condenses and is separated from the gaseous phase through a flash separator.

The remaining vapor stream, which still contains a considerable amount of ammonia together with hydrogen and nitrogen, is then sent directly to a second condensation stage operating at the same pressure level. Here, the temperature is further reduced to approximately $-30\text{ }^{\circ}\text{C}$ in order to recover additional ammonia and increase the overall separation efficiency.

The liquid streams obtained from the two condensation stages are then mixed and expanded to final storage conditions of approximately $-30\text{ }^{\circ}\text{C}$ and 3 bar. These conditions were selected as a compromise between refrigeration requirements and storage pressure. Lower pressures would require further cooling to maintain ammonia in liquid phase, increasing the refrigeration duty of the

process. At the same time, although ammonia can also be stored at significantly higher pressures, lower storage pressures are generally preferred from a transport and handling point of view.

After the expansion step, the resulting mixture was found to be partially vaporized because of the vapor–liquid equilibrium behaviour of the system. For this reason, an additional flash separator was introduced in order to separate the liquid ammonia product from the remaining vapor fraction. The vapor stream leaving the final separator was not recycled back to the synthesis loop. Even though this stream still contains a certain amount of ammonia, recovering it through additional separation stages was considered energetically inconvenient compared to the relatively small amount of ammonia that could still be obtained. Moreover, recycling this stream would require recompression up to the reactor operating pressure of 250 bar and would also reintroduce ammonia into the synthesis loop, negatively affecting the conversion achieved inside the reactors because of equilibrium limitations.

The remaining gaseous stream from the main separation section, mainly composed of unreacted hydrogen and nitrogen, is instead recycled back to the synthesis loop in order to improve the overall utilization of the reactants.

Recycle loop

Due to the limited single-pass conversion, the unreacted hydrogen and nitrogen are recycled back to the reactor inlet. This recycle loop is essential to achieve high overall conversion and efficient utilization of the reactants.

The recycle stream is recompressed, mixed with the fresh feed, and reintroduced into the synthesis section. The presence of ammonia in the recycle stream influences the inlet composition of the reactors and contributes to limiting the achievable conversion due to equilibrium effects.

In industrial Haber–Bosch processes, a purge stream is typically required to prevent the accumulation of inert species within the synthesis loop. Although the present system considers only hydrogen and nitrogen as feed components, and therefore does not inherently require a purge, a small purge stream is nevertheless included to reproduce a more realistic industrial configuration. In particular, a purge fraction of approximately **2%** is adopted, consistent with conventional industrial practice, ensuring stable operation while having a negligible impact on the overall mass balance.

Process performance and limitations

Under the selected operating conditions, the process produces approximately **12 t/h of ammonia with a purity of 99.9%** .

The structure of the process is dictated by fundamental thermodynamic and kinetic constraints:

- high pressure is required to favor ammonia formation
- high temperature is necessary to ensure acceptable reaction rates
- low single-pass conversion requires the implementation of a recycle loop

In addition, the separation step based on ammonia condensation is energy-intensive and plays a key role in determining both the recycle composition and the overall process efficiency.

4.2 Conceptual Design of the Membrane-Integrated Process

Starting from the conventional Haber–Bosch process described in the previous section, a modified configuration including a membrane separation unit was developed. As discussed in Chapter 3, both immobilized molten salt (IMS) membranes and Na^+ -gated nanochannel membranes were initially considered as possible candidates for ammonia separation. However, the Na^+ -gated membrane was selected for this work because of its higher mechanical stability and its compatibility with relatively high-pressure operating conditions. IMS membranes were also considered during the preliminary evaluation phase. However, in order to operate within the typical pressure range of the membrane, a significant pressure reduction would be required. This pressure decrease would also lead to a reduction in stream temperature, causing the process conditions to fall below the minimum temperature required to maintain the immobilized molten salt phase in its operating state. As a consequence, an additional heating stage would be necessary after depressurization in order to restore suitable operating conditions for the membrane, making the overall configuration energetically unfavorable for the present process design. For this reason, IMS membranes were considered more suitable for applications closer to the reactor section, where higher operating temperatures can be maintained more easily.

The reactant preparation and reaction sections remain essentially unchanged compared to the reference process. Hydrogen and nitrogen are compressed and heated to the operating conditions required for ammonia synthesis before entering the three-reactor synthesis loop with intermediate cooling between each reactor stage. Therefore, the main modification introduced in this configuration concerns the ammonia separation section.

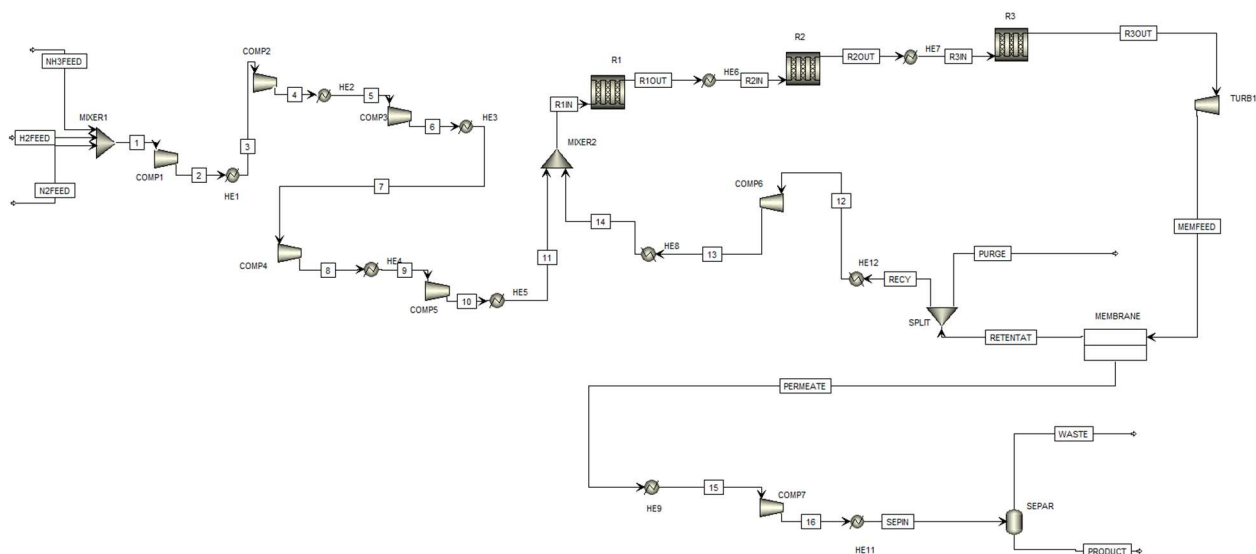


Figure 16. Flowsheet of the membrane-assisted Haber–Bosch process configuration

In the reference configuration, ammonia recovery is achieved through a two-stage condensation system. In the membrane-assisted configuration, the first condensation stage is replaced by a membrane separation unit. After leaving the third reactor, the process stream pressure is varied from 250 bar to lower values before entering the membrane module.

In the present work, IMS and Na^+ -based membranes were considered as representative state-of-the-art technologies for ammonia separation. However, the objective of this study is not to reproduce the exact operating limits of currently available membranes, but rather to perform a more exploratory analysis aimed at identifying favourable operating regions for membrane-assisted ammonia synthesis.

For this reason, different operating conditions were investigated through sensitivity analyses in order to evaluate their influence on process performance and to assess whether currently available membrane technologies could potentially be adapted to industrial Haber–Bosch conditions.

The associated pressure reduction also leads to a decrease in temperature, allowing the stream conditions to approach the operating range considered suitable for ammonia-selective membranes. It also represents a compromise between ammonia recovery, membrane area, and downstream compression requirements. Higher feed pressures increase the driving force for ammonia permeation, allowing higher recovery for the same membrane area.

The membrane properties adopted in the model were selected according to values reported in the literature for Na⁺-gated membranes. In particular, an NH₃/H₂ selectivity of approximately 4000 and an NH₃/N₂ selectivity close to 10000 were considered, together with an ammonia permeance of 250 GPU. Using these membrane properties, a permeate stream containing approximately 99% ammonia was obtained while imposing an ammonia recovery of 96%. The membrane area was then calculated accordingly in order to satisfy the selected recovery target.

Inside the membrane module, ammonia is selectively separated from the reactor effluent, while the retentate stream, mainly composed of unreacted hydrogen and nitrogen, is recycled back to the synthesis loop together with the fresh feed streams. Similarly to the reference configuration, a purge stream was maintained inside the loop.

