

**NUMERICAL INVESTIGATION OF INTEGRATED AMMONIA
SYNTHESIS UTILIZING MULTI-STAGE AMMONIA PRODUCTION**

BY

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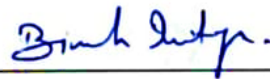
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[To my family]

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NOMENCLATURE

a_i	Activity of Species	
A_s	Surface Area	m^2
AEM	Anion Exchange Membrane	
ASU	Air Separation Unit	
AWE	Alkaline Water Electrolysis	
b_i	Correlation Constant for Calculation of Effectiveness Factor	
B2A	Biomass to Ammonia	
CBM	Bare Module Cost of Equipment	USD
CCSU	Carbon Capture Storage and Utilization	
CEPCI	Chemical Engineering Plant Cost Indices	
$C_{p,reactor}$	Purchase Cost of Equipment	USD
C_{pf}, C_{pg}	Heat Capacity of Feed Gas, Reactor Gas	kJ/kgK
$C_{revenue}$	Annual Value of Revenue	USD
DE	Differential Evolution	
f_i	Fugacity of Species	atm
FBM	Bare Module Factor	
F_c	Faraday Constant	
FCI	Fixed Capital Investment	USD
fcr	Fixed Cost Factor	
GHG	Greenhouse Gases	
h	Enthalpy	kJ/kg
HER	Hydrogen Evolution Reaction	
I	Current	A
IDCR	Internal Direct Cooling Reactor	
INV	Total Initial Investment	USD
ITM	Ion Transport Membrane	
K_a	Equilibrium constant of reaction	
K_1, K_2, K_3	Cost Correlation Constants	
k_A, k_B	Rate Constants	
l	Bed Length	m
LCOA	Levelised Cost of Ammonia	USD
LHV	Lower Heating Value	MJ/kg
LMTD	Log Mean Temperature Difference	C
m	Total Mass Flow Rate	kg/h
MOF	Metal Organic Framework	
N	Molar Flow Rate	$kmol/h$
n	Number of Total Electrolyzer Cells	
N_i	Molar Flow of Component	
NPV	Net Present Value	USD
OER	Oxygen Evolution Reaction	
P	Pressure	atm
p_i	Partial Pressure	atm

PEM	Proton Exchange Membrane	
PSA	Pressure Swing Adsorption	
PV	Present Value	
Q	Heat Rate	kW
R	Universal Gas Constant	kJ/kmolK
r	Rate of Reaction	kmol/m ³ h
S ₁	Surface Area of Cooling Tubes per Unit Length of Reactor	m ² /m
S ₂	Cross-sectional Area of Reactor Beds	m ²
SMR	Steam Methane Reforming	
SOEC	Solid Oxide Electrolysis Cell	
T	Temperature	K, °C
TEMA	Tubular Exchangers Manufacturers Association	
TES	Thermal Energy Storage	
TRL	Technology Readiness Level	
TVA	Tennessee Valley Authority	
U	Overall Heat Transfer coefficient	kJ/m ² hK
W	Work	kW
X _{N2}	conversion of nitrogen	
y _i	mole fraction of species	

Greek Letters

α	Constant For Calculation of Rate of Reaction (Dyson)	
β	Non-Adiabatic Behaviour Parameter	
γ	Volatility	
ΔH	Heat Of Reaction	kJ/kmol
ε	Effectiveness Factor	
η	Efficiency	
λ	Capacity Parameter	
v	Specific Volume of Water	m ³ /kg

ABSTRACT

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With increasing effects of climate change and greenhouse effect, alternatives to fossil fuels, especially those generated from renewable sources, have come into focus. Among these prospects, ammonia has received particular attention, due to its multifaceted capabilities in solving this problem, as it is able to behave as a carrier for hydrogen, to store energy ready to be produced either via fuel cell electrolyzers or directly as a combustible fuel. Ammonia produced from renewable energy, especially at the small scale, is thus considered a pathway to establishing a carbon-free fuel economy, but high cost of production, as well as an interest in maximizing useful output in general, means that the integration of such green ammonia production plants with other energy generation systems is incumbent. In this work, a differential approach is used to accurately model the performance of a catalytic ammonia reactor, and it is then used in a multigeneration system having power and ammonia as outputs, with the system performance being evaluated in terms of the first and second law of thermodynamics, using a mathematical model. A review of the current state of green ammonia production, and its use in integrated energy systems will also be conducted, and optimum operating parameters for the proposed plant will also be deduced from relevant parametric analyses. |

ملخص الرسالة

الاسم الكامل: أديب عدنان

عنوان الرسالة: دراسة عددية لتركيب الأمونيا المتكامل باستخدام إنتاج الأمونيا متعدد المراحل

التخصص: ماجستير العلوم في الهندسة الميكانيكية

تاريخ الدرجة العلمية: ديسمبر ٢٠٢٤

مع تزايد تأثيرات تغير المناخ وتأثير الاحتباس الحراري، أصبحت البدائل للوقود الأحفوري، وخاصة تلك المولدة من مصادر متجددة، موضع تركيز. ومن بين هذه البدائل، حظيت الأمونيا باهتمام خاص، نظرًا لقدراتها المتعددة الأوجه في حل هذه المشكلة، حيث إنها قادرة على التصرف كحامل للهيدروجين لتخزين الطاقة الجاهزة للإنتاج إما عن طريق أجهزة التحليل الكهربائي لخلايا الوقود أو مباشرة كوقود قابل للاشتعال. وبالتالي، تعتبر الأمونيا المنتجة من الطاقة المتجددة، وخاصة على نطاق صغير، مسارًا لإنشاء اقتصاد وقود خالٍ من الكربون، ولكن التكلفة العالية للإنتاج، فضلاً عن الاهتمام بتعظيم الناتج المفيد بشكل عام، يعني أن دمج محطات إنتاج الأمونيا الخضراء مع أنظمة توليد الطاقة الأخرى أمر ضروري. في هذا العمل، يتم استخدام نهج تفاضلي لنمذجة أداء مفاعل الأمونيا الحفزي بدقة، ثم يتم استخدامه في نظام متعدد التوليد مع الطاقة والأمونيا كمخرجات، مع تقييم أداء النظام من حيث القانون الأول والثاني للديناميكا الحرارية، باستخدام نموذج رياضي. كما سيتم إجراء مراجعة للحالة الحالية لإنتاج الأمونيا الخضراء واستخدامها في أنظمة الطاقة المتكاملة، وسيتم أيضًا استنتاج معايير التشغيل المثلى للمصنع المقترح من التحليلات البارامترية ذات الصلة.

CHAPTER 1

Introduction

Ammonia can be considered to be one of the most important chemicals in the world, with the development of the Haber-Bosch process for its industrial manufacturing beginning an agricultural revolution that led to an exponential growth in human population. 100 years later, ammonia sees renewed interest as a vector for the fuel of the new age, hydrogen. Concurrently, the environmental effect of its manufacture is also concerning.

Recent work has been done on the manufacture of ammonia from renewable sources, with hydrogen being produced from water electrolysis, and nitrogen from air. The required power for these processes would be provided from renewable energy sources such as solar photovoltaics or wind, as well as the energy requirements for the manufacture of ammonia itself. Ammonia produced in this manner from entirely renewable sources has been dubbed “Green Ammonia” and is a topic of great interest in the current energy landscape.

The past one hundred years of ammonia manufacture have led to great advancements in the Haber-Bosch process, and as the “Green Ammonia” paradigm shift approaches, these technologies must be leveraged in order to achieve both goals of improving ammonia manufacture in terms of process performance and reducing environmental effect by stopping reliance on fossil fuels. Simultaneously, the evaluation of green ammonia technologies in terms of their feasibility must also be done to understand whether they are mature enough to be deployable at large scales or not.

CHAPTER 2

Literature Review

2.1 Introduction

The production of ammonia through the development of the Haber-Bosch process remains a landmark moment in science and history. The ability to produce large amounts of ammonia from elemental substances, allowed for the widespread production and use of nitrogenous fertilizer, thereby drastically increasing agriculture yields worldwide, which directly correlate to increases in worldwide population [1], created the discipline of chemical engineering as it is known today [2], and also won Fritz Haber the Nobel Prize in Chemistry in 1920 [3].

Following on from Haber's milestone achievement, numerous improvements have been made to the process to achieve objectives such as improved efficiency, increased yield, operation at reduced temperatures and pressures, or use of different feedstocks for elemental nitrogen and hydrogen in order to reduce overall environmental impact.

Recently, ammonia has gathered renewed attention due to the movement away from non-renewable fossil fuels, and its ability to act as a vector for one of the most viable renewable fuel options, hydrogen [4], [5]. Considerable study has been done regarding the production of hydrogen using entirely renewable sources, known as "green hydrogen" [6], and the prospect of storing and transporting the produced hydrogen via ammonia, producing "green ammonia" [5], [7], [8]. The advantages of ammonia are multiple; ammonia is more easily stored and transported than hydrogen, and the existing infrastructure for the production and transport of ammonia such as pipelines and shipping routes, allows for reduced operational costs compared to hydrogen storage

and transport [5]. Ammonia can also be produced with entirely renewable resources, and from cheap raw materials, namely water and air. While the majority of current ammonia production relies on methane reforming for production of elemental hydrogen for use in the Haber-Bosch process [9], the prospect of green hydrogen, mainly via water electrolysis [10], means that ammonia may soon be produced cheaply, and with minimal adverse environmental effect.

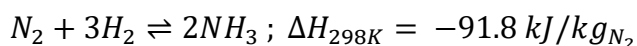
In this work, we will discuss the current state of ammonia production, first by detailing the cornerstone of the technology, i.e the Haber-Bosch process, and discuss its current industrial applications. Following this, we will discuss the ammonia production technology which is experiencing the most attention and research effort currently, which is Green Ammonia production, and will discuss in detail the three primary thrusts of green ammonia production, namely modification of the Haber-Bosch process to utilize renewable resources and feedstocks, production of ammonia via electrochemical processes, and finally we will discuss the production of ammonia via biological and biosynthesis processes.

2.2 Haber-Bosch process and Industrial Applications

The various benefits of nitrogenous compounds were already well known and documented in Haber's time, particularly the demand for nitrogen in the agricultural sector. As such, the extraction of nitrogen and nitrogenous compounds such as ammonia and ammonium sulphate from sources such as saltpeter and coal distillation, received widespread attention [3]. However, neither source was able to meet the expected demands of the time, and thus a process to harness nitrogen from the most abundant source available, i.e, the atmosphere, was necessary. While many attempts had been made to develop such a process, it was not until the early 20th century, did Haber, collaborating with Robert le Rossignol, devised the process of producing ammonia from elemental

nitrogen and hydrogen. Nitrogen was produced by separating from the air, and hydrogen from electrolysis of water in the laboratory setting, and from methane reforming industrially. The reaction is carried out using iron catalyst in a high pressure and temperature environment to produce ammonia, allowing the great demand of nitrogen and nitrogenous fertilizers to be met. The other innovation made by Haber was the recirculation of unreacted gaseous nitrogen and hydrogen over the iron catalyst, thereby increasing the yield of the process. These innovations, along with the adaption of the technology to an industrial scale by Carl Bosch, allowed for the proliferation of ammonia synthesis and nitrogen capture, paving the way for the modern agriculture and fertilizer industry as we know it today. Today, ammonia production consumes 1% of the global electricity generated, and it is estimated, as of 2008, that almost 50% of total births since 1908 would not be possible without the agricultural revolution predicated on nitrogen fertilizers [1], and thus the Haber-Bosch process.

The synthesis of ammonia from its elemental components occurs through the reaction;



This is an equilibrium reaction, with the forward reaction, i.e. the production of ammonia from nitrogen and hydrogen, being exothermic, while the reverse reaction, i.e. the decomposition of ammonia, is endothermic. Following Le Chatelier's Principle, we can deduce that the production of ammonia would be favored by low temperatures and high pressures, which would cause the equilibrium position to shift to the right and the forward reaction to be favored. However, at ambient temperatures, the reaction does not proceed in this manner. The energy required for the dissolution of the $N \equiv N$ triple bond is very large, and consequently the activation energy required for the reaction to proceed is not reached in the gaseous phase until the reactants reach a

temperature of around 3000°C, a condition at which the equilibrium is shifted to the left and ammonia production is inhibited. The presence of iron catalyst, however, resolves this issue, as it allows the reaction to proceed at a lower activation energy, and at reduced temperatures [11]. However, the reaction is still not possible at ambient conditions. In Haber's time, the industrial-scale production was carried out at temperatures around 500°C and at pressures in the range of 150-200 atm [2], which maximizes the single-pass equilibrium conversion, which was generally on the order of 15%. This necessitates the use of gas recycle, wherein unreacted gases are looped through the synthesis reactor, thus increasing the overall yield, with any ammonia produced being extracted from the outlet stream by condensation [12].

The operating conditions for the ammonia synthesis process have remained more or less unchanged in the intervening century, but considerable work has been done in regard to improving the performance of the process. Catalyst chemistry has received continuous attention, with the primary objective in developing an ammonia synthesis catalyst being to improve single-pass conversion rates, reduce operating temperatures, and overall, to obtain catalysts with improved catalytic activity, thereby achieving a higher overall yield overcoming the limitations imposed by thermodynamic equilibrium. At low temperatures, the reaction rate is typically too slow to practically produce ammonia, even though the theoretical equilibrium tends toward nearly 100% conversion of N_2 to NH_3 . The breaking of nitrogen's triple bond requires substantial energy input, resulting in a markedly high activation energy threshold for the reaction to proceed, which is not available at low temperatures.

Most contemporary ammonia synthesis catalysts used in the Haber-Bosch process achieve conversion rates of approximately 10-15% while operating in the 425-450 °C range at pressures

as low as 100 atm. Consequently, enhancing the reaction rate at temperatures below this range becomes crucial, as it would exponentially increase the conversion per pass in the ammonia synthesis loop. Thus, the catalyst's catalytic activity plays a pivotal role, and if new catalysts exhibit high activity, it becomes feasible to conduct ammonia synthesis at lower temperatures and pressures, resulting in improved overall energy efficiency.

Ammonia synthesis through catalysis hinges on the interaction between nitrogen and hydrogen on the catalyst's surface. This interaction takes place through two distinct processes: chemisorption and physisorption, with the former being more influential than the latter. Chemisorption involves a strong chemical bond formation between the surface of the catalyst and the reactants, resulting in a stable and lasting attachment. In contrast, physisorption is characterized by weaker, physical forces (such as van der Waals interactions) that facilitate a temporary and less stable association between the surface and reactants [13]. The catalysts generally used in ammonia synthesis generally fall into one of two categories: fused-iron and supported-metallic catalysts, with fused-iron catalysts being the more widely used. These catalysts are derived from various iron oxides, including hematite (Fe_2O_3), magnetite (Fe_3O_4), and wüstite (Fe_{1-x}O) [14], [15]. The key advantage of iron lies in its ability to prevent hydrogen poisoning, a common issue with other transition metals, making it a highly effective catalyst for ammonia synthesis, even at reduced temperatures. Typically, industrial iron catalysts are multipromoted with additives such as K_2O , BaO , and Al_2O_3 in small quantities, enhancing their structural and electronic properties. On the other hand, supported metallic catalysts consist of a metallic catalyst material, such as ruthenium or cobalt, deposited on the surface of a support material like activated carbon or a metal oxide. These metallic catalysts typically constitute around 2-10% of the catalyst's weight. The use of support materials

serves to reduce cost, and it also has promotion effects. Supporting the metallic catalyst material helps mitigate the high cost of ruthenium and cobalt compared to iron, aligning their overall costs. Moreover, support materials can be tailored to specific catalysts to achieve promotional effects that significantly alter catalyst activity.

Over the past century, the Haber–Bosch process has undergone continuous optimization through the development of new catalysts [16], better understanding of operating of reaction kinetics [17], [18], and of operating conditions [19], [20], leading to a significant reduction in the minimum energy input required. Initially exceeding 60 GJ per ton of ammonia in the 1950s, modern plants can operate at energy requirements as low as 27.4 GJ per ton of ammonia. This progress has resulted in an overall increase in energy efficiency, rising from 36% to the present range of 62–65%. The most substantial efficiency improvement came from the shift to using methane instead of coal feedstock for hydrogen production through steam methane reforming, rather than gasification. However, this change has brought with it its own issues, namely higher CO₂ emissions, as well high energy and temperature requirements of the water gas-shift reaction. The requirement for more sustainable and environmentally friendly feedstock and processes has necessitated the study of different technologies, giving rise to the concept of “Green Ammonia”[12].

2.3 **Green Ammonia Production**

Due to concerns about environmental impacts and the contribution of ammonia production to GHG emissions[21], there is a growing need for regulations to limit these emissions. These regulations may lead to significant technological changes in the ammonia industry, with a focus on reducing emissions and improving environmental sustainability.

Efforts have been underway to develop cleaner and more environmentally friendly methods for ammonia production to address these concerns and reduce the industry's environmental footprint. Green ammonia, which refers to ammonia production with minimal or no carbon dioxide emissions, has garnered significant attention from various sectors including academia, industry, and governments. Its appeal lies in its reliability, stability, and sustainability, making it suitable for a range of applications such as power generation using technologies like furnaces, fuel cells, gas turbines, and internal combustion engines, as well as in agriculture as a fertilizer, among others. However, green ammonia production primarily relies on renewable energy sources [22], and unfortunately despite the perceived mass proliferation of technologies such as solar photovoltaics and wind, the cost of green ammonia is still very high [23], being more than \$600 per ton NH_3 compared to existing commercial processes being valued at \$300 per ton NH_3 . Despite this, green ammonia, based on green hydrogen production, still remains the best option for the oncoming paradigm shift for ammonia production, as it moves away from reliance on fossil fuels with the rest of the world, and adopts more sustainable feedstock. Figure 1 shows the process flow for green ammonia production.

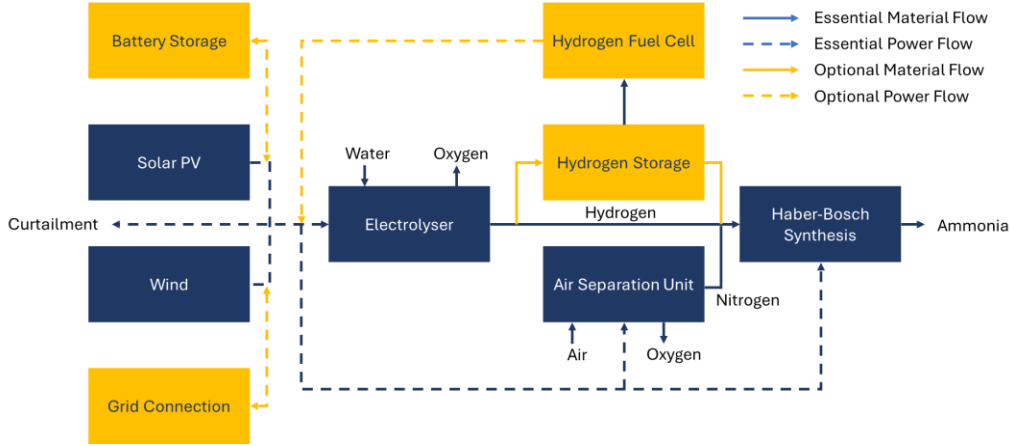


Figure 1: Schematic of green ammonia production (redrawn from [5], [24])

Several studies and analyses have explored different aspects of green ammonia. Some have examined the import/export market of green ammonia, assessing its advantages and disadvantages as a hydrogen carrier, production costs, and supply and demand constraints [5]. Others have looked at offshore green ammonia production, considering factors like land availability and transportation to major demand centers [25]. Economic evaluations have been conducted, including the levelized cost of ammonia (LCOA) analysis in various locations worldwide [26]. The choice of hydrogen production route, such as alkaline water electrolysis (AWE), polymer electrolyte membrane water electrolysis (PEM), and solid oxide electrolysis cell (SOEC), has been assessed for its impact on green ammonia production costs, with SOEC being identified as the most energy-efficient method [27]. Additionally, techno-economic comparisons have shown that hydrogen recovery via green ammonia reforming has superior CO₂ and cost reduction potential with increased capacity and technical advancements, compared to other common hydrogen production methods [28].

The challenge of finding an economical and sustainable method for ammonia production has gained importance due to global warming concerns. MacFarlane et al. [29] classified the various routes for ammonia production are based on their environmental impact. Ammonia is traditionally produced using the Haber-Bosch process, with feed hydrogen being produced from methane

reforming. The dependence on fossil fuels for feedstock results in considerable greenhouse emissions, and the need to reduce this adverse environmental impact is the primary influence in developing green ammonia production technologies. However, efforts are being made to capture carbon emissions after ammonia production, thus reducing overall carbon emissions to zero. This results in what is known as Generation 1 Ammonia, or "blue ammonia."

Generation 2 ammonia production involves using greener feedstocks for nitrogen and hydrogen. This approach aims to transform the conventional Haber-Bosch process into a renewable and more environmentally friendly source of ammonia production. By using cleaner and more sustainable feedstocks, the environmental impact of ammonia production can be reduced. Nitrogen is separated from the air through air separation technology and hydrogen may be produced from technologies such as water electrolysis, with the power requirement being met by renewable power generated from wind or solar. Currently, the capacity for a daily production of 30 kg of NH_3 using power generated from a 20kW wind turbine has been practically demonstrated [30].

Generation 3 green ammonia production departs from the traditional Haber-Bosch process and instead relies on the electroreduction of N_2 directly to ammonia, wherein nitrogen reduction occurs at the cathode surface of an electrochemical cell, where applied electrical potential provides the energy required to break the $\text{N}\equiv\text{N}$ triple bond [29], [31]. This allows the electroreduction process to occur at ambient pressures, however, the technology has not yet left the laboratory setting. Overall, Generation 3 production explores alternative methods that emphasize high stability, sustainability, and the use of renewable energy sources, with the aim to revolutionize ammonia production by making it more efficient, sustainable, and more environmentally friendly.

Table 1 summarizes the different ammonia generation technologies and their performance relative to each other.

Table 1: Comparing the efficiency of different route (power-to-ammonia, biomass-to-ammonia, methane-to-ammonia, and coal-to-ammonia), and production generation

Green ammonia production generation	Energy Sources	Material Sources	Useful Output	H ₂ Production Technology	N ₂ Production Technology	NH ₃ Production Technology	System efficiency (%)	Ammonia production rate (kg/hr)	Year	Reference
Biosynthesis	Solar Energy, Wind Energy	Biomass, Air, Water	Power, NH ₃ , Heat			Haber-Bosch Process	60.1	3376.94	2022	[32]
Generation 1	Natural Gas	Air		Steam Methane Reforming	Air Separation (Cryogenic)	Haber-Bosch Process			2022	[33]
Generation 1	Liquefied Natural Gas	Air, Water	NH ₃ , Fuel gas, CO ₂ Capture	Steam Methane Reforming	Air Separation (Cryogenic)	Haber-Bosch Process	42.69	35700	2023	[34]
Generation 1	Natural Gas	Air, N ₂	Power, Hot Water, H ₂ , NH ₃	High Temperature Steam Electrolysis		Haber-Bosch Process	51.83	574.56	2020	[35]
Generation 1	Solar Energy, Wind Energy	CH ₄ , N ₂	NH ₃ , CO ₂ Captured	Steam Methane Reforming		Electrochemical Reduction of N ₂		9.248×10^{-7}	2020	[36]
Generation 2	Wind Energy	Air, Water	NH ₃	Water Electrolysis		Haber-Bosch Process		2.7	2017	[37]
Generation 2	Wind Energy	Water, N ₂	NH ₃ (as NH ₄ HCO ₃)	Water Electrolysis (PEM)	Air Separation (Pressure Swing Adsorption)	Haber-Bosch Process		2.2643	2022	[38]
Generation 2	Solar Energy (PV)	Air, Water	NH ₃	Water Electrolysis (PEM)	Air Separation (Cryogenic)	Haber-Bosch Process	26.08	792	2021	[39]
Generation 2	Wind Energy, Solar Energy, Grid Power	Air, Water	NH ₃	Water Electrolysis (Alkaline)	Air Separation (PSA)	Haber-Bosch Process	67	2283.11	2020	[40]

Generation 2	Wind Energy, Solar Energy, Grid Power	Air, Water	NH ₃	Water Electrolysis (PEM)	Air Separation (PSA)	Haber-Bosch Process	61.14	60.12	2020	[41]
Generation 2	Solar Energy	Water, N ₂	NH ₃	Water Electrolysis (PEM)		Haber-Bosch Process	1.9	0.000982	2020	[42]
Generation 2	Solar Energy (PV), Wind Energy	Air, Water	NH ₃	Water Electrolysis	Air Separation (Cryogenic)	Haber-Bosch Process		12500	2018	[43]
Generation 2	Solar Energy	Air, Water	NH ₃	Water Electrolysis (PEM)	Air Separation (Cryogenic)	Haber-Bosch Process		14086.76	2020	[44]
Generation 2	Hydropower	Air, Water	NH ₃	Water Electrolysis (PEM)	Air Separation	Haber-Bosch Process	45	3000	2022	[45]
Generation 3		Air, Water	NH ₃			Electrochemical Reduction of N ₂		6.9768×10 ⁻⁸	2013	[46]
Generation 3		N ₂ , Li ₃ N	NH ₃			Electrochemical Reduction of N ₂		0.01252	2021	[31]
Generation 2		H ₂ , N ₂	NH ₃	-	-	Haber-Bosch Process	-		2021	[47]
Generation 2		H ₂ , N ₂	NH ₃	-	-	Haber-Bosch Process	-	0.9-18 mg/g sorbent	2017	[48]
Generation 2	Wind power	Air, Water	NH ₃	water electrolysis	air separation (PSA)	Haber-Bosch Process	-	0.2-0.8	2019	[49]
Generation 2		H ₂ , N ₂	NH ₃	-	-	Haber-Bosch Process	-	1.8 mol/h	2016	[50]
Generation 2	Wind power	Air, Water	NH ₃	water electrolysis	air separation (PSA)	Haber-Bosch Process	-	1.2×10 ⁻⁶ - 1.8×10 ⁻⁶ mol/gcat.s	2018	[51]
Generation 2		N ₂ , NH ₃	NH ₃	-	-	Haber-Bosch Process	-	2.5 mol/mol sorbent	2022	[52]
Generation 2		H ₂ , N ₂	NH ₃	-	-	Haber-Bosch Process	-	27.2 μmol/gcat.s	2022	[53]
Generation 3		H ₂ , N ₂ or N ₃ ⁻	NH ₃			Electrochemical Reduction of N ₂	72%	0.12 mol/h.m ²	2003	[54]
Generation 3	Solar Power	H ₂ , N ₂	NH ₃			Electrochemical Reduction of N ₂	5.5% (energy)	4.41×10 ⁻⁹ mol/s.cm ²	2017	[55]
Generation 3		water and air	NH ₃			Electrochemical Reduction of N ₂	-	1.14×10 ⁻⁵ mol/s.m ²	2013	[56]
Generation 3		H ₂ , H ₂ O, N ₂	NH ₃			Electrochemical Reduction of N ₂	-	9.3×10 ⁻⁷ mol/s.cm ²	2020	[57]
Generation 3	Solar Power	H ₂ , N ₂	NH ₃			Electrochemical Reduction of N ₂	-	1.88 mg	2017	[58]

These different generations of green ammonia production represent evolving strategies to address the environmental challenges associated with ammonia synthesis while ensuring economic viability and sustainability. Each generation builds on the previous one to achieve more eco-friendly and efficient ammonia production and is primarily differentiated based on the mode of hydrogen production, whether it be based on production from fossil fuels, or water electrolysis. Figure 2 shows the current scenario of global hydrogen production.