Although the membrane shows very high selectivity values, and the permeate stream reaches a high ammonia purity, direct ammonia condensation at atmospheric pressure would still require excessively low temperatures. In fact, even cooling the permeate stream down to approximately −33 °C at 1 bar would still result in a partially vaporized mixture because of the residual presence of hydrogen and nitrogen.

For this reason, the ammonia-rich permeate stream leaving the membrane is first cooled to approximately 30 °C while maintaining the permeate pressure close to 1 bar. The stream is then compressed up and cooled before entering a flash separator in order to reach the desired recovery. Under these conditions, most of the ammonia condenses and is recovered as a liquid product stream, while the remaining gaseous phase, mainly composed of hydrogen, nitrogen, and residual ammonia, is separated in the flash unit.

The vapor stream leaving the separator was not recycled back to the synthesis loop. Although it still contains a certain amount of ammonia, recycling this stream would require recompression back to the reactor operating pressure, increasing the overall energy consumption of the process. Moreover, reintroducing ammonia into the recycle loop would negatively affect the conversion achieved inside the reactors because of equilibrium limitations.

Even with the additional condensation stage, the cooling duty required in this configuration is still expected to be lower compared to the conventional Haber–Bosch process, since only the ammonia-rich permeate stream must be cooled instead of the entire reactor outlet stream. Overall, this configuration allows part of the ammonia to be removed directly through the membrane unit while reducing the dependence on deep cryogenic separation and maintaining efficient reactant recycling within the synthesis loop.

4.3 Simulation Tools and Assumptions

The development of both the conventional Haber–Bosch process and the membrane-integrated configuration required the use of simulation software capable of reproducing the thermodynamic, kinetic, and energetic behaviour of the system.

The reference process was mainly simulated using Aspen Plus® V15, which is widely used for the modelling of industrial chemical processes. Aspen Plus allowed the construction of the entire process flowsheet, including compressors, heat exchangers, reactors, separators, recycle loops, and auxiliary units. The simulation results were then exported to Excel spreadsheets in order to analyse the trends of the main process variables and evaluate the overall energy and economic performance of the system.

For the membrane-assisted configuration, the work started from a theoretical basis taken from the literature together with preliminary models already available within the research laboratory. In particular, the membrane separation unit was initially developed using Aspen Custom Modeler® (ACM), which allows the implementation of customized models for unit operations that are not directly available in Aspen Plus. Once the membrane model was completed, it was integrated into Aspen Plus in order to simulate the entire membrane-assisted process.

In both configurations, Aspen Energy Analyzer® was also used to evaluate the thermal integration of the process and to analyse the main heat duties associated with the heat exchangers present in the synthesis loop and separation section.

The ammonia synthesis reaction was described using the Temkin–Pyzhev kinetic model, which is commonly adopted for the simulation of Haber–Bosch systems employing iron-based catalysts. This model allows a realistic representation of the reaction behaviour under the high-pressure and high-temperature conditions typical of industrial ammonia synthesis.

From a thermodynamic point of view, the Peng–Robinson equation of state was selected as the property method. This model is particularly suitable for non-ideal gaseous mixtures operating at high pressure and provides a reliable description of the phase equilibrium behaviour of hydrogen, nitrogen, and ammonia mixtures.

The entire process was analysed under steady-state conditions, while the synthesis reactors were modelled as Plug Flow Reactors (PFRs), consistently with the reactor configurations typically adopted in industrial ammonia production.

To simplify the numerical solution of the model and reduce computational complexity, pressure drops across equipment and pipelines were neglected. Although pressure losses are present in real industrial systems, this assumption allowed the analysis to focus mainly on the effects of membrane integration on the overall process performance without introducing additional convergence difficulties.

Regarding the membrane separation section, the membrane module was modelled by discretizing the permeation zone into a fixed number of cells. This approach improves the accuracy of the model by allowing a better representation of local transport phenomena and composition variations along the membrane length. However, an excessively high number of cells generated convergence problems within the simulation environment, especially due to the presence of the internal recycle loop. For this reason, a compromise number of cells was selected in order to maintain both numerical stability and satisfactory prediction accuracy.

The membrane model was developed by implementing the governing permeation and mass balance equations for each discretization cell. The model uses as input the membrane area, operating pressure, ammonia permeance, and membrane selectivities toward hydrogen and nitrogen. Based on these parameters, the permeation rate of each component is calculated for every cell of the membrane module.

For each species i , the permeated molar flow rate is calculated according to:

$$\dot{n}_{i,perm} = P_i \cdot A \cdot (p_{i,f} - p_{i,p})$$

where $\dot{n}_{i,perm}$ is the permeated molar flow rate, P_i is the permeance of species i , A is the membrane area associated with the cell, and $p_{i,f}$ and $p_{i,p}$ are the partial pressures on the feed and permeate sides, respectively.

The permeances of hydrogen and nitrogen are obtained from the ammonia permeance and the corresponding membrane selectivities:

$$P_{H_2} = \frac{P_{NH_3}}{\alpha_{NH_3/H_2}}$$

$$P_{N_2} = \frac{P_{NH_3}}{\alpha_{NH_3/N_2}}$$

For each discretization element, the retentate stream is calculated through a component mass balance:

$$\dot{n}_{i,ret} = \dot{n}_{i,feed} - \dot{n}_{i,perm}$$

The retentate leaving a given cell is subsequently used as the feed stream for the following cell:

$$\dot{n}_{i,feed}^{j+1} = \dot{n}_{i,ret}^j$$

where j denotes the cell index. In this way, the model accounts for the progressive removal of ammonia and the resulting variation in gas composition and partial pressures along the membrane length.

To ensure numerical stability and avoid non-physical solutions, upper and lower bounds were assigned to the main model variables using the variable library available in Aspen Custom Modeler. Thermodynamic property calculations were incorporated through the Aspen property package interface, allowing the model to update gas properties consistently throughout the simulation. Finally, isothermal operation was assumed, and the same temperature was imposed on both the feed and permeate sides of the membrane module.

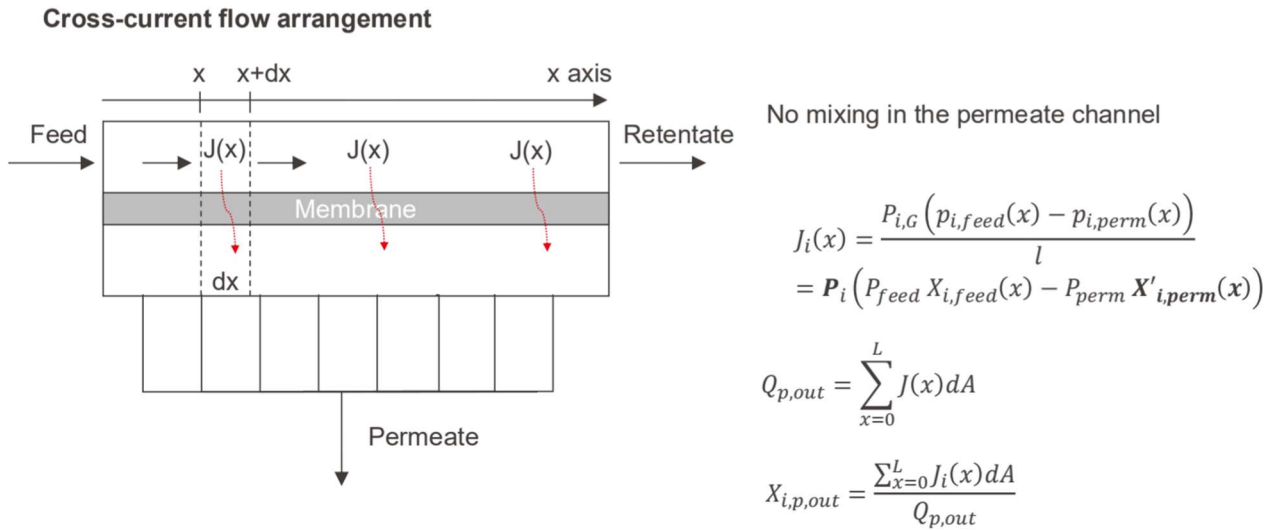


Figure 17. Cross-current membrane model adopted for the simulation of ammonia separation

Furthermore, additional simplifying assumptions were adopted during the simulations. Membrane fouling and long-term membrane degradation phenomena were neglected, while the hydrogen and nitrogen feed streams were assumed to be perfectly purified before entering the synthesis loop. Moreover, heat losses to the external environment were not considered. No chemical reactions were assumed to occur within the membrane module, as the separation unit was exclusively devoted to species permeation. Membrane permeance and selectivity were assumed to remain uniform over the

entire membrane surface, with no spatial variations in membrane properties. Furthermore, ideal plug-flow behaviour was assumed on the feed side of the membrane, neglecting any axial back-mixing effects.