Water electrolysis [59] is considered as the most viable option currently for the production of green hydrogen, using electrolytic methods to split water into hydrogen and oxygen, with the hydrogen serving as the feedstock for ammonia synthesis.

These methods generate green hydrogen, which can subsequently be used in ammonia production through various routes, including electrochemical and photochemical processes, which can be broadly categorized under Generation 3 production technology [60].

In addition to the previously mentioned ammonia production technologies, the distributed green ammonia approach involves the direct synthesis of ammonia from water and nitrogen, eliminating the need for the traditional Haber-Bosch (H-B) process. Various methods fall under this category, including electrochemical, photochemical, biological, and metallocomplex N_2 fixation. Many of these methods are still in the early stages of research and development, ranging from Technology Readiness Levels (TRL) 1 to 4 [61], [62], [63].

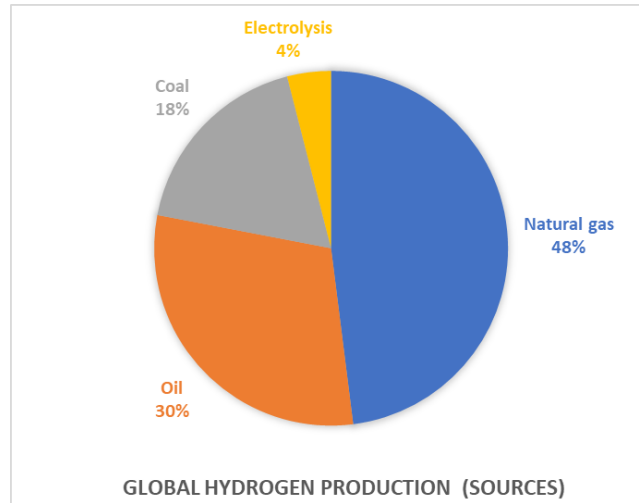
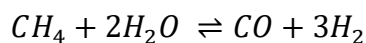


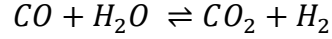
Figure 2: Global hydrogen production sources (redrawn from El-Shafie)[64]

2.3.1 Generation 1: Haber-Bosch Process with carbon capture

The most popular process for hydrogen production for use in ammonia synthesis is steam methane reforming (SMR) [56]. While this method proves to be cost-effective when the price of natural gas is low, in times of high natural gas prices, the preference shifts towards its direct production, especially in regions with surplus renewable energy resources. Additionally, increased awareness regarding eventual depletion of fossil fuel resources, and the contributions of natural gas use to phenomena such as greenhouse effect and pollution mean that an incentive exists to search for alternatives. Steam methane reforming accounts for the large part of CO₂ emissions involved in ammonia production, due to the combustion of methane fuel in the furnace, which provides the energy needed for the high-temperature endothermic reaction. It is also the main contributor to the large carbon footprint of ammonia production, which accounts for more than 1% of the global CO₂ emissions.

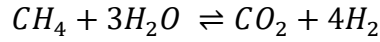
The methane reforming process can be described chemically by the following reactions;





The first is the primary methane reforming reaction, while the second is the water gas shift reaction, and serves the purpose of converting the produced CO to CO₂ which can be more easily captured.

The two can be combined as one step reaction;



As stated previously, this is a highly endothermic reaction, with the required energy being provided by the combustion of additional methane, further increasing the CO₂ production of the overall process. As such, reducing the use of methane in ammonia production would be a significant step towards reducing global CO₂ emissions.

The integration of a carbon capture, utilization, and storage (CCSU) unit into an existing Haber-Bosch plant increases both the cost and complexity of the plant. However, given the growing emphasis on decarbonization, such integrated processes with carbon capture have the potential to significantly contribute to achieving global mid-century decarbonization goals.

Various technologies are in operation to realize this objective, both in terms of capture and storage. Regarding carbon capture, amine absorption is considered the most popular [65], wherein compounds such as mono-, di, and tri-ethanolamines are used to separate carbon dioxide from the effluent stream via an exothermic reaction with the active -NH₂ group of the amine compounds. However, this process has drawbacks, such as the high energy requirement for regeneration of the absorbent compounds for reuse, as well as the formation of corrosive carbonate salts in absorbent mixture, which may cause damage to the plant equipment [66].

Carbon capture may also be carried out through cryogenic separation [67], with the effluent stream being cooled and the carbon dioxide being separated as condensed liquid CO₂. This has the added benefit of providing liquid CO₂ for ease to transport and storage, however there is a large energy cost associated with the cooling required for condensation, and thus the economic viability of such an approach would need to be evaluated on a system-by-system basis. Recently, the use of polymer and mixed matrix membranes [68] to separate carbon dioxide has also received attention. Wang et al[69] considered the use of inorganic palladium-based hydrogen permeation membranes for use in separation of hydrogen and carbon species from effluent of water gas shift reaction, predicting a maximum methane conversion rate of 64% operating at 400 °C.

Regarding storage of captured CO₂, the most common method is the injection into high depth geological formations, such as cave systems, salt mines and coal deposits [70]. CO₂ is also often injected into depleted oil reserves, and the ocean. In the context of injection into oil and natural gas reservoirs, the pressure from the buildup of injected CO₂ allows for easier extraction of fossil fuels [71], [72]. Ocean injection is also considered as a commercially viable alternative, however it requires considerable infrastructure, and also necessitates deep injection as otherwise the CO₂ is able to rise through the water and be released into the atmosphere. Overall, while these methods allow for storage of CO₂, they do not address the issue of use, disposal, or overall reduction of CO₂. As such, methods of CO₂ utilization such as for use in the manufacture of urea, in the drinks industry, or via processes such as methanation should be considered with greater interest [12].

Methanation is also considered an option for carbon capture, wherein nickel catalyst is used to convert CO and CO₂ to CH₄, thereby reducing carbon in effluent and recovering energy in the

form of CH₄ fuel [73]. This process also has the added benefit of storing hydrogen in the vector of methane, which allows for ease of transport and storage, although this application would perhaps be better suited in plants producing green hydrogen, utilizing sourced CO₂, rather than in SMR-based plants. The chemical reaction can be considered as the reverse of that followed in methane reforming and is thus highly exothermic [74]. The evolved energy can thus be used as a heat source for applications such as process heat, power generation, district heating, etc.

2.3.2 Generation 2: Haber-Bosch Process Utilizing Renewable Resources

The easiest way to integrate renewable resources into ammonia production is to substitute feedstocks, particularly that for hydrogen, thereby reducing reliance on fossil fuels and CO₂ emissions. Consequently, there has been a growing trend in recent years towards the establishment of prototype small-scale production facilities [75]. In fact, farmers and researchers in the USA have identified a correlation between fertilizer demand and wind speeds, making the utilization of stranded wind energy as energy source for hydrogen production via water electrolysis an increasingly viable strategy for ammonia production. If certain economic incentives, such as carbon taxation, come into play, decentralized on-site ammonia production may gradually replace centralized manufacturing [76]. Similarly, ammonia production has been suggested as a solar-hydrogen technology [77], promoting distributed manufacturing in both developing and developed economies.

One common approach is the "power to ammonia" process, which utilizes renewable energy sources to split water and produce green hydrogen, known as water electrolysis. This green hydrogen is then used in the Haber-Bosch process for green ammonia production. This method

has demonstrated successful green ammonia production with an efficiency of approximately 83% when integrated with a high-temperature operating system and heat integration techniques.

Figure 3 shows the different routes for hydrogen production and how they can be consolidated into existing Haber-Bosch based ammonia production technologies.

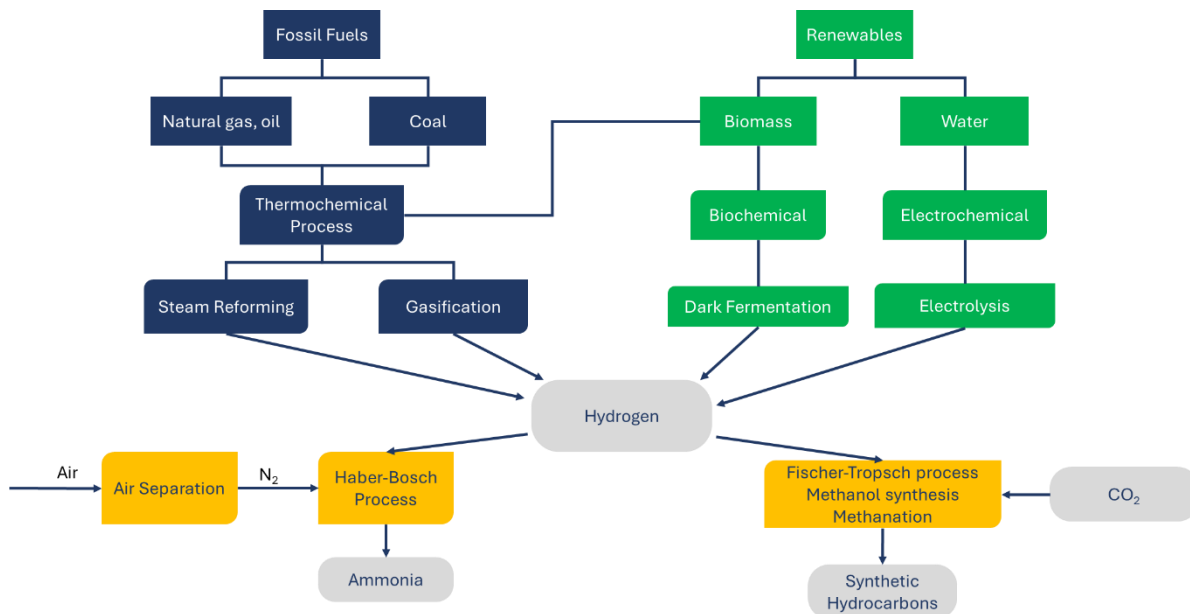
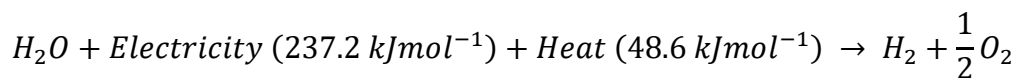


Figure 3: Hydrogen production pathways and routes (redrawn from [78])

2.3.2.1 Water Electrolysis

Water electrolysis is an electrochemical process where energy is supplied in the form of electricity to dissociate water, producing elemental hydrogen and oxygen. The reaction can be represented as [10],



The theoretical cell voltage is 1.23V, but the experimentally required value is observed to be 1.48 V, with the surplus voltage being required in order to overcome kinetic and ohmic resistance of

the electrolyte and electrolyzer cell components[27], [79], [80]. The underlying principle of water electrolysis has been used to develop four primary technologies, which differ in their electrolyte, operating conditions, and ionic agents (OH^- , H^+ , O^{2-}). These technologies include alkaline water electrolysis, PEM water electrolysis, and solid oxide water electrolysis. Despite the variations in electrolyte and conditions, they share similar operating principles [80]. Provided that the supply electricity is produced from renewable sources such as wind or solar, or perhaps from nuclear power generation, and the other primary feedstock of nitrogen is also captured from the air similarly without the use of fossil fuels, the entire production process for ammonia can be carried out without any carbon emissions, and at reduced capital cost [10].

Overall, alkaline electrolysis has the highest industrial adoption and production scale till now, followed by PEM electrolysis, which has entered pilot applications and is rapidly progressing toward industrial deployment. Solid Oxide technologies, while showing encouraging results in terms of energy efficiency, are still at the laboratory experimentation stage, as are most other technologies. As a result, alkaline electrolyzers tend to be the most economically viable, with PEMs being more expensive, and other technologies not yet being suitable for realistic cost evaluation [81]. Table 2 summarises the current scenario for water electrolysis-based hydrogen technologies.