4.4 Key Performance Indicators

In order to compare the conventional Haber–Bosch process with the membrane-assisted configuration, several performance indicators were considered. The analysis focused not only on the energy performance of the process, but also on how the membrane integration affects the behaviour of the synthesis loop and the recycle stream composition.

Since the reactor section was kept identical to the reference configuration, particular attention was given to the variation of the overall conversion depending on the separation strategy adopted. In particular, the ammonia concentration inside the recycle stream was monitored, since higher ammonia contents in the recycle loop negatively affect the conversion achieved inside the reactors because of thermodynamic equilibrium limitations. For this reason, the effect of the membrane separation on the recycle composition represented one of the main aspects investigated during the simulations.

The recycle flow rate was also evaluated in order to understand how the membrane integration influences the circulation of unreacted hydrogen and nitrogen inside the synthesis loop. Variations in recycle composition and recycle flow rate can directly affect reactor performance, separation efficiency, and the overall energy demand of the process.

Particular attention was also given to the total ammonia production obtained under the selected operating conditions, together with the final ammonia purity achieved by the different separation configurations. These parameters are especially important because the ammonia purity directly influences the downstream condensation and storage conditions.

The membrane separation section was mainly analysed in terms of ammonia recovery, permeate purity, and membrane area requirements. The influence of membrane selectivity on the achievable ammonia purity was investigated in order to identify the separation targets required to obtain suitable downstream operating conditions. Since the permeate stream still contains residual hydrogen and nitrogen, the effect of ammonia purity on the condensation temperature required in the second separation stage was also considered.

The effect of membrane permeance was evaluated as well, mainly because of its direct relation with the membrane area required for the separation process. The trade-off between permeance and membrane area was therefore considered an important aspect not only from an energy point of view, but also from a potential economic perspective.

From an energy point of view, the main contributions associated with cooling duties, refrigeration requirements, heating duties, and compression work were analysed for both process configurations. Particular attention was given to the additional recompression required after the membrane separation stage and to its impact on the overall process energy demand. Possible alternative configurations aimed at reducing the recompression penalty were also considered and will be discussed in the following chapters.

In addition to the total energy demand, the specific energy consumption referred to ammonia production was also considered in order to provide a more consistent comparison between the two process configurations.

Overall, the analysis of these parameters allows a direct comparison between the conventional Haber–Bosch process and the membrane-assisted configuration, providing a better understanding of the potential advantages and limitations associated with membrane integration inside the synthesis loop.

5. Results and Discussion

After defining the process parameters and operating conditions, a series of sensitivity analyses were carried out in order to evaluate the evolution of the process under different operating scenarios. The objective of these analyses was to identify the key process performance indicators (KPIs) and determine the conditions under which the system could achieve advantages in terms of energy consumption and economic performance, while also identifying the most suitable characteristics required for the implementation of a membrane-assisted process capable of competing with the conventional Haber–Bosch process.

The investigated variables and monitored performance indicators are summarized in Table 5.

Process Section	Variable Investigated	Parameters Varied	Performance Indicators Monitored
Reference Process	Feed composition	H ₂ /N ₂ ratio	Overall conversion, conversion in each reactor
Reference Process	Reactor feed composition	NH ₃ concentration in Reactor 1 feed	Overall conversion, conversion in each reactor
Reference Process	Separation section	First condenser temperature	Cooling duty, NH ₃ concentration in recycle stream
Membrane Process	Membrane selectivity	NH ₃ /H ₂ selectivity	NH ₃ recovery, recycle stream composition
Membrane Process	Membrane permeance	NH ₃ permeance	Required membrane area
Membrane Process	Operating pressure	Membrane feed pressure	Compression duty, cooling duty, electricity consumption
Membrane Process	Operating temperature	Membrane feed temperature	Heating duty, cooling duty, overall energy consumption
Membrane Process	Membrane lifetime, Membrane cost	Membrane lifetime, Membrane unit cost	Annualized membrane cost

Table 5. Summary of the Sensitivity Analyses Performed

The conventional Haber–Bosch process was first analysed in order to identify its main limitations and characteristic operating features. Based on the results obtained from this reference configuration, further analyses were subsequently performed on the membrane-integrated process. Additional investigations were conducted to evaluate its energetic and economic feasibility, as well as to identify the main limiting factors and the trade-offs associated with the implementation of such a process configuration.

Overall, the present work represents an exploratory study aimed at investigating new process intensification opportunities arising from the use of selective membranes for ammonia recovery and optimization of the conventional ammonia synthesis loop.

5.1 Reference Case: Conventional Haber–Bosch Process

The reference process was analysed in order to investigate its main limitations and identify the operating conditions affecting process performance. Starting from pure hydrogen and nitrogen streams, as previously described in Chapter 4, ammonia is produced using three plug flow reactors (PFRs) arranged in series with progressively increasing reactor volumes. This configuration was selected to promote longer residence times and consequently higher conversion values, in agreement with the scientific literature. A recycle loop is included to allow the recirculation of unreacted reactants, thereby reducing operating costs.

Finally, a separation section is implemented in order to recover ammonia, while part of the process stream is purged from the system. Under these operating conditions, the process is capable of producing approximately 12 tons per hour of ammonia with a final purity of 99.9%.

Based on the described configuration, several analyses were carried out with the aim of identifying the main process KPIs and evaluating their influence on the overall process performance.

The first analysis focused on the hydrogen-to-nitrogen ratio. In particular, the hydrogen feed flowrate was varied in order to investigate its effect on the process behaviour. Starting from the previously defined operating conditions (1004 kmol/h of hydrogen and 344 kmol/h of nitrogen), the hydrogen flowrate was progressively modified, leading to the trend shown below.

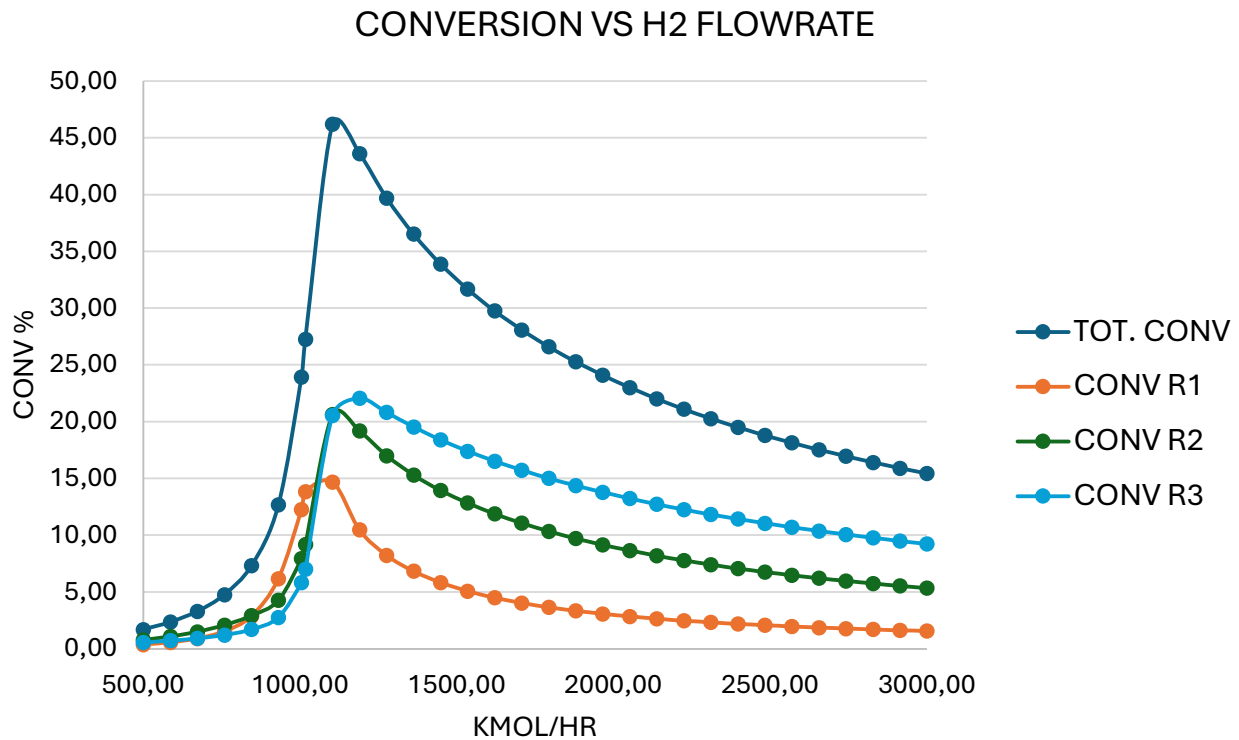


Figure 18. Conversion vs H_2 Flowrate

As can be observed from the obtained trends, increasing the hydrogen-to-nitrogen ratio leads to an increase in conversion, reaching maximum values for compositions close to the stoichiometric H_2/N_2 ratio of 3:1. Under these conditions, a maximum overall conversion of approximately 46% was achieved. Moving away from this ratio resulted in a progressive decrease in conversion across all three reactors, reaching minimum overall conversion values close to 15%. It can be observed that, beyond a certain point, higher conversion values are achieved in reactors 2 and 3. As the hydrogen flow rate increases, the conversion rises in all three reactors. However, due to the progressively larger reactor volumes, higher conversion values are attained in the larger reactors. In addition, the conversion is influenced by the ammonia concentration, which becomes lower at higher hydrogen flow rates, further contributing to the increase in conversion.