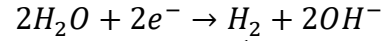
Table 2: Summary of main renewable hydrogen production technologies (reproduced from [12])

Method of production	Technology (TRL)	Readiness Level	Feedstock
Alkaline electrolysis	9		H_2O + electricity
PEM electrolysis	7-8		H_2O + electricity
Solid Oxide electrolysis	3-5		H_2O + electricity + heat
Biomass gasification	4		Biomass + heat
Biological	1-3		Biomass + microbes (+light)
Photoelectrochemical	1-3		H_2O + light
Thermochemical	1-3		H_2O + heat

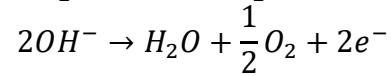
2.3.2.1.1 Alkaline water electrolysis

Alkaline water electrolysis is an electrochemical method used for splitting water into its components in the presence of electricity. This process involves two separate half-cell reactions: the hydrogen evolution reaction (HER) at the cathode and the oxygen evolution reaction (OER) at the anode.

At cathode (Hydrogen Evolution):



At anode (Oxygen Evolution):



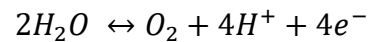
The produced H_2 has a purity over 99%, and can be collected from the cathode surface, while the remaining hydroxyl ions (OH^-) migrate under the influence of an electric circuit, passing through a porous separator to reach the anode. At the anode, the hydroxyl ions (OH^-) are discharged, leading to the production of half a molecule of oxygen (O_2) and one molecule of water (H_2O). The alkaline water electrolyzer operates at relatively low temperatures ranging from 30 to 80 °C and employs a concentrated alkaline solution, typically 5M KOH or NaOH. In this setup, the electrodes are typically made of stainless steel coated with nickel (Ni), and a diaphragm composed of asbestos/ ZrO_2 -based materials is used to separate the two compartments [82], [83], [84], [85]. The hydroxyl ion (OH^-) serves as the primary ionic charge carrier in this process, facilitated by the presence of KOH/NaOH, and water flows through the porous structure of the diaphragm to enable the electrochemical reaction to occur [86]. Alkaline electrolyzers with zero gap configuration, i.e. with electrolyte membrane, are known as anion exchange membrane (AEM) electrolyzers [87]. The reduced internal resistance due to the thin electrolyte membrane allows for higher current densities and thus higher performance. However, AEMs are still in a development stage compared to more mature alkaline water electrolysis technology.

The primary advantage of alkaline electrolysis systems is the maturity of the technology, with multiple multi-megawatt level facilities being currently deployed worldwide and at an industrial scale [88], [89]. Alkaline electrolysis outperforms PEM electrolysis in terms of lower installation and initial investment costs, and requires lower current densities and lower specific energy, around 4.4 kWh/kg of H₂ compared to about 4.7 kWh/kg for PEM. However, it does require larger cell areas and the purity of H₂ is slightly lower compared to PEM [90]. As such, in recent times, it has fallen out of favor, at least in academic circles, as work shifts toward development of PEM technology for widespread commercialization.

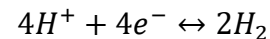
2.3.2.1.2 PEM electrolysis

Proton exchange membrane (PEM) electrolysis is considered as the second most viable and established technology for the production of hydrogen from water [12]. PEM electrolyzers use a solid electrolyte such as sulfonated polystyrene, instead of soluble electrolyte like KOH in alkaline electrolysis. The name of the technology derives from the use of the Nafion electrolyte membranes, which allow for the travel of H⁺ ions, or more simply, protons. At the anode, water is dissociated to produce oxygen, electrons and hydrogen ions. The H⁺ ions, or protons, travel from the anode to the cathode through the cathode, where they combine with available electrons to produce hydrogen [91]. The reaction mechanism is described below;

At cathode:



At anode:



PEM is considered as having benefits in terms of safety over alkaline electrolysis. It also has a higher charge density, resulting in reduction of size for electrolyzers having equal production rates.

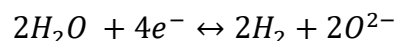
However, it does not offer the same level of flexibility in terms of large-scale production and is currently more expensive than alkaline systems. The durability and higher costs of PEM components is currently the largest hurdle currently standing in the way of PEM technology proliferation [90]. This is an area where further study in terms of analytical and on-field deployment is required [64], with more technology development leading to more widespread adoption and reducing of initial investment and overall technology costs.

Alkaline and PEM electrolysis is considered as being the most viable options for H₂ generation utilizing renewable feedstocks and has thus seen the most attention in the context of both hydrogen and ammonia generation. The TRL for Haber Bosch process utilizing alkaline and PEM electrolysis is 9 and 7, respectively, and already multiple plants have been deployed utilizing water electrolysis for the production of green hydrogen and ammonia.

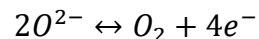
2.3.2.1.3 Solid oxide water electrolysis

Solid oxide electrolyzers (SOEC) is a new frontier of water electrolysis and is currently undergoing extensive development. Compared to alkaline and PEM electrolyzers, solid oxide electrolyzers operate at much higher temperatures in the range of 900 °C, and require a heat input for operation, with the cell efficiency increasing with increase in temperature [92]. However, higher temperatures also result in rapid degradation of the solid electrolyte. The half-cell reactions are described below [91];

At cathode:



At anode:



The advantages in SOEC lie in the low electrical power input required for hydrogen dissociation, lower cell areas, lower current density requirements and the overall high energy efficiency of the cell, which can exceed 80%. However, due to the high temperatures involved, material reliability and the generally nascent nature of the technology, large-scale deployment of SOEC has not yet been possible.

Table 3 summarises different Generation 2 technologies and their performance from the literature.

Table 3: Comparison table of different Generation 2 applications with regards to ammonia production, operating conditions, and sources used (material and energy)

Input/Sources	Operating temperature (°C)	Operating pressure (Bar)	Method of hydrogen production	Method of nitrogen production	Catalyst	Ammonia production rate	Year	Reference
Water & Air/ Solar power	298 K	100 KPa	Water electrolysis (PEM)	air separation (cryogenic)	-	0.22 kg/s	2019	[39]
Water/ Solar Power	313.15 K	101.3 KPa	Water electrolysis (Alkaline)	-	PtB & IrRuOx	0.83 kg/s	2022	[93]
Water & Nitrogen/ Solar Power	300	10	Water electrolysis (PEM)	-	Pre-reduced iron-based (KM1R)	2.73×10^{-7} kg/s	2020	[42]
Water & Air/ Wind power	400	20-60	water electrolysis	air separation (PSA)	Iron-based	7.5×10^{-4} kg/s	2017	[37]
H ₂ , N ₂	150-400	1-2.5	-	-	Iron-based	9×10^{-7} - 1.8×10^{-5} kg/s (per g sorbent)	2017	[48]
Water & Air/ Wind power	400	25-100	water electrolysis	air separation (PSA)	wustite-based iron catalyst	8.52×10^{-6} - 1.53×10^{-4} kg/gcat.s	2019	[49]
H ₂ , N ₂	492	25	-	-	wustite-based iron catalyst	8.52×10^{-6} kg/s	2016	[50]
Water & Air/ Wind power	400	20	water electrolysis	air separation (PSA)	wustite-based iron catalyst	2.05×10^{-8} - 3.07×10^{-8} kg/gcat.s	2018	[51]
N ₂ , NH ₃	(25)100/300 (abs/des)	276 kPa	-	-	-	4.26×10^{-2} kg/mol sorbent	2022	[52]
H ₂ , N ₂	460	30	-	-	Iron-based (AmoMax10RS)	4.63×10^{-4} kg/gcat.s	2022	[53]

2.3.2.2 Applications

Renewable energy sources such as solar, wind, photovoltaics, and geothermal energy have been applied to power the hydrogen (H_2) production sub-system through water electrolysis. For instance, integrated systems combining ammonia (NH_3) synthesis with fuel cell technology have been developed for solar photovoltaic power plant applications [39]. In this setup, excess power generated by the solar photovoltaic plant is used for ammonia production. During periods of low solar energy availability, some of the produced ammonia is employed as fuel to generate useful power. This integrated approach enables the storage of surplus energy from the solar photovoltaic plant in the form of NH_3 . At peak power output, the production rates are 97.2 mol/s for H_2 and 64.8 mol/s for NH_3 . The overall energy and exergy efficiencies, along with the maximum energy discharge capacity, are 15.83%, 16.67%, and 7924.2 kWh, respectively.

In another study, an integrated photovoltaic -driven ammonia production system utilizing renewable H_2 generated by a proton exchange membrane electrolyzer (PEM) was analyzed [39]. At the lowest solar irradiation intensity of 200 W/cm^2 , energy and exergy efficiencies of 26.08% and 30.17%, respectively, were reported. As solar irradiation intensity increased (while maintaining a constant air flow rate), efficiencies decreased due to low energy and exergy output despite higher solar radiation levels. At nitrogen (N_2) and hydrogen (H_2) production rates of 10.58 mol/s and 2.35 mol/s, respectively, the ammonia production rate reached 12.9 mol/s.

Karaca and Dincer [93] carried out experimental assessment of a photoelectrochemical cell green hydrogen generator using a novel mesh electrode geometry to utilize solar energy to enable water splitting for hydrogen generation. From thermodynamic analysis of the system, a linear correlation

between the surface illumination of the electrodes and the rate of hydrogen production, and consequently, the solar-to-hydrogen efficiency, is observed. The same linear increase in rate of production is also observed as solar irradiance increases, however the efficiency is observed to slightly decrease with rise in solar irradiance, as the PEC cell reaches the upper bound of the possible rate of production, and so input solar energy is wasted. Overall, the cell is observed to achieve an energy efficiency of 6.30% and exergy efficiency of 6.38% at a surface illumination of 870 cm^2 . Environmental impact and life cycle assessments for this design was carried out [94], and it was observed that when the rate of production of hydrogen is $47.1 \text{ } \mu\text{g/s}$, the ozone depletion potential reaches a value of 4.14 mg CFC-11 equivalent per kg of hydrogen. Global warming potential for the PEM cell is observed to be 1.052 kg CO_2 equivalent per kg hydrogen. The major disadvantage of this system is observed to be the process loss due to the high energy bandgap of the semiconductors, limiting the amount of solar energy that can be harnessed.

Sousa et al [45] conducted technoeconomic study of a green ammonia production plant utilizing PEM electrolysis and Haber-Bosch synthesis based on experimental data. The plant utilized an adiabatic reactor having three beds, and the overall ammonia conversion as found to be 26%, with the levelized cost of ammonia being calculated to be about $1250 \text{ } \text{€}/\text{MT}_{\text{NH}_3}$, which is three times the cost as produced from current conventional sources. However, this cost is expected to be reduced with further proliferation and depreciation of renewable electricity and electricity production costs, as well as proper site selection.

Siddiqui et al [42] experimentally investigated the performance of a direct synthesis ammonia reactor using solar energy captured using photovoltaic cells. Green hydrogen is produced using

proton exchange membrane electrolyser, using solar energy from PV cells as input. A tubular reactor with specific dimensions was employed, using 50 grams of an iron oxide industrial catalyst. The catalyst is activated by passing hydrogen gas through it at a flow rate of $16.7 \text{ cm}^3/\text{s}$ for 7 hours. The activation process takes place at a temperature of 300°C , with a gradual temperature increase of 10°C per minute. During steady state operation, the reactor operates at 300°C and 10 bar. The ammonia synthesis rate achieved is 0.016 mmol/s , resulting in low overall energy and exergetic efficiencies of 1.9% and 1.8%, respectively. The solar-to-hydrogen sub-process demonstrates better efficiencies, with energy efficiency at 2.4% and exergy efficiency at 2.1%. The proton exchange membrane-based water electrolysis subsystem shows higher energy and exergy efficiencies of 19% and 15.3%, respectively.

Cussler et al. [37] designed a pilot plant for small-scale ammonia production at lowered pressures, in the range of 20 to 60 bar, and achieved production performance comparable with industrial plants. The feed is provided by nitrogen produced via air separation, and hydrogen produced via electrolysis, with the required power for all processes being generated by wind turbines. The primary innovation of this technique is the use of absorbent material, such as magnesium chloride, to remove ammonia from the system as it forms, in lieu of a condenser. Using absorbent material, high synthesis rates of ammonia at pressures as low as 25 bar was found to be viable, with the performance expected to improve further with improved recycling of unreacted gas flows. However, this technique is constrained by the stability [48] and availability of the absorbent materials, with being noted that the best performing materials often lack the robust, long-term capabilities required to scale up this technology.

Further optimization study of this technology [49] concluded that while absorption allows for swifter removal of ammonia than condensation at the same pressure, this effect diminishes as the operating pressure of the absorber increases. Furthermore, while at high pressures, the partial pressure of ammonia is low compared to the reaction pressure, allowing for ease of extraction, at lower pressures the partial pressure significantly reduces, and thus the pressure differential between the absorber and ammonia vapor becomes more influential in achieving high yields. This would require higher mass of absorber, if the cost of increased piping and cost of cooling is deemed too large.

Malmali et al. [50], [51] studied the use of reactive separation using calcium chloride absorbents for production of ammonia at reduced pressures, observing that the primary parameter contributing more significantly to the reaction kinetics was temperature rather than pressure. However, the reactor pressure is observed to affect reaction rate, which increases with increase in pressure, and the subsequent increase in ammonia concentration in reactor exit stream allows for higher absorption. As stated above, the recycling flow also has significant effect, with higher recycling resulting in higher rates of reaction for the ammonia synthesis process, with this requiring increased equipment investment and may potentially also be practically unviable. Regardless, this process allows for high production of ammonia at pressures as low as 25 bar, provided that the absorber is able to remove ammonia as it is produced effectively.

Optimization study of these systems [52] found the potential for production of ammonia having purity of 97.5% using calcium chloride absorbent and absorption temperature of 25 °C at a pressure of 276 kPa, with ammonia removal being carried out via desorption at 300 °C. Further parametric

study [50] corroborated the conclusion that performance increased at lower absorption and higher desorption temperatures, and that the reaction, absorption and desorption temperatures are more influential in the process than operating pressure. Furthermore, while recycling of flow is observed to increase performance, it is not a singular solution, and consideration of factors such as the operating temperatures, volumetric flow rate is required for optimal production, especially for continuous operation.

Ishaq et al. [47] experimentally developed a cascaded ammonia synthesis reactor, operating at lowered conditions of 310-390 °C temperature and 6-12 bar pressure, using industrial KMR catalyst. The system consists of two ammonia reactors containing the activated catalyst, fed by nitrogen and hydrogen feed gas. Output stream from the first reactor is used as input stream for the second, and an ammonia trap is placed after the second reactor to capture the ammonia produced. It is observed that changes in temperature and pressure significantly influence ammonia conversion rates in the cascaded ammonia synthesis system. Increasing the temperature from 310 °C to 370 °C at 12 bar pressure led to higher ammonia conversion rates in both synthesis reactors, with substantial percentage increases. Additionally, elevating the pressure from 6 to 12 bar at 370 °C also resulted in improved ammonia conversion ratios.

2.3.3 Generation 3: Electrochemical Ammonia Production

Electrochemical synthesis allows for the direct production of green ammonia from atmospheric nitrogen and water, using renewable energy sources such as solar or tidal energy. This process is entirely distinct from the Haber-Bosch process and has several advantages over the conventional Haber-Bosch process, such as lower sensitivity to power fluctuation and intermittency, lower sensitivity to feed purity, and higher energy efficiencies [29], [95]. Electrochemical reduction would also allow for the production of ammonia at ambient temperatures and pressures, using unrefined feedstock such as air and water at ambient conditions [46], [96]. This flexibility, coupled with the use renewable sources for power input, makes this technology very lucrative for achieving the green ammonia paradigm shift.

In this process, hydrogen or water is typically oxidized, i.e loses electrons, at the anode to produce oxygen. This oxidation generates protons (H^+) as a result. Protons generated at the anode travel through a solid or liquid electrolyte to reach the cathode. On the cathode side, nitrogen reacts with the protons under mild conditions to produce ammonia. The reactions are detailed in Table 4.

Table 4: Feed Reactants and Half-Reactions in the Electrochemical Synthesis of Ammonia (reproduced from [97])

Feedstock	Anode		Cathode	
	Reactant	Reaction	Reactant	Reaction
H_2/N_2 or air	H_2	$H_2 \rightarrow 2H^+ + 2e^-$	N_2 or air	$N_2 + 6H^+ + 6e^- \rightarrow 2NH_3$
H_2O/N_2 or air	H_2O	$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$	N_2 or air	$N_2 + 6H^+ + 6e^- \rightarrow 2NH_3$
H_2O/N_2 or air	O^{2-}	$2O^{2-} \rightarrow O_2 + 4e^-$	H_2O and N_2 or air	$3H_2O + N_2 + 6e^- \rightarrow 3O^{2-} + 2NH_3$

The use of electrochemical processes allows for the operation of such systems across different temperature ranges. At temperatures of around 500 °C, comparable to conditions used for the

Haber-Bosch process, the performance of the electrochemical synthesis cell relies heavily on the selectivity, material conductivity, and catalytic behavior of the electrolyte and electrode material [97]. Along with this, the equilibrium remains significantly influential, with the high temperature favoring the decomposition of ammonia into hydrogen and nitrogen. This leads to hydrogen losses of up to 40%, and generally lower faradic efficiency than expected [98], [99].

At lower temperatures, between 100 °C to 500 °C, the use of molten electrolytes [54] has been observed to have favorable effect on the performance of the electrolyzer, achieving faradic efficiencies of more than 70% and energy efficiencies of more than 50%, with some systems achieving faradic efficiencies of almost 90% [55], albeit at the loss of energy efficiency.

At sub 100 °C, while the equilibrium favors the production of ammonia, the electrokinetics of the reaction become the limiting factor and performance diminishes to sub-10% faradic efficiency. However, recent advances have shown promise, with Du et al [31] achieving near 100% faradic efficiency operating at ambient temperature and 50 bar pressure, utilizing lithium-based electrolyte and by augmenting the behavior of the electrode and electrolyte interface. Lan et al [46] reported the production of ammonia at ambient temperature and pressure utilizing electrochemical process. Their system used Nafion membranes as solid electrolyte, and the system is able to produce ammonia directly from water and air.

Regardless, while Generation 3 technologies are promising, they are still only at the laboratory stage, and thus robust, high-performance systems at these conditions, comparable to that of contemporary Haber-Bosch plants, utilizing renewable energy and feedstock consisting of air and

water, still remains the ultimate objective of Generation 3 technology. Furthermore, they are still not financially viable, and require much more work regarding electrode material, catalyst applications, and improvements to Faradaic efficiency.

Electrochemical processes offer the best potential for ammonia synthesis under mild conditions, with the electrochemical reduction of N_2 being possible at both lowered temperatures and pressures compared to the traditional Haber-Bosch process. Rod et al. [100] carried out density functional theory analysis to assess the possibility of nitrogen reduction at reduced conditions in the presence of metal surface catalysis, ultimately concluding that electrochemical processes would allow for this form of synthesis. Marnellos and Stoukides had earlier carried out synthesis of ammonia using solid electrolyte, achieving minimum H_2 conversion of 78%, at temperatures around 550 °C and N_2 partial pressures of less than 2 kPa [101].

Recently, catalysis of ammonia synthesis, especially for the electrochemical reduction of nitrogen, or Generation 3 ammonia production, has received increased attention. Attempts to develop catalysts to allow for ammonia production at more favorable conditions have been encouraging, with Hattori et. al [102] developing a low-temperature ammonia synthesis method utilizing a stable electron-donating heterogeneous CaFH catalyst, which is a solid solution of CaF_2 and CaH_2 formed at low temperatures. This catalyst can facilitate ammonia production from N_2 and H_2 gases at just 50 °C, and it exhibits an extremely low activation energy of only 20 kJ mol⁻¹. This activation energy is less than half of what has been reported for conventional catalysts. The remarkable catalytic performance of cubic CaFH is attributed to the weak ionic bonds between Ca^{2+} and H^- ions in the solid solution, as well as the easy release of hydrogen atoms from H^- sites.

The same research group [103] also studied the capability of metallic iron particles to catalyze ammonia synthesis at temperatures of around 100 °C when used in conjunction with BaH_2 . Ruthenium based catalysts have been considered as the next step in ammonia catalysis, but industrial applications have been difficult due to their comparatively lower stability and higher cost [104], especially compared to industrial iron-based catalysts. However, they do outperform iron-based catalysts in terms of operation at low pressures, and considerable research has been performed in recent years to understand and improve their viability [96 - 109].

Gomez et al [57] carried out technical and life-cycle assessment for an electrochemical proton exchange membrane-based synthesis system for production of ammonia. This process is able to use renewable sources throughout the entire process, with hydrogen being produced by electrolysis, nitrogen by air separation, and ammonia being synthesized in an electrochemical cell with molten hydroxide electrolyte, with the required power being at least 17 MWh per metric ton ammonia, at a Faradaic efficiency of 56%. Life cycle assessment for a similar electrochemical ammonia synthesis reactor using iron-based catalysts was conducted by Bicer and Dincer [58], considering the environmental effect of such a system, reporting a global warming potential of 1.09 kg CO_2 per kg NH_3 , which is half the value of 2.5 kg CO_2 per kg NH_3 for a Haber-Bosch plant.

Table 5 summarizes the existing literature on Generation 3 technologies.

Table 5: Comparison table of different Generation 3 technologies with regards to ammonia production, operating conditions, and operating conditions

Input/Sources Reactants	Output Electrolyte	Operating temperature (°C)	Operating pressure (Bar)	Cathode Reaction	Anode Reaction	Catalyst	Electrode Material	Faradaic Efficiency	Ammonia production rate	Year	Reference
H ₂ N ₂ or H ₂ N ³⁻ /No energy source	LiCl-KCl-CsCl-Li ₃ N	400	1.013	1/2N ₂ +3e ⁻ =N ³⁻	3/2H ₂ +N ³⁻ =NH ₃ +3e ⁻	-	Nickel	-	5.68×10 ⁻⁷ kg/s.m ²	2003	[54]
H ₂ & N ₂ /Solar Power	NaOH-KOH	180-260	1.013	N ₂ +6e ⁻ =2N ³⁻	2N ³⁻ +3H ₂ =2NH ₃ +6e ⁻	nano-Fe ₃ O ₄	Nickel	14.2%	7.51×10 ⁻¹⁵ kg/s.m ²	2017	[55]
EtOH, N ₂	LiNTf ₂	25	15	$3\text{Li}^+ + 1/2\text{N}_2 \xrightarrow{3\text{e}^-} \text{Li}_3\text{N} \xrightarrow{3\text{EtOH}} \text{NH}_3 + 3\text{Li}^+$		-	Nickel	99%	2.55×10 ⁻¹⁵ kg/s.m ²	2022	[31]
water and air	Nafion	25	1.013	2H ⁺ +2e ⁻ =H ₂ 2H ⁺ +1/2O ₂ +2e ⁻ =H ₂ O 6H ⁺ +N ₂ +6e ⁻ =2NH ₃	H ₂ O=2H ⁺ +1/2O ₂ +2e ⁻	Pt	Carbon	≈ 0.5%	1.94×10 ⁻⁷ kg/s.m ²	2013	[46]
H ₂ (water) & N ₂	molten hydroxide	200	≈ 1.013	N ₂ +6H ⁺ +6e ⁻ =NH ₃	3H ₂ O=6H ⁺ +3/2O ₂ +6e ⁻	noble metal-based	-	83%	1.58×10 ⁻¹⁵ kg/s.m ²	2020	[57]
H ₂ & N ₂ /Solar Power	NaOH-KOH	170 >	1.013	N ₂ +6e ⁻ =2N ³⁻	2N ³⁻ +3H ₂ =2NH ₃ +6e ⁻	nano-Fe ₃ O ₄	Nickel	-	1.88×10 ⁻⁶ kg	2017	[58]

2.3.3.1 Electrocatalysis using Metal-Organic Frameworks (MOF)

Another material that has seen promise as catalyst in recent years are metal organic frameworks (MOF). MOFs have an open structure and can also behave as precursors for oxide and sulfide molecules, and this nature has seen their application in fields such as energy storage, and other electrocatalytic fields. Recently, there has been interest in their application in ammonia synthesis [110 - 113]. However, it has also been posited that the lower electric conductivity of MOFs may hinder the electrochemical process, and as such, extensive research into the underlying mechanism and reactions involved in the electrocatalytic effect of MOFs in ammonia synthesis is still required [123]. Table 6 summarizes the current state of the art regarding Ru-based and MOF-based catalysis in electrochemical reduction of N₂.

Table 6: Summary table of metal and metal organic framework (MOF) catalysis performance in Generation 3 Ammonia Production

Catalyst	Operating Temperature (°C)	Operating Pressure (bar)	Faradaic Efficiency (%)	Ammonia Production Rate	Year	Reference
Cs-Ru/Sib2200	400	6.08		0.591 mol/gcat/h	2020	[105]
Ru/B2CA	490	10		189 mmol/gcat/h	2022	[106]
CsRu/CeO ₂ (2-4%)	260	1		1.18 mmol/gcat/h	2021	[107]
Ru-CNT GDE	25	1.01	13.5	2.1*10 ⁻⁹ mol/cm ² s	2020	[108]
Ba-(Ru/AC) ₀	400	10		38.0 mmol/gcat/h	2022	[109]
1.4 nm Ru NCs	400	10		17.13 mmol/gcat/h	2022	[110]
3Cs-2wt%Ru/Ba ₅ Ta ₄ O ₁₅	400	1		263.7 mmol/gcat/h	2021	[111]
Ba-Ru/gC-Al ₂ O ₃	400	10		5611 umol/g/h	2019	[112]
Co/C12A7:e-	340	1		912 umol/g/h	2019	[113]
Ru/C12A7:e-	360	1		2760 umol/g/h	2017	[114]
Ni/Al ₂ O ₃	35	1.01		471 umol/g/h	2019	[115]
CoO QD/RGO	25	1.01	8.3	21.5 ug/h/mgcat	2019	[116]
OV-Ti ₂ O ₃	25	1.01	19.29	37.24 ug/h/mgcat	2022	[117]

TiO ₂ /JE-CMTs	25	1.01	10.76	20.03 ug/h/mgcat	2022	[118]
HT Au@MOF			60.9	49.5 ug/h/mgcat	2022	[119]
Zn-Co ₃ O ₄			11.9	22.71 ug/h/mgcat	2021	[120]
Fe-TCPP			16.23	44.77 ug/h/mgcat	2021	[121]
HE-MOF			14.75	42.76 ug/h/mgcat	2023	[122]

2.3.4 Ammonia Synthesis at Low Pressures

The production of ammonia at mild conditions has long since been considered a “holy grail” of the industry, allowing for reduced investment and material cost, and less maintenance. To that end, considerable research has been carried out for achieving this goal, particularly in regard to Generation 2 technologies using the Haber-Bosch process, and Generation 3 technologies using entirely novel electroreduction techniques.