These results highlight how the hydrogen-to-nitrogen ratio significantly affects not only the overall process conversion but also the behaviour of each individual reactor within the synthesis loop. In particular, the analyses confirmed that an H_2/N_2 ratio close to 3:1 is the most favourable condition for achieving maximum conversion.

Subsequently, an additional analysis was carried out in order to investigate the effect of ammonia concentration in the feed stream entering the first reactor. In this case, the ammonia flowrate was varied in order to evaluate its impact on the overall conversion behaviour of the process.

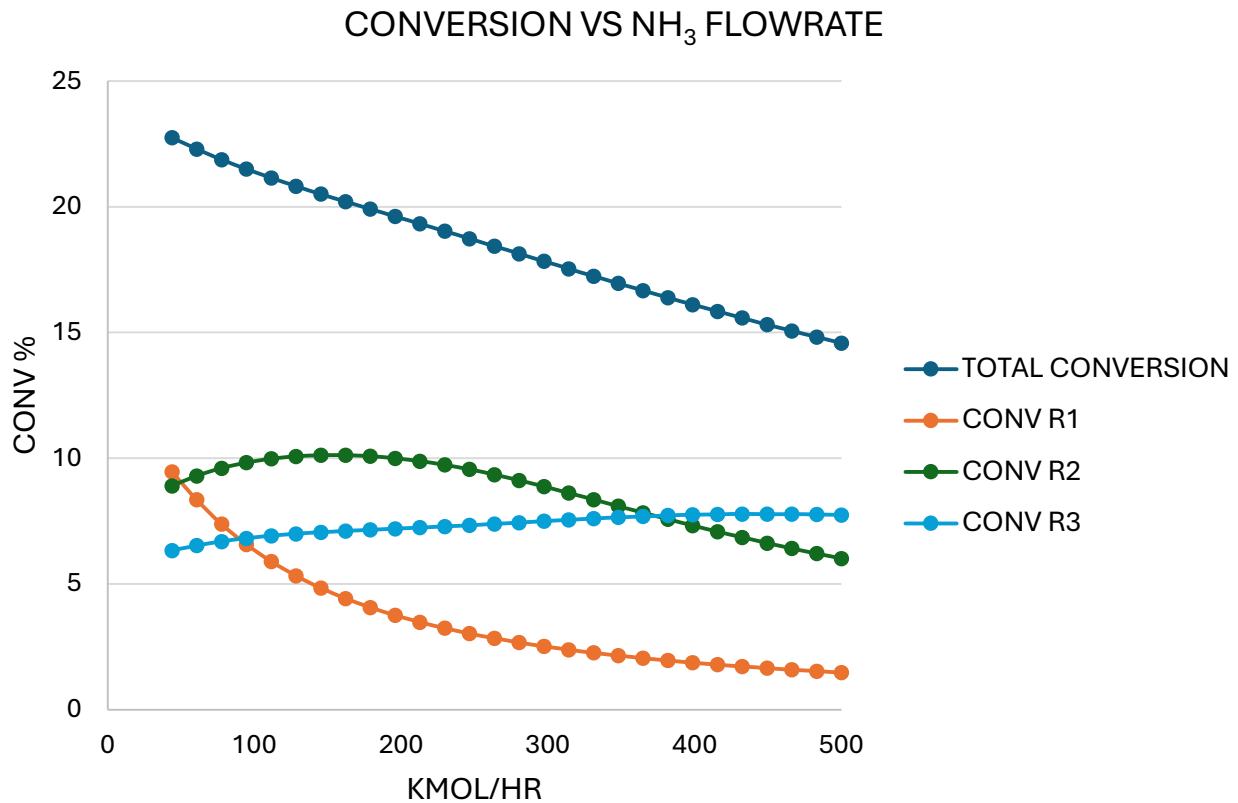


Figure 19. Conversion vs NH_3 Flowrate

The obtained results show that increasing the ammonia concentration in the feed stream entering the first reactor leads to a significant decrease in overall conversion. In particular, while the total conversion exhibits a strongly decreasing trend, the behaviour of the individual reactors differs.

The first reactor shows a simple parabolic decrease in conversion as the ammonia concentration increases. In the second reactor, a slight increase in conversion is initially observed, likely due to the lower conversion achieved in the first reactor, followed by a subsequent decrease. A similar slight increase is also observed in the third reactor. Nevertheless, in all cases, the overall conversion stabilizes at significantly lower values compared to the reference condition.

These results highlight the importance of achieving efficient ammonia separation in order to avoid contamination of the feed stream entering the first reactor. An inefficient separation stage would not only reduce the overall conversion but also lead to a substantially larger recycle stream, consequently increasing the overall energy demand of the process. Therefore, the analyses confirmed that both separation efficiency and operating separation conditions strongly influence the overall process performance and energetic efficiency.

Subsequently, the condensation temperature in the first condenser located downstream of the third reactor was varied in order to evaluate its effect on the energy demand of the two heat exchangers. The analysis was performed not only in terms of the overall energy consumption, but also to investigate how the energy duty was distributed between the two units under different operating conditions.

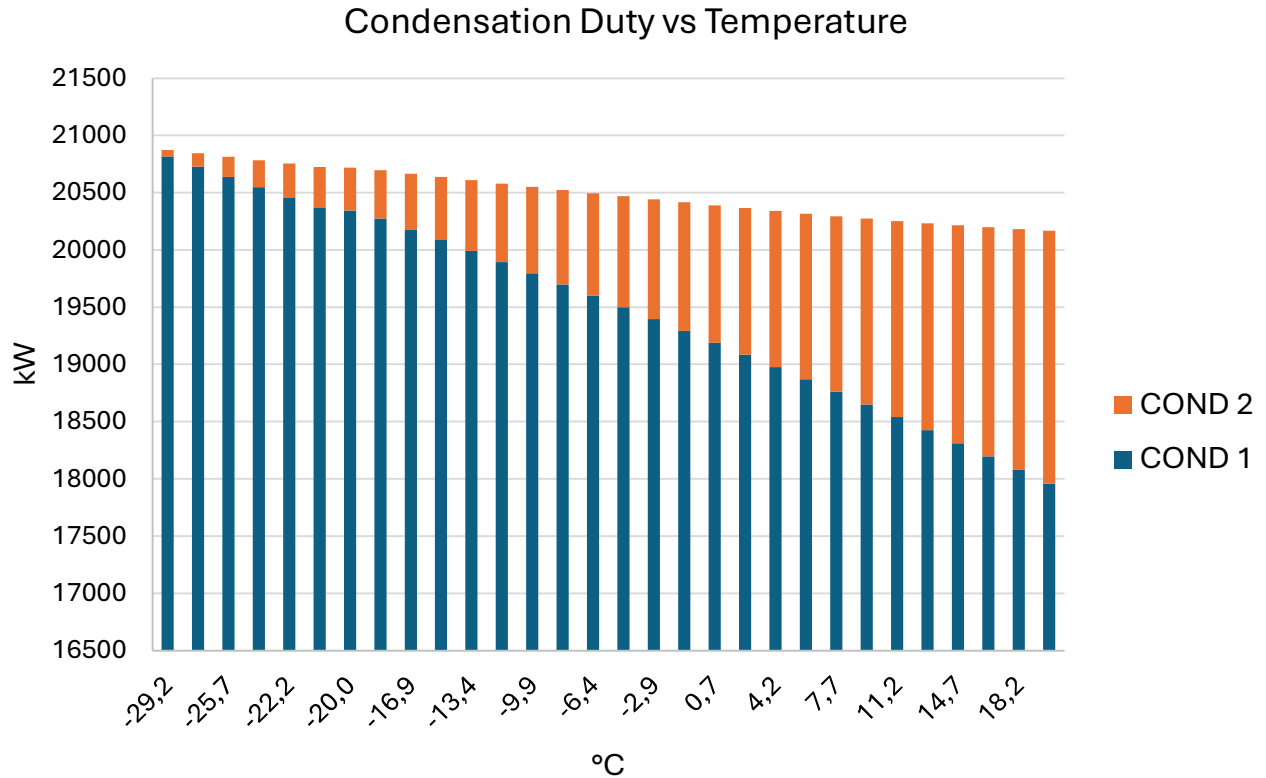


Figure 20. Condensation Duty vs Temperature

The obtained results show how variations in the operating temperature of the first condenser directly affect the energy required within the separation section. As expected, performing the first separation stage at higher temperatures leads to lower energy consumption in the first condenser. However, this reduction is compensated by an increase in the energy required in the second condenser.