The Haber-Bosch process while being very mature in technology, is constrained by the underlying nature of the ammonia synthesis equilibrium reaction, and the condition constraints involved therein. As mentioned previously, in absence of catalyst, the reaction kinetics do not allow the synthesis of NH₃ below temperatures of 3000 °C, at which point the equilibrium is shifted towards the reactants instead of products. While iron-based catalysts do allow for the reaction to proceed at temperatures of around 500 °C, high pressures of 150 bar and above are still required. Till now, lower pressures have not been able to be used for the synthesis of ammonia via the Haber-Bosch process due to the ammonia equilibrium reaction favoring high pressures and suitable catalysts having not been available which are able to operate at lower pressures. Recently however, catalysts have been developed which allow the reaction to progress at industrially comparable rates of reaction at lower pressures [124], [125], as well as the use of chloride absorbers in absorption-resorption technologies for efficient and fast separation of NH₃ has allowed for the operation of

Haber-Bosch process plants at below 100 bar pressure. It should be noted that water electrolysis produces hydrogen at pressures of about 50 bar, and as such lower ammonia synthesis pressures would reduce the overall compression work for the system, lowering energy requirements and improving efficiencies.

Cussler et al. [37] designed a pilot plant for small-scale ammonia production at lowered pressures, in the range of 20 to 60 bar, and achieved production performance comparable with industrial plants. The feed is provided by nitrogen produced via air separation, and hydrogen produced via electrolysis, with the required power for all processes being generated by wind turbines. The primary innovation of this technique is the use of absorbent material, such as magnesium chloride, to remove ammonia from the system as it forms, in lieu of a condenser. Using absorbent material, high synthesis rates of ammonia at pressures as low as 25 bar was found to be viable, with the performance expected to improve further with improved recycling of unreacted gas flows, as the absorbent material allows for faster separation of product ammonia, shifting equilibrium towards the synthesis of ammonia. However, this technique is constrained by the stability [48] and availability of the absorbent materials, with being noted that the best performing materials often lack the robust, long-term capabilities required to scale up this technology.

Further optimization study of this technology [49] concluded that while absorption allows for swifter removal of ammonia than condensation at the same pressure, this effect diminishes as the operating pressure of the absorber increases. Furthermore, while at high pressures, the partial pressure of ammonia is low compared to the reaction pressure, allowing for ease of extraction, at lower pressures the partial pressure significantly reduces, and thus the pressure differential between the absorber and ammonia vapor becomes more influential in achieving high yields. This

would require higher mass of absorber, if the cost of increased piping and cost of cooling is deemed too large.

Malmali et al. [50], [51] studied the use of reactive separation using calcium chloride absorbents for production of ammonia at reduced pressures, observing that the primary parameter contributing more significantly to the reaction kinetics was temperature rather than pressure. However, the reactor pressure is observed to affect reaction rate, which increases with increase in pressure, and the subsequent increase in ammonia concentration in reactor exit stream allows for higher absorption. As stated above, the recycling flow also has significant effect, with higher recycling resulting in higher rates of reaction for the ammonia synthesis process, with this requiring increased equipment investment and may potentially also be practically unviable. Regardless, this process allows for high production of ammonia at pressures as low as 25 bar, provided that the absorber is able to remove ammonia as it is produced effectively.

Optimization study of these systems [52] found the potential for production of ammonia having purity of 97.5% using calcium chloride absorbent and absorption temperature of 25 °C at a pressure of 276 kPa, with ammonia removal being carried out via desorption at 300 °C. Further parametric study [50] corroborated the conclusion that performance increased at lower absorption and higher desorption temperatures, and that the reaction, absorption and desorption temperatures are more influential in the process than operating pressure. Furthermore, while recycling of flow is observed to increase performance, it is not a singular solution, and consideration of factors such as the operating temperatures, volumetric flow rate is required for optimal production, especially for continuous operation.

Ishaq et al. [47] experimentally developed a cascaded ammonia synthesis reactor, operating at lowered conditions of 310-390 °C temperature and 6-12 bar pressure, using industrial KMR catalyst. The system consists of two ammonia reactors containing the activated catalyst, fed by nitrogen and hydrogen feed gas. Output stream from the first reactor is used as input stream for the second, and an ammonia trap is placed after the second reactor to capture the ammonia produced. It is observed that changes in temperature and pressure significantly influence ammonia conversion rates in the cascaded ammonia synthesis system. Increasing the temperature from 310 °C to 370 °C at 12 bar pressure led to higher ammonia conversion rates in both synthesis reactors, with substantial percentage increases. Additionally, elevating the pressure from 6 to 12 bar at 370 °C also resulted in improved ammonia conversion ratios, from 5.42% to 9.16%.

The other promising avenue for low pressure ammonia synthesis is electrochemical reduction of N_2 , or Generation 3 Ammonia production. Electrochemical processes offer the best potential for ammonia synthesis under mild conditions, with the electrochemical reduction of N_2 being possible at both lowered temperatures and pressures compared to the traditional Haber-Bosch process. Rod et al. [100] carried out density functional theory analysis to assess the possibility of nitrogen reduction at reduced conditions in the presence of metal surface catalysis, ultimately concluding that electrochemical processes would allow for this form of synthesis. Marnellos and Stoukides had earlier carried out synthesis of ammonia using solid electrolyte, achieving minimum H_2 conversion of 78%, at temperatures around 550 °C and N_2 partial pressures of less than 2 kPa [101].

Recently, the catalysis of ammonia synthesis, especially in the context of electrochemical reduction of nitrogen, or Generation 3 ammonia production, has received increased attention. Attempts to develop catalysts to allow for ammonia production at near ambient conditions have been encouraging. Hattori et. al [102] developed a low-temperature ammonia synthesis method utilizing a stable electron-donating heterogeneous CaFH catalyst, which is a solid solution of CaF_2 and CaH_2 formed at low temperatures. This catalyst can facilitate ammonia production from N_2 and H_2 gases at just 50 °C, and it exhibits an extremely low activation energy of only 20 kJ mol⁻¹. This activation energy is less than half of what has been reported for conventional catalysts. The remarkable catalytic performance of cubic CaFH is attributed to the weak ionic bonds between Ca^{2+} and H^- ions in the solid solution, as well as the easy release of hydrogen atoms from H^- sites. The same research group [103] also studied the capability of metallic iron particles to catalyze ammonia synthesis at temperatures of around 100 °C when used in conjunction with BaH_2 . Ruthenium based catalysts have been considered as the next step in ammonia catalysis, but industrial applications have been difficult due to their comparatively lower stability and higher cost [104], especially compared to industrial iron-based catalysts. However, they do outperform iron-based catalysts in terms of operation at low pressures, and considerable research has been performed in recent years to understand and improve their viability [96 - 109].

In recent years, metal-organic frameworks (MOFs) have emerged as promising catalysts, possessing an open structure and being able to serve as precursors for oxide and sulfide molecules, which facilitate their application in fields such as energy storage and various electrocatalytic processes. While recent interest has focused on their potential use in ammonia synthesis, the relatively low electrical conductivity of MOFs may impede the electrochemical process.

Therefore, extensive research into the underlying mechanisms and reactions involved in the electrocatalytic effect of MOFs in ammonia synthesis remains necessary [123].

2.3.5 Integration of Ammonia Synthesis with Multi-Generation Systems

Investigations into the generation and synthesis of ammonia from renewable resources has received increased attention, both in academia and industry, due to the existence of an already well-established transport infrastructure and the ability of ammonia to act as a hydrogen carrier. Existing ammonia synthesis plants can also be easily integrated with renewable technologies [126], as well as power generation, desalination, and chemical production systems, thus further leveraging existing technology to meet global climate goals, while operating at reduced costs.

Ishaq and Dincer [126] proposed modifications to existing ammonia plants based on steam reforming technology, utilizing solar technologies and absorption cooling in order to reduce overall environmental impact. Solar thermal energy is harnessed using a solar heliostat field and transmitted through molten salt to provide energy required for absorption cooling and steam reforming process. The absorption cooling unit separates produced ammonia and uses a portion as refrigerant. Heat exchangers between the absorber and generator serve to reheat the strong solution before reaching the generator, thus maintaining the cycle. The remaining thermal energy is used to produce steam from water for reformers, which operates at 730°C and 5 bar, leading to the formation of CO and H₂. CO generated in this process proceeds to the water gas shift reactor, operating at 440°C and 14.4 bar, where it reacts with steam to produce CO₂ and H₂, with the produced CO₂ being used to produce methanol. The system incorporates a pressure swing adsorption unit to separate oxygen for natural gas autothermal reforming and nitrogen for ammonia synthesis. A portion of the hydrogen produced in the natural gas reforming unit is directed to the

cascaded ammonia production unit for ammonia synthesis. Key findings of the study include that the system's operation yields 13.31 mol/s of CH_3OH and provides a cooling capacity of 625.9 kW. Furthermore, it produces 10 mol/s of H_2 and 2.4 mol/s of NH_3 . The overall energy and exergy efficiencies are determined to be 66.83% and 68.55%, respectively.

Siddiqui and Dincer [127] carried out exergoeconomic and optimization studies for a novel design of a combined plant to produce ammonia, hydrogen and electricity using both solar and wind energy to drive a PEM electrolyzer and pressure swing adsorption separator for generation of hydrogen and nitrogen, respectively. The produced hydrogen and nitrogen would be used to provide feed for an ammonia synthesis reactor, as well as an ammonia fuel cell for electricity generator. Under design conditions of ammonia fuel cell operating temperature of 25 °C, the system's total cost rate is \$63,345 per hour, with an overall exergy efficiency of 29.7%. However, the optimal operating point, considering design solar intensity and wind speed, results in a lower total cost rate of \$59,755 per hour and a slightly improved exergy efficiency of 30.4%. At high wind speed and solar intensity, the optimal exergy efficiency is 27.3% and total cost rate is \$51,262 per hour.

Yuksel et al [128] proposed a novel design for a multigeneration plant based on gas Brayton cycle, with power, hydrogen, heating and cooling, drying and freshwater as outputs. The highly integrated system involves a Brayton cycle using methane gas fuel, combined with a supercritical CO_2 power cycle. This setup is further complemented by the organic Rankine cycle, proton exchange membrane (PEM) electrolyzer for hydrogen production, ammonia production system, freshwater production unit using reverse osmosis, cooling cycle, and dryer unit. The overall energy

and exergy efficiency of the plant has been determined to be 69.08% and 65.42%, respectively, with the production rates of ammonia and hydrogen calculated to be 0.2462 kg/s and 0.0631 kg/s, with an overall power generation of 26,435 kW.

The same authors also proposed a design for a combined plant producing power, hydrogen, methane, ammonia and urea, based on solar power input [129]. The system integrates a PEM electrolyzer, NH_3 reactor, methanation unit in conjunction with a carbon capture system for production of hydrogen, ammonia, methane and urea. The system is analysed in terms of energy, exergy and cost, with the multigeneration system attaining energetic and exergetic efficiencies of 66.12% and 61.56%, respectively. At higher solar intensities, the exergy efficiency increased from 57.64% to 65.73%. The cost of hydrogen (H_2) generation reaches 1.58 \$/kg H_2 , with higher solar radiation intensity reducing this value to a minimum of 1.50 \$/kg H_2 . The overall levelized energy cost of the proposed plant was found to be 0.084 \$/kW.