The presence of a double-stage condensation and separation configuration therefore provides greater operational flexibility for the process. Although the variation in condenser temperature slightly affects the total thermal energy required by the two condensers, the most relevant aspect is the possibility of adopting different process configurations while maintaining similar overall process performances.

In all investigated cases, the main thermal energy consumption within the separation section was associated with the two condensers and with the heat exchanger located on the recycle stream, which is required to restore the process temperature to approximately 450 °C before entering the synthesis loop again.

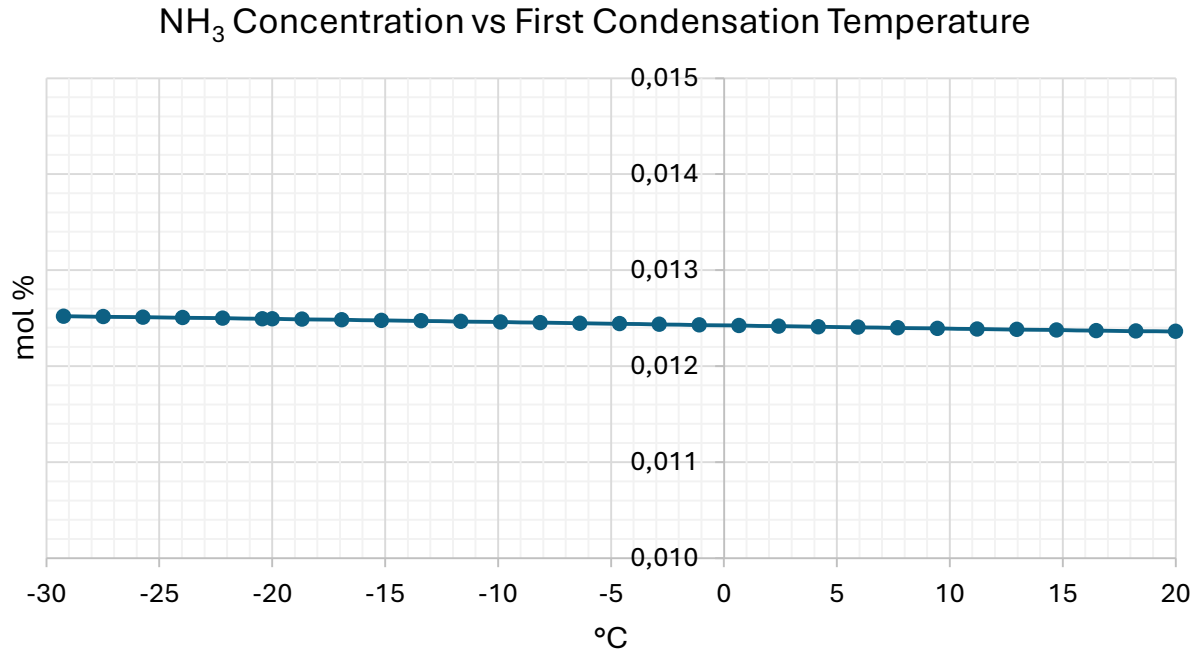


Figure 21. NH₃ Concentration vs First Condensation Temperature

The results also show that the temperature of the first condensation stage has only a limited effect on the ammonia concentration within the recycle stream. This behaviour was expected, since variations in the first condensation temperature are partially compensated by the presence of the second condenser, which removes most of the remaining ammonia from the process stream.

Energy Use Details								
		Current [cal/sec]	Target [cal/sec]	Saving Potential [cal/sec]	Energy Cost Savings [\$/Yr]	Energy Cost Savings [%]	ΔTmin [C]	Status
▶	Fired Heat (1000)	3,48E+06	0	3,48E+06	1.953.903	100,00	25,0	
▶	Total Hot Utilities	3,48E+06	0	3,48E+06	1.953.903	100,00		✓
▶	HP Steam Generation	1,862E+06	2,511E+06	-6,482E+05	213.261	34,81	10,0	
▶	Cooling Water	9,78E+05	1,538E+06	-5,604E+05	-15.731	-57,30	5,0	
▶	Refrigerant 2	1,241E+05	1,242E+05	-32,37	-14	-0,03	3,0	
▶	Refrigerant 1	4,859E+06	1,697E+05	4,689E+06	1.696.755	96,51	3,0	
▶	Total Cold Utilities	7,823E+06	4,343E+06	3,48E+06	1.894.271	154,25		✓

Table 6. Energy Consumption Traditional HB

The utility savings reported by Aspen are calculated by comparing the current process configuration with the thermally integrated target configuration obtained through pinch analysis. The results show that thermal integration significantly reduces the demand for Refrigerant 1, while slightly increasing the consumption of Refrigerant 2 and cooling water. At the same time, the recovered process heat completely satisfies the heating requirements previously supplied by external hot utilities and enables additional high-pressure steam generation. Overall, the integration strategy leads to a more efficient utilization of the available thermal energy and a reduction in utility-related operating costs.

Under these operating conditions, the process allows an effective thermal integration strategy capable of recovering all the energy required for the heating stages, consequently reducing the overall cooling demand. Furthermore, the process configuration enables the production of high-pressure steam, providing benefits not only from an energetic point of view but also in terms of overall economic savings.

	Name	Fluid	Rate	Rate Units	Cost per Hour	Cost Units
►	Electricity		5929,18	KW	459,512	USD/H
►	Cooling Water	Water	0,243302	MMGAL/H	29,1962	USD/H
►	Refrigerant - Propane	Refrigerant	9,70529	KLB/H	0,281453	USD/H
►	Refrigerant - Freon 12	Refrigerant	979,209	KLB/H	83,2328	USD/H

Table 7. Utilities Cost Traditional HB

The economic evaluation of both capital and operating costs was carried out using the Aspen Process Economic Analyzer extension integrated within Aspen Plus.

Assuming continuous plant operation throughout the year (24 h/day, 365 days/year) and a utility cost of approximately **572 USD/h**, as estimated by Aspen Plus, the total annual utility cost amounts to approximately **5 million USD per year**, including both thermal and electrical energy consumption. Furthermore, it can be observed that the largest contribution to the utility cost is associated with electricity consumption, which is more than four times higher than the cost related to thermal energy requirements.

A partial reduction in utility expenses was achieved thanks to the generation of high-pressure steam as a by-product of the process, resulting in an estimated annual saving of approximately 213 thousand USD.

Parameter	Value
NH₃ production	~12 t/h
NH₃ purity	99.9%
Reactor configuration	3 PFR reactors in series
Reactor pressure	250 bar
Reactor inlet temperature	450 °C
H₂/N₂ feed ratio	~3:1
Purge fraction	2%
Total overall conversion	23.96 %
Total recycle flowrate	35.2 t/h
Total refrigeration duty	18,2 MW
Total compression duty	5.9 MW
Total utility cost	5 M\$/year

Table 8. Overall Performance Traditional HB

5.2 Effect of Membrane Integration

The integration of a membrane separation process introduces different effects on the overall process in terms of both thermal and electrical energy consumption. Several alternative configurations are currently under development for the implementation of membrane-based separation systems, mainly due to the operating conditions required by the process itself. For this reason, several analyses were carried out on the membrane-assisted configuration in order to identify the key parameters governing membrane integration.

First of all, the membrane affects both process conversion and yield. This behaviour derives from its separation capabilities, which are indirectly influenced by the membrane selectivity towards hydrogen and nitrogen. In addition, ammonia permeance also represents an important parameter to be monitored. Literature studies have shown that membrane systems typically involve a trade-off between the permeance of the desired product and the selectivity towards the other components of the mixture.

In this new process configuration, the membrane represents the only unit influencing the ammonia concentration within the recycle stream, since the separated permeate is entirely sent to a condensation process, while the vapor fraction remaining after separation is subsequently purged from the system.

To evaluate the impact of membrane selectivity, a sensitivity analysis was performed by varying the ammonia selectivity with respect to hydrogen while keeping the ammonia-to-nitrogen selectivity fixed at 10,000, as reported in the literature for Na⁺-gated membranes. This choice was made considering that ammonia selectivity is typically lower with respect to hydrogen than nitrogen. Furthermore, since the process feed contains approximately three times more hydrogen than nitrogen, variations in ammonia-to-hydrogen selectivity are expected to have a more pronounced impact on the overall separation performance.

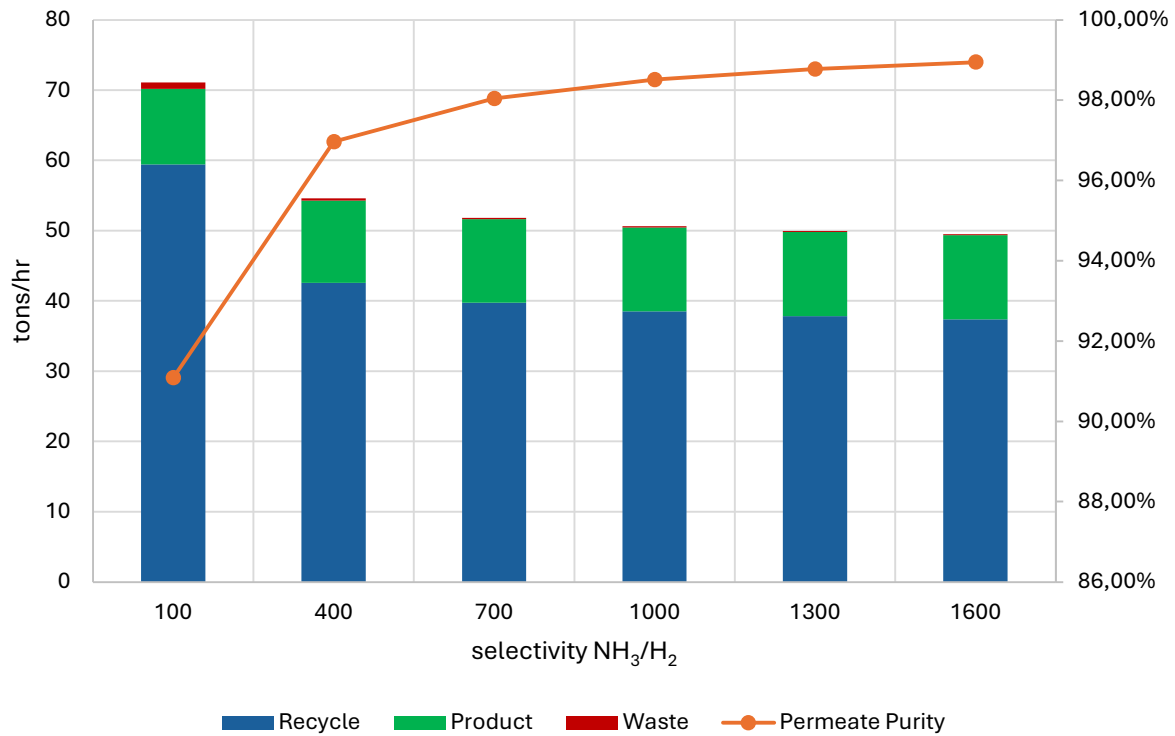


Figure 22. Impact of Selectivity

The next step was to analyze the impact of ammonia permeance on the membrane area required to achieve the separation target, while maintaining a fixed ammonia recovery of 96%.

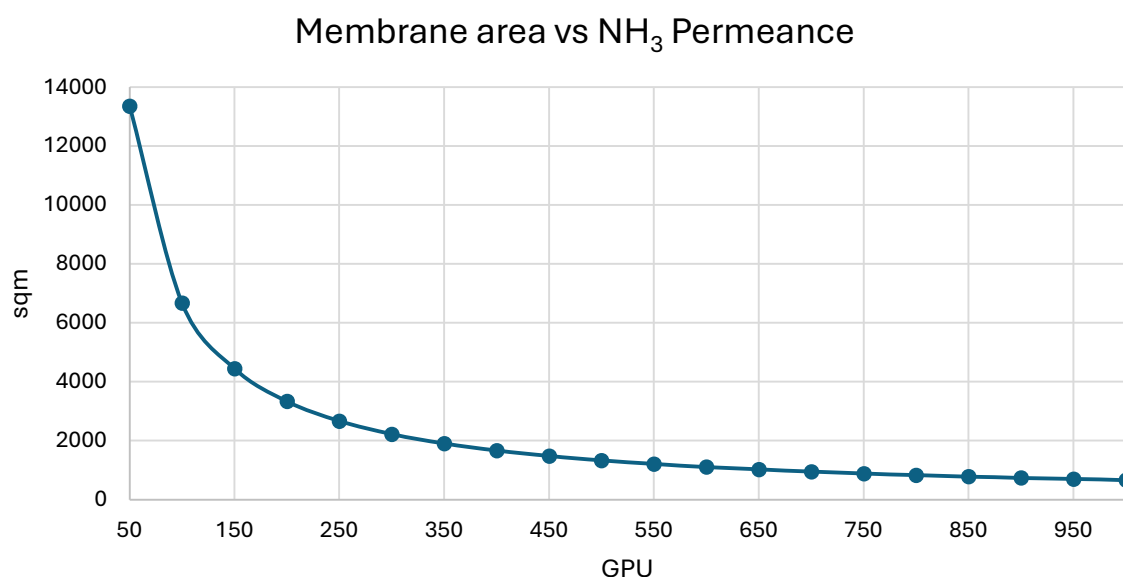


Figure 23. Membrane area vs NH_3 Permeance

From the graph, it can be observed that ammonia permeance has a more pronounced effect at lower values, while a plateau is reached at approximately 350 GPU, beyond which further increases in permeance result in only marginal reductions in the required membrane area. Both sensitivity analyses on selectivity and permeance were carried out considering a permeate pressure of 3 bar and a feed pressure of 250 bar.

5.3 Energy Efficiency Improvements

With regard to energy efficiency, several process configurations were investigated by varying the key operating parameters and evaluating their impact on overall process performance.

First, the possibility of expanding the stream leaving the third reactor followed by recompression after the membrane separation unit was analyzed, with the aim of maintaining the original reaction conditions. A key constraint was the requirement to keep the compressor inlet temperature below 200 °C in order to prevent equipment damage. This necessitated an additional cooling step, which increased the overall energy demand of the process.

The obtained results showed that the expansion stage reduced the thermal duty associated with the heat exchanger located downstream of the third reactor while simultaneously enabling energy recovery through the turbine. However, the positive effect of energy recovery was entirely offset by the energy required for recompression, which is inherently more energy-intensive than the amount recoverable through expansion. Furthermore, neither the turbine nor the compressor operates at 100% efficiency, resulting in additional energy losses in the form of heat.

The energy analysis revealed that decreasing the membrane operating pressure significantly increases the energy required for recompression to the reaction pressure of 250 bar. The compression duty increased from approximately 6.8 MW for membrane operation at 200 bar to about 12 MW when separation was performed at 50 bar.

While electricity consumption decreases as the membrane operating pressure increases, the thermal energy demand exhibits a slight increase, rising from 17.9 MW to 18.9 MW when moving from the 50 bar configuration to the 200 bar configuration.