Ozturk and Dincer [39] performed a case study for an integrated ammonia synthesis system, based on green hydrogen and solar thermal power for the context of Istanbul, Turkey. The ammonia production incorporates a polymer electrolyte membrane (PEM) electrolyzer, a cryogenic air separation unit, and a reactor for ammonia synthesis. The process commences with air compression, followed by heat extraction in a heat exchanger, and the recovered heat serves hot water needs. The cooled air then undergoes expansion via a turbine, where a generator produces electricity. Nitrogen separated from the column and hydrogen generated by the PEM electrolyzer are utilized in the reactor for ammonia synthesis, with the electricity requirements for the electrolyzer and compressor being met through photovoltaic panels. Thermodynamic and

parametric study of the plant was conducted, and it was found that the multigeneration system exhibits its highest energy and exergy efficiencies when solar radiation intensity is at a minimum, reaching 26.08% and 30.17%, respectively. This contradictory behavior is due to the low efficiencies of the solar photovoltaic panels and resulting large energy and exergy losses. The PEM electrolyzer consumes 3410 kW of electricity, and the ammonia reactor releases 585.4 kW of heat. Enhanced power output from the photovoltaic panels can be achieved at greater solar radiation intensity and expanded panel area. The system demonstrates the capacity to produce 0.22 kg/s of ammonia, utilizing 0.04 kg/s of H_2 generated by the PEM electrolyzer and 0.18 kg/s of N_2 from the cryogenic air separation unit.

Furthermore, Ozturk et al. designed an integrated multigeneration plant utilizing geothermal energy to produce H_2 , NH_3 , freshwater, drying, and power [128]. The study reported a total exergy destruction of about 13 707 kW in the system, with ammonia production being the most efficient sub-system at 74.26%, followed by drying at 75.16%. The overall energy and exergy efficiencies depended on the temperature of the geothermal renewable energy source, with 59% and 55% energy and exergy efficiencies reported at 180 °C.

Several theoretical studies have also proposed synergistic wind and solar-driven hybrid systems for cascaded ammonia synthesis [41], [127]. For example, an investigation in Toronto explored the effects of wind speeds and solar radiation intensities on system efficiencies and the production of H_2 and NH_3 , assuming solar and wind sources to be 15% and 45%, respectively. In this report, a maximum power output of 12 155 kW was achieved during average days, resulting in an overall energy efficiency of 24.2%, an exergetic efficiency of 26.06%, and maximum production rates of

42.2 mol/s for H_2 and 9.92 mol/s for NH_3 . Conversely, power production was minimal during December (around 5000 kW), with energy and exergy efficiencies of 18% and 19.21%, respectively.

Karaca et al [94] developed and analysed a novel renewable-based integrated power system tailored for Antigua and Barbuda. This proposed system has an overall power capacity of 60 MW, with 40 MW being produced from wind and 20 MW from solar, and strategically incorporates various sub-components in a thermodynamically optimized manner to yield multiple valuable outputs within a distinctive integrated energy system framework. To address energy storage needs during off-peak periods, the integrated system adopts compressed air storage with undersea air balloons as the storage medium, providing an efficient mechanical energy storage solution. The thermal energy generated from the cooling stages during the air compression process is stored for subsequent utilization in the power production process through compressed air. Additionally, the proposed system serves the local community by supplying desalinated potable water using a multistage water distillation method. The electricity generation capacity is 316 GWh, and during the charging phase, it operates with energy and exergy efficiencies of 45.4% and 37.6%, respectively, while during the discharging phase, the efficiencies are 23.5% and 24.9%, respectively. Additionally, the system can provide 124.07 tons of fresh water daily for Antigua and Barbuda. The daily compressed air storage capacity is estimated at 1388 m³. The initial cost for wind turbines and solar photovoltaic panels is assessed at 129 million US\$. Moreover, the proposed system has the potential to reduce CO₂ emissions by 88% compared to the existing power plant in Antigua and Barbuda, which currently relies on heavy fuel oil.

Demir and Dincer [130] focused on the development and thermodynamic analysis of an innovative solar energy-based multigeneration system designed for ammonia synthesis, freshwater production, and electricity generation. The system comprises various components, including a solar thermal subsystem, a thermal energy storage (TES) system, a solar-driven Rankine cycle, a desalination unit, a proton exchange membrane (PEM) electrolyzer, and an ammonia synthesis subsystem. The goal is to explore the synergies and efficiencies of these integrated components in providing multiple useful outputs within a sustainable and energy-efficient framework. The energy and exergy efficiencies of the solar-driven system are found to be 70.3% and 12.1%, respectively. The air separation unit has minimal impact, contributing less than 0.3% to the overall system's energy and exergy efficiencies. The exergy efficiency of the ammonia synthesis unit is found to be 59.3%, while the net power production capacity of the system is calculated at 17.6 MW. The ammonia production capacity is determined as 0.85 kg/s, and the freshwater production capacity is calculated as 143.97 kg/s. Notably, the solar receiver is identified as the main contributor to exergy destruction and losses within the system, accounting for 70.8 MW.

Juangsa and Aziz [131] proposed an integrated system to produce ammonia, and power. Oxidation of AlN is used to generate ammonia, as opposed to the traditional Haber-Bosch process, with combustion of syngas being used to generate the high temperatures required. Power is produced through the use of a steam Rankine cycle, and the maximum power output is found to be about 250 MW at an energy efficiency of 69.3%, and the maximum ammonia yield from the oxidation of AlN reached is 88%.

Wen and Aziz[132] developed the operation strategy for an integrated system consisting of solar and wind energy capture, steam Rankine cycle, hydrogen and ammonia production, and electrical

energy storage subsystems for the context of 10 major cities in China, and also studied the parametric effect and performance variation due to changing weather conditions. The overall system demonstrated maximum energy and exergy efficiencies of 50% and 73.1%, respectively, with the solar subsystem having corresponding maximum energy and exergy efficiencies of 33.7% and 59.4%. The wind subsystem operates at a maximum energy and exergy efficiencies of 43.5%. The backup power subsystem achieves maximum energy and exergy efficiencies of 59.5% and 60.9%, respectively. In the hydrogen production subsystem, the net hydrogen yield reached 994.5 ton per year, at maximum energy and exergy efficiencies of 51.3% and 50.1%. Finally, the ammonia synthesis subsystem produced 7201 ton per year of ammonia, achieving maximum energy and exergy efficiencies of 73.8% and 54.3%.

Su et al [133] evaluated an integrated system utilizing supercritical carbon dioxide and oxy-fuel combustion of biomass, Ion Transport membrane (ITM) and Claude cycle for production of power and liquid carbon-dioxide and nitrogen. Optimization of the plant for minimization of payback time and operating cost was also carried out, with the minimum payback time being found to be 5.7 years, corresponding to an annual operating cost of 46.58 million \$ per year.

Ishaq and Dincer [41] proposed a design for the production of ammonia from green hydrogen produced using PEM electrolyzer, and nitrogen separated from air, with the system being powered entirely with renewable power, with the proposed system having an energetic efficiency of 61% and an exergetic efficiency of 65.5%. The system utilized two ammonia synthesis reactors in cascade configuration, with the second reactor having the outlet stream of the first as inlet feed

stream, with the ammonia conversion being observed to increase with this change, as well as reducing costs related to the reheating and repressurizing of ammonia during storage.

Karaca and Dincer [93] analysed a novel design for a photoelectrochemical green hydrogen generator, having a mesh electrode of a conic geometry, and found that the design had energy and exergy efficiencies of about 6.3%.

Sanchez and Martin [43] evaluated the industrial production of ammonia at a rate of 300 ton/day, with all the required energy being produced from renewable sources, and hydrogen being produced by electrolysis. A rigorous mathematical model was developed and evaluated for both indirectly and directly cooled ammonia reactor, and cost analysis and optimization for the systems was also carried out. Solar energy is observed to perform better than wind energy as primary energy source but has the disadvantage of requiring large area, with 2.9 million photovoltaic panels being required to operate the system. The preference of reactor model is more nuanced, as direct cooling performs better in terms of economics, but the capital cost of solar field dominates in all cases.

Palone et al [134] analysed a plant configuration for the production of ammonia and methanol from waste plastic using three reactor chemical looping, wherein an oxygen carrier is used to carry out the three processes of reduction, syngas production and oxidation. The production efficiency for methanol is found to be around 44%, and that for ammonia is 55%, with the carbon emissions for the system being found to be significantly less than that from traditional processes.

Khasani et al. [135] proposed a system for the concurrent production of ammonia and power utilizing low-rank coal, involving coal drying and chemical looping for hydrogen and power generation, cryogenic air separation for the production of nitrogen and exergy recovery processes to improve overall efficiency. The system is evaluated using Aveva Pro/II and is found to have the capability to produce ammonia at an efficiency of about 58%, and power at an efficiency of 60%. The performance can be further augmented by increasing the single pass conversion of nitrogen, which would result in improved energy efficiency as well. Furthermore, reducing the operating conditions to reduced temperature and pressure would allow for reduced equipment and more compact design, allowing for reduction in capital cost and thus overall plant costs.

A trend that emerges in the literature, particularly in the various modeling works for integrated power and ammonia generation systems, which is the use of Gibbs minimization[136] and equilibrium calculation methods in order to model and calculate output ammonia from ammonia synthesis systems. The point that is to be noted is that the ammonia equilibrium at any given operating condition is not achieved in practical industrial reactors [19], [20], [137], as the time required for equilibrium to be reached is not practicable and the large temperatures involved with industrial ammonia synthesis favors the equilibrium shifting toward the decomposition of ammonia to nitrogen and hydrogen. As such, the single pass conversion of nitrogen to ammonia does not reach the equilibrium prediction, requiring recirculation, as well as variation of operating conditions such as temperature and pressure. Much of the work also carries out cost analysis, and it can be observed that disregarding reactor features such as piping involved in recirculation, as well as renewal of catalyst to ensure optimal performance will result in discrepancies between estimated and actual costs for such plants. These models may thus be overestimating the amount

of ammonia that is practically available from the proposed configurations. A more robust approach can be considered, using the breadth of ammonia reactor model literature [81]-[90] to more accurately estimate the amount of ammonia that can be practically produced, as well as the required operating conditions and costs associated with plant operation. Accuracy of such models can also be improved by considering the catalyst chemistry [145] and specific reaction steps [146] involved in ammonia synthesis, although that would require a great amount of computational power. Table 7 summarises the different multigeneration system modeling literature and the approaches used for modeling ammonia reactors.

Table 7: Summary table of multigeneration systems, comparing sources, outputs, energy efficiency and ammonia production

Input	Output	System Efficiency	Ammonia production rate	Ammonia Reactor Model	Year	Reference
HDPE, Air, Water	NH ₃ & CH ₃ OH	55% (η_{NH_3}), 43.7% ($\eta_{\text{CH}_3\text{OH}}$)	910 kg/hr	Gibbs Reactor	2023	[134]
Air, Natural Gas, N ₂	Power, Hot Water, H ₂ , NH ₃	51.83%	574.56 kg/hr	Control volume	2021	[35]
Wind Energy, Solar Energy, Water	Power, Heat, NH ₃	50%	822.03 kg/hr	Control volume	2022	[147]
Solar Energy, Air, Seawater	Power, Freshwater, NH ₃	70.30%	3060 kg/hr	Control volume	2021	[148]
Solar Energy, Seawater, Air,	Power, CH ₄ , NH ₃ , (NH ₂) ₂ CO	66.12%	38628 kg/hr	Control volume	2022	[129]
Solar Energy, Wind Energy, Water, Air	Power, NH ₃ , H ₂	28.50%	7455.6 kg/hr	Control volume	2021	[127]
CH ₄ , Seawater	Power, NH ₃ , H ₂ , drying, freshwater, heating and cooling	69.08%	886.3 kg/hr	Control volume	2021	[128]
Air, Biomass	NH ₃ , Power	69.30%	200000 kg/hr		2019	[149]

2.3.6 **Biological processes for green ammonia production**

Synthesis of ammonia from biological sources or by using various biological processes has also received attention and can be considered as an alternative to Generation 3 electrochemical processes. The ability to produce ammonia from organic material is widely observed in nature, and utilizing such processes allows for production of ammonia at near ambient conditions while requiring less resources and minimizing adverse effects on the environment. The indirect synthesis of ammonia can be carried out through processes such as microbial electrolysis cells [150] and dark fermentation[151], which utilize microorganisms and biological processes to facilitate the production of hydrogen gas from organic matter, which can then be used for ammonia synthesis.

Biomass to ammonia (B2A), i.e., biosynthesis, is considered a pathway to green ammonia production and it is mainly categorized into biomass gasification and chemical looping combustion. Wen and Aziz [32] designed and analyzed a renewable multi-generation system using the biomass chemical-looping for the ammonia production, utilizing the biomass-to-ammonia-to-power approach as a means of storing energy, observing a maximum energy efficiency of 60.1%, with maximum exergy efficiency equal to 56.3%. Furthermore, the system has the capacity to produce 29,582 tons per year of ammonia and 3,525,305 tons per year of hot water, while concurrently capturing 171,550 tons per year of carbon dioxide.

Ammonia production through use of biological organisms and processes has also been a topic of great interest. The use of microalgae such as *Chlorella vulgaris* [152], *Cladophora glomerata* [153], and *Nannochloropsis* [154] for the production of hydrogen and subsequent use in Haber-Bosch process for production of ammonia has been studied.

Ammonia generation from coal and biomass has also been studied [155], with eucalyptus being used as a feed source. Biomass is gasified in a fluidized bed gasifier, and byproducts such as methane and tar are removed through high temperature filtering. Cost of conversion of biomass to ammonia is found to be nearly 30% higher than that for natural gas to ammonia conversion. Biomass to ammonia also has low carbon dioxide avoidance compared to natural gas and coal feedstocks.