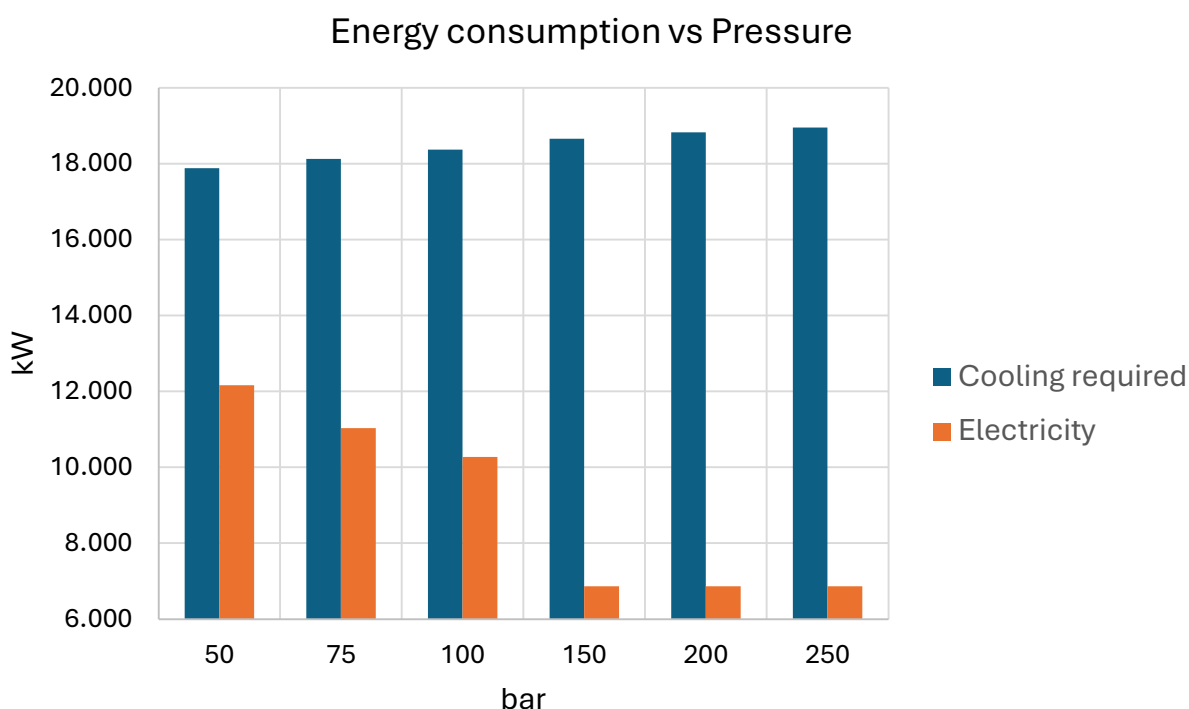


Figure 24. Energy consumption vs Pressure

Subsequently, the impact of the separation temperature on the process operating at 250 bar and 450 °C was analyzed. In the conventional process, the stream is first cooled to approximately −20 °C and then reheated after the separation stage in order to restore the temperature required for reintroduction into the first reactor. In the membrane-assisted configuration, however, it is not necessary to cool the entire stream to −20 °C, since the membrane allows separation to occur at significantly higher temperatures. This makes it possible to avoid cooling the entire stream leaving the third reactor, acting only on the product stream.

The analyses showed that a greater reduction in the temperature of the stream leaving the third reactor results in a higher energy demand for the individual heat exchanger. However, this increase is partially compensated by the reduced cooling duty required for the permeate stream and, at the

same time, leads to an increase in the heating duty of the recycle stream. Overall, the total energy consumption increases as the membrane feed temperature decreases, indicating that higher membrane feed temperatures are preferable from an energy perspective.

Furthermore, although an initial evaluation of the process streams suggests a clear energetic advantage, this benefit is significantly reduced when operating with a permeate-side pressure of 1 bar. In this case, since ammonia must subsequently be stored at pressures higher than 1 bar to avoid excessively low temperatures, an additional compression step is required together with two cooling stages, one before and one after the compressor, to ensure that the compressor temperature does not exceed 200 °C. Compression at lower temperatures is not feasible, as it would lead to the formation of two-phase mixtures inside the compressor, potentially causing equipment damage.

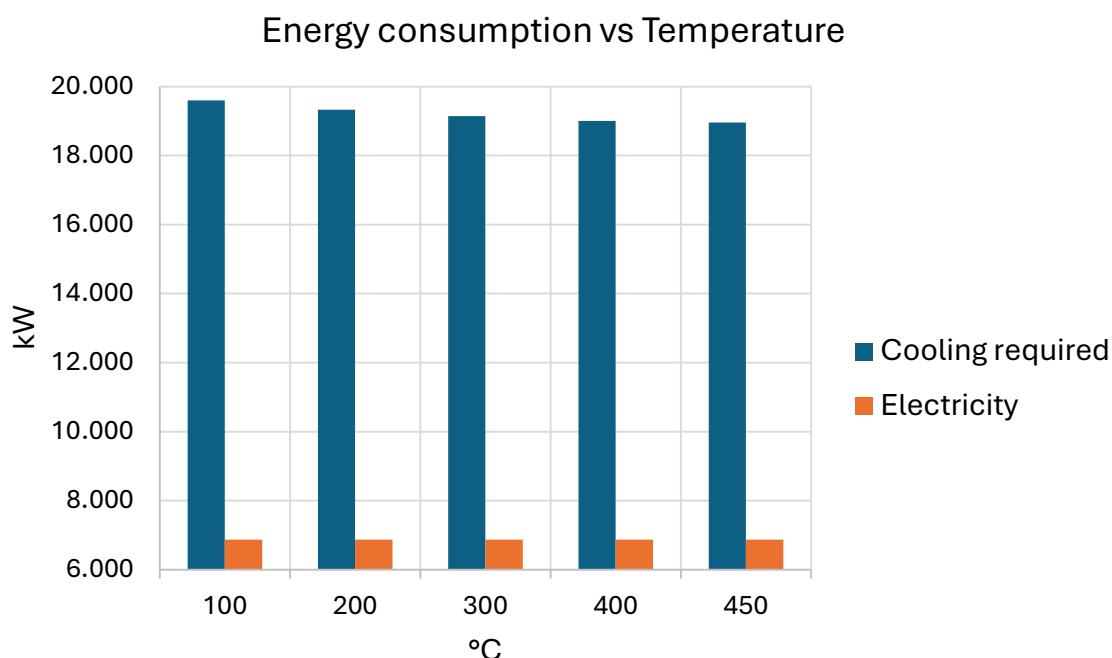


Figure 25. Energy consumption vs Temperature

The cooling duties obtained ranged from 19.5 MW at a membrane feed temperature of 100 °C to 18.9 MW at 450 °C.

Regarding electricity consumption, no significant variation was observed, since different operating temperatures did not result in changes in the flow rates circulating through the process reactors. As a result, the electrical power demand remained constant at approximately 6.87 MW.

Overall, the results indicate that the most favorable operating conditions are achieved when the membrane operates under conditions that closely approach those of the reaction section.

Energy Use Details								
		Current [cal/sec]	Target [cal/sec]	Saving Potential [cal/sec]	Energy Cost Savings [\$/Yr]	Energy Cost Savings [%]	ΔT_{min} [C]	Status
▶	Fired Heat (1000)	8,347E+05	0	8,347E+05	468.587	100,00	25,0	
▶	Total Hot Utilities	8,347E+05	0	8,347E+05	468.587	100,00		✓
▶	HP Steam Generation	2,326E+06	2,036E+06	2,902E+05	-95.490	-12,48	10,0	
▶	Cooling Water	1,75E+06	1,2E+06	5,5E+05	15.438	31,42	5,0	
▶	Refrigerant 2	1,092E+06	1,097E+06	-5558	-2.471	-0,51	3,0	
▶	Total Cold Utilities	5,168E+06	4,333E+06	8,347E+05	-82.522	-35,77		✓

Table 9. Energy Consumption HB with Membrane

Table 9 reports the thermal energy consumption of the membrane-based configuration operating at process conditions with a permeate-side pressure of 3 bar.

5.4 Economic Evaluation

As previously performed for the reference process, the economic assessment was carried out by evaluating different process configurations. The results showed that, as the membrane operating conditions progressively approach those of the reaction section, the utility costs decrease, reaching a minimum value of approximately 4.4 million USD per year.

However, while a reduction in utility costs can be achieved, an additional cost associated with membrane implementation must also be considered. For this reason, the membrane area required for the separation was calculated for each configuration. Under the most favorable conditions, the required membrane area was estimated to be approximately 2700 m².

Based on this value, the economic impact of membrane integration was further evaluated by considering different membrane lifetimes ranging from 2 to 8 years.

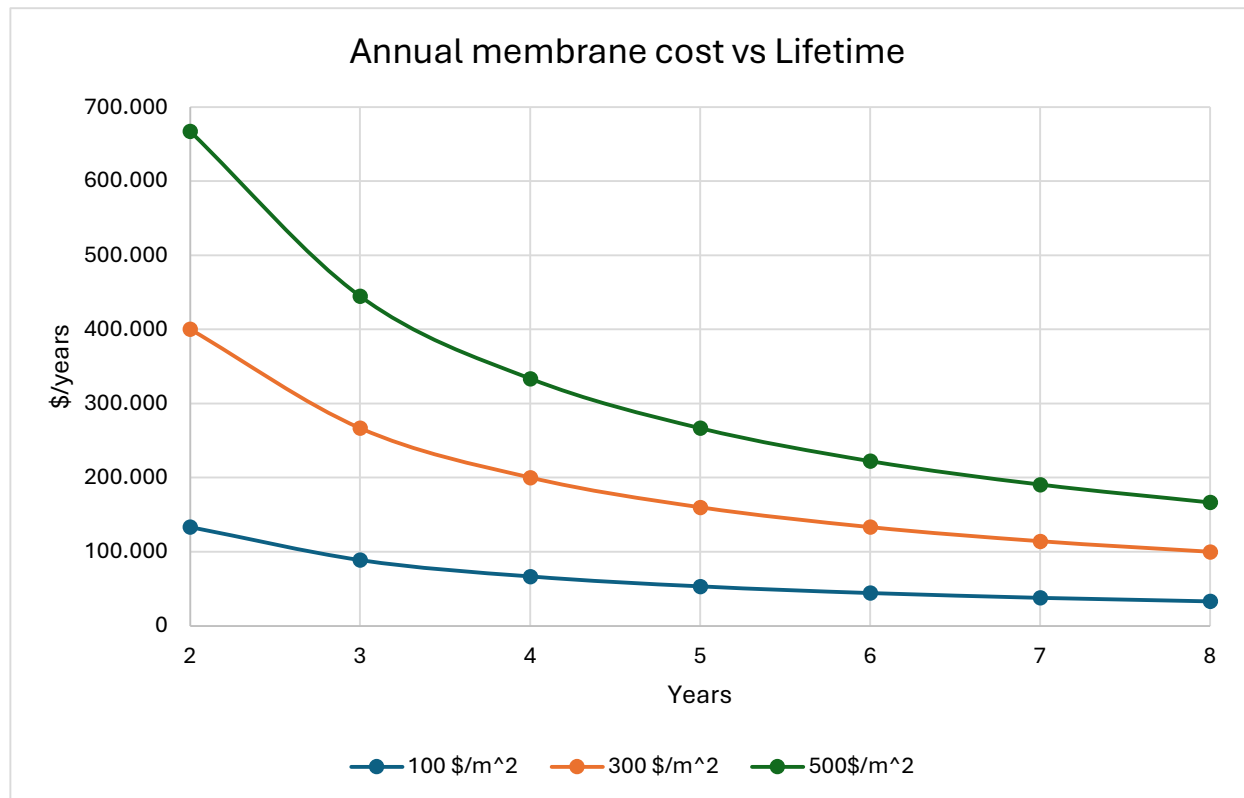


Figure 26. Annual membrane cost vs Lifetime

The graph shows that, as expected, the highest annual membrane cost is obtained for the combination of the shortest membrane lifetime and the highest specific membrane cost, reaching approximately 667 thousand USD per year.

By combining the membrane-related annual cost with the utility costs previously estimated for the process, the total annual operating cost ranges from approximately 5.1 million USD in the most conservative scenario to about 4.45 million USD in the most favorable case.

	Name	Fluid	Rate	Rate Units	Cost per Hour	Cost Units
▶	Electricity		5923,34	KW	459,059	USD/H
▶	Cooling Water	Water	0,349151	MMGAL/H	41,8981	USD/H
▶	Refrigerant - Propane	Refrigerant	85,3722	KLB/H	2,47579	USD/H

Table 10. Utility Cost HB with Membrane

Table 10. reports the utility costs associated with the investigated membrane-based process configurations.

5.5 Comparative Assessment

Following the analyses performed, it can be concluded that varying the operating pressure is not advisable, as it leads to an increase in electricity consumption. In the case of temperature variation, an energy benefit would be expected; however, this advantage is largely offset by the existing

thermal integration and by the fact that the conventional process employs a turbine to reach the storage conditions.

In the membrane-based configuration, the stream leaving the membrane separation unit is at only a few bar. Therefore, it is not possible to achieve cooling through pressure reduction, and heat exchangers are required to remove the entire amount of heat from the stream.

Parameter	Conventional HB	Membrane Case
NH₃ production (t/h)	~12	~12
NH₃ purity (%)	99.9	99.9
Total refrigeration duty (MW)	18.2	18.1
Total compression duty (MW)	5.9	5.9
Total utility cost (M\$/year)	5	4.4
Membrane area (m²)	—	2670
Membrane annual cost (T\$/year)	—	50 - 450

Table 11. Comparative Assessment

All this leads to the results reported in Table 11, which show that, under the most favourable conditions investigated—namely operation at process conditions with a permeate-side pressure of 3 bar—the benefit in terms of thermal energy consumption is almost negligible. However, an economic advantage is observed in utility costs due to the reduced use of expensive refrigerants. Furthermore, operating at a permeate-side pressure of 3 bar eliminates the need for recompression to product liquefaction.

5.6 Process Limitations and Discussion

The implementation of membrane-based separation technologies within the conventional Haber–Bosch process represents a current challenge that is attracting significant research interest. The increasing demand for fertilizers is directly linked to a growing global demand for ammonia, as fertilizer production remains strongly dependent on ammonia synthesis.

Over the years, the conventional Haber–Bosch process has undergone several process intensification and optimization efforts, becoming a highly mature and well-established technology that is difficult to replace. Nevertheless, its considerable energy consumption, coupled with the continuous growth in ammonia demand, results in an increasing overall energy requirement. The results obtained in this study highlight that the integration of a membrane separation unit is strongly dependent on the reaction conditions, mainly as a consequence of the limited conversion achievable within the synthesis loop. The pressure and temperature conditions currently adopted in industrial Haber–Bosch plants prevent the direct replacement of the conventional separation section

due to the thermal and mechanical stability limitations of currently available membranes. Furthermore, alternative catalytic systems aimed at reducing the severity of the operating conditions would, with the technologies currently available, lead to significantly lower conversion levels, offsetting any potential energy savings.

The introduction of a membrane separation unit also results in additional fixed costs. However, when integrated into a highly optimized process, these costs may be partially compensated by operational savings.

6. Conclusions and Future Perspectives

This chapter summarizes the main findings of the present work and discusses the future developments that could improve the feasibility of membrane integration within the Haber–Bosch process.

6.1 Main Findings

The membrane-assisted configuration appears particularly attractive when limited changes in pressure and temperature are required between the reaction and separation sections, thereby reducing the energy demand associated with cryogenic separation.

In summary, although the membrane-based configuration successfully reduces the amount of gas that must be sent to the refrigeration section, the overall reduction in cooling duty remains limited, decreasing only from approximately 18.2 MW in the conventional process to 18.1 MW in the membrane-assisted configuration. This modest improvement can be attributed to several factors. First, ammonia must still be condensed downstream of the membrane unit to obtain the final liquid product. Second, modern Haber–Bosch plants already benefit from extensive heat integration, which limits the potential for further reductions in utility consumption. In addition, the membrane process requires additional compression and cooling stages for the permeate stream, partially offsetting the benefits associated with the reduced gas flow rate entering the refrigeration system. As a result, the economic advantage observed for the membrane-assisted configuration does not primarily originate from a substantial decrease in overall energy consumption, but rather from a reduced utilization of expensive refrigeration utilities. This finding highlights a critical limitation of current membrane technologies for ammonia recovery. The main bottleneck is not the separation of ammonia itself, but the mismatch between the operating conditions required by available membranes and those of the Haber–Bosch synthesis loop. While ammonia synthesis typically

occurs at approximately 450 °C and 200–250 bar, most currently available ammonia-selective membranes operate at significantly lower temperatures and pressures, requiring additional process steps to adjust the gas conditions before and after separation.

Therefore, future research should focus on the development of ammonia-selective membranes capable of operating directly under Haber–Bosch conditions. Such membranes would eliminate the need for intermediate cooling, pressure reduction, recompression, and reheating stages, potentially enabling much larger reductions in both energy consumption and operating costs. Recent studies have already demonstrated promising high-temperature and high-pressure ammonia-selective membrane concepts, although their operating limits remain well below industrial Haber–Bosch conditions.

6.2 Industrial Relevance

The results obtained in this work highlight that the main limitation of membrane integration within the Haber–Bosch process is the mismatch between the operating conditions required for ammonia synthesis and the operating limits of currently available membrane technologies. The need for additional cooling and recompression steps partially offsets the potential benefits of membrane separation. Furthermore, the introduction of a membrane unit involves an additional fixed cost associated with membrane installation and replacement.

6.3 Future Work

Future developments should focus on the design of ammonia-selective membranes capable of operating under conditions closer to those of the Haber–Bosch synthesis loop. Improvements in thermal and mechanical stability, together with lower manufacturing costs and longer membrane lifetimes, could significantly enhance the feasibility of membrane-assisted ammonia production.

An alternative approach could be the direct integration of the membrane within the reactor itself. In such a configuration, ammonia would be continuously removed as it is produced, potentially shifting the reaction equilibrium toward higher conversions while reducing the need for downstream separation. Although significant technological challenges remain, membrane reactors may represent a promising direction for future ammonia synthesis processes.

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