Aziz [152] studied the use of microalgae for the production of hydrogen via gasification, producing syngas and hydrogen. The hydrogen is separated and stored in the storage media of toluene, converting it into methylcyclohexane, and the remaining syngas is used as fuel source for a power generation cycle. The system is modeled using SimSci Pro, with biological gasification being modeled at pressures of 25 and 30 MPa, using the process of supercritical water gasification. The overall energy efficiency of the system is found to be above 60%, and a work output of more than 280 MW is observed.

Following this work, Wijayanta and Aziz [153] studied the use of different microalgae for the production of hydrogen and subsequent storage as ammonia, using Haber-Bosch process. Gasification was carried out using hydrothermal gasification with alumina as the fluidizing particle, and it is observed that the amount of hydrogen produced, as well as overall energy efficiency for the system decreases with increase in gasification temperature. However, higher gasification temperature allows for greater electricity production. Overall, an energy efficiency of 38% is observed, considering both amount of ammonia produced, and power generated.

Tatemichi et al [156] considered the production of ammonia from food-by-products, a feedstock that allows for reduction in overall waste and thus has favorable environmental effect, using modified *Escherichia coli* bacteria. They found that the presence of glucose diminished the production capability of the process and following modifications to the bacteria to overcome these drawbacks, a yield of 47% was achieved using okara, a by-product of tofu manufacturing process, as a feedstock.

2.4 Conclusion and future pathways

An extensive review of ammonia production methods, global outlook and future prospects have been carried out. The processes, limitations and benefits of different ammonia production schemes, grouped together as specific Generations of production, have also been examined, and the large body of work covering each topic is summarized. It is generally concluded that;

- Traditional ammonia production via the Haber-Bosch process utilizing H_2 produced from fossil fuels, also known as blue/grey hydrogen, remains the most popular method for the large-scale production of ammonia. This accounts for 2% of global fossil fuel consumption, produces more than 1% of global CO_2 emissions. It is the most mature production route, and thus the product ammonia also tends to be the cheapest, being priced between \$430 - \$595 per ton_{NH_3} [157]
- The use of blue hydrogen in traditional Haber-Bosch process with carbon capture, known as Generation 1 ammonia production, is the easiest to be implemented in the industrial scale, and has already been implemented at industrial scale. Multiple analytical studies considering the implementation of carbon capture in pre-existing production plants have indicated that it would result in substantially reduced CO_2

emissions. Blue ammonia with carbon capture is slightly higher priced than gray ammonia at \$470 - \$650 per ton_{NH3}

- The increased popularity of green hydrogen, encouraged by climate initiatives such as the Kyoto Protocol and COP20, along with the proliferation of cheap wind and solar power, has allowed for the production of ammonia via the Haber-Bosch process from entirely renewable sources, known as Generation 2 production, with hydrogen being produced by water electrolysis and nitrogen by air separation. While these processes are able to achieve production rates similar to existing industrial plants, the cost of production remains high, which hinders widespread adoption. Green ammonia production, while garnering much attention, still remains expensive at \$900- \$1050 per ton_{NH3}.
- Generation 3 ammonia production, which is an entirely electrical process involving the electrochemical reduction of nitrogen, is considered the ultimate goal for achieving an entirely green ammonia production methodology, with energy being provided by renewable sources and production being carried out at milder conditions. However, this is still a technology in adolescence, having not yet escaped laboratory environments or achieving production rates on par with Generation 1, or Generation 2, and thus price estimations are not yet possible.

Regarding further research and development, the path forward for green ammonia production involves 3 avenues.

- Generation 2 production still lags Generation 1 and traditional Haber-Bosch production in terms of cost of production. However, the flexibility to use energy sources as stranded wind

as well as the scope for smaller scale operation make it attractive in scenarios requiring local production of ammonia, such as near farming areas experiencing high wind speeds. Furthermore, the added cost of Generation 2 ammonia stems from the higher cost of H_2 production and subsidizing this cost would lead to a narrowing of the price gap between blue or brown ammonia, and cleaner green ammonia.

- Another route toward reduction of Generation 2 production costs, and Haber-Bosch technology costs as a whole, may be milder operating conditions and more effective catalysis. Extensive experimental work has been done in both the operation of Haber-Bosch process-based ammonia plants at reduced pressure utilizing absorbent material and absorption-desorption processes, which would lead to better single-pass ammonia conversion, and thus reduction in energy requirements for feed compression and recycling. Work has also been done regarding the use of materials such as $CaFH$ and BaH_2 in process catalysis, which have shown the prospect of allowing for the production of ammonia at temperatures as low as $50\text{ }^{\circ}C$, however their use in more industrial scale scenarios has not yet been verified.
- Research regarding electrochemical reduction of N_2 is witnessing great interest, and the production of ammonia directly from air and water has been achieved in the laboratory setting. Further research regarding the electrochemical process, particularly the effect of different electrolytes, electrodes, operating conditions and effect of catalytic material, is still needed in order for Generation 3 technology to reach similar technological milestones and performance as Generation 1 and Generation 2.

CHAPTER 3

Objectives

3.1 Research Gaps

While green ammonia has received increased attention in both academic literature and in industry as a component in addressing the growing concerns regarding the adverse effects of climate change, and in realizing the promise of a green hydrogen economy, a prevalent trend in the literature is the utilization of Gibbs minimization and equilibrium calculation methods for modeling and determining the output of ammonia in synthesis systems, especially in models considering large scale production, or multigeneration with other outputs, such as power and desalinated water. However, it is crucial to recognize that practical industrial reactors do not achieve ammonia equilibrium under given operating conditions. Single-pass conversion from nitrogen to ammonia falls short of equilibrium predictions, necessitating recirculation and adjustments in operating parameters. Consequently, there is a risk of overestimating the practically available amount of ammonia in proposed configurations. To enhance accuracy, a more robust approach is proposed, leveraging the extensive literature on ammonia reactor models to estimate producible ammonia and overall performance more precisely.

Such a reactor model can then be used to more accurately model integrated multigeneration systems having multiple outputs, such as power, water, ammonia, hydrogen, etc. The increased accuracy in the mathematical modeling of the reactor model would thus also result in increased accuracy in the modeling and analysis of the overall system.

3.2 Specific Objectives

The objectives of the study may be summarized as follows;

- To mathematically model and analyse the performance of an ammonia reactor using a differential approach
- To mathematically model and analyse a multigeneration system having multiple usable outputs, including power and ammonia
- To use the formulated ammonia reactor modeling in the modeling and analyses of multigeneration systems
- To carry out parametric analysis for the multigeneration system, and evaluate overall performance

3.3 Roadmap

In the following chapters, the evaluation of green ammonia production will be carried out. First, a more accurate method for modeling the ammonia synthesis reaction occurring within the ammonia reactor will be identified, validated against industrial data and optimization will be carried out to identify the ideal operating conditions. Secondly, the different reactor arrangements that can be considered for use in an ammonia synthesis loop will be considered and evaluated based on both their thermodynamic and economic performance. Finally, a large-scale green ammonia plant, including an air separation unit for the production of nitrogen, a water electrolyzer stack for the production of hydrogen, and refrigeration for ammonia separation is considered, and its performance evaluated and compared with other comparable systems from the literature.

CHAPTER 4

Investigation and Optimization of Operating Conditions for Improved Ammonia Synthesis Reactor Performance

4.1 Introduction

A mathematical model has been formulated to simulate and estimate the performance of ammonia synthesis reactors. The simulation code is created using Python 3, based on a differential volume approach, utilizing thermodynamic libraries and a Runge-Kutta solution algorithm. The work is validated against both literature and industrial plant data. The behavior of the ammonia reactor with variation in top temperature, feed temperature, reactor pressure, and under different feed compositions is studied. The effect of the use of different reaction rate equations to calculate the rate of synthesis reaction is also explored. Different rate of reactions leads to different estimations of reactor behavior. In this regard, both the Temkin-Pyzhev equation and the modified equation proposed by Dyson and Simon operate within a 5% deviation from plant data. However, the Temkin-Pyzhev equation performs slightly better for the non-adiabatic case, and the modified equation performing better for adiabatic reactors. Finally, an optimization study to find the best operating parameters for maximization of ammonia production for both plant designs is carried out, using Differential Evolution (DE) algorithm. A comparative analysis of adiabatic and non-adiabatic ammonia synthesis reactors reveals optimal nitrogen conversion at 650 K and 700 K respectively, with non-adiabatic reactors achieving higher conversion rates (30.6%) compared to adiabatic systems (23.4%). Both configurations demonstrate improved performance with increased operating pressure and reduced inert gas presence, while feed stream ammonia and inerts inhibit synthesis by promoting decomposition. In inert-free conditions, conversion rates reach 26%

and 36% for adiabatic and non-adiabatic reactors respectively. While non-adiabatic reactors show superior N_2 conversion, their extended length requirements may offset advantages when considering material constraints. Optimization studies demonstrate that higher pressures, minimal inerts, and lower feed temperatures maximize ammonia production, with adiabatic reactors requiring lower initial ammonia concentrations. Under optimized conditions, performance improvements of 21.4% and 3.21% were achieved for adiabatic and non-adiabatic reactors respectively, compared to industrial standards. For both adiabatic and non-adiabatic optimal cases, the peak temperature inside the bed also increases, and the reaction is seen to become stagnant at earlier bed lengths, suggesting the prospect of reducing reactor size for economic improvements.

4.2 Literature Review

In 1909, the German chemist Fritz Haber developed a nitrogen fixation process, and the subsequent industrial adaptation of this process by Carl Bosch led to the first industrial production process of ammonia, which is nowadays called the Haber-Bosch (HB) process. The Haber-Bosch process can be said to be singularly responsible for the first global chemical revolution, in which ammonia has been used extensively in agriculture, contributing greatly to worldwide population growth and reduction of famine [1]. Currently, ammonia is the second most produced chemical in the world, with a total production of 176 million metric tons annually, and it is predicted to increase by 2.3% per year.

Due to the global shift toward use of renewable energy and resources [158], [159]. Specifically, ammonia is suggested to leverage its capability as a space vector and carrier of hydrogen to solve the issue of hydrogen energy transport and distribution. Hydrogen is considered the fuel of the future, allowing for a free-carbon energy approach, but its use raises challenges because of its low volumetric density and high flammability. Ammonia, having high energy density, and high

hydrogen content, makes it a promising chemical store for hydrogen [159]. The realization of this application will no doubt lead to an increase in its future demand and the development in production of renewable energy.

As such, the processes of ammonia production have received renewed attention [7], [8], with particular focus being on understanding and modeling the behavior of ammonia synthesis reactors. Numerous studies on modeling and simulation of an auto-thermal ammonia synthesis reactor exist. The mathematical modeling of ammonia reactors follows from the modeling of ammonia synthesis rate, with the added consideration of parameters such as reactor dimensions, heat transfer coefficients, feed rate and inlet and internal reactor conditions. This has been the subject of much study, with Annable [139] carrying out study for an adiabatic single catalyst bed reactor, followed by Baddour et al. [138], who carried out steady state analysis for the industrially deployed Tennessee Valley Authority reactor configuration, which utilizes internal direct cooling. Subsequent work by Murase et al. [19], Upreti and Deb [160], Babu and Angira [143], Carvalho et al.[144], Khademi and Sabbaghi [161], Suhan et al.[20], and Shamiri and Aliabadi[137] have focused on the mathematical modeling of both adiabatic and non-adiabatic models using differential volume and length approach for mass and energy balance, as well as the optimization of reactor operation conditions based on cost and ammonia production rate.

Table 8 summarises the reactor modeling work, and reaction model used in the literature.

Table 8: Comparison table for different kinetic models used in literature

Reference (year)	Kinetic Model	Type of Reactor	Deviation from industrial data
Annable [139]	Temkin and Pyzhev[162]	Adiabatic	-
Baddour [138] (1965)	Temkin and Pyzhev[162]	Non-adiabatic	2.28%
Murase [19] (1970)	Temkin and Pyzhev[162]	Non-adiabatic	3.57%
Upreti and Deb [160] (1997)	Temkin and Pyzhev [162]	Non-adiabatic	-
Babu and Angira [143] (2005)	Temkin and Pyzhev [162]	Non-adiabatic	-
Carvalho et al. [144] (2014)	Temkin and Pyzhev [162]	Non-adiabatic	-
Khademi and Sabbaghi [161] (2017)	Modified Temkin and Pyzhev [140]	Non-adiabatic and Adiabatic	1.30%
Suhan et al. [20] (2022)	Modified Temkin and Pyzhev [140]	Adiabatic	6.29%
Shamiri and Aliabadi [137] (2021)	Modified Temkin and Pyzhev [140]	Adiabatic	0.10%

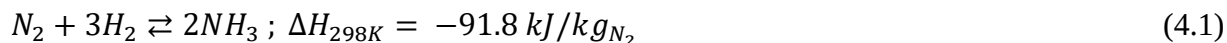
Baddour et al. [138] and Murase et al. [19] are the earliest work and compare their mathematical models against plant data from an autothermal ammonia reactor from the Tennessee Valley Authority, observing predicted results very close to actual behavior. However, several typographical errors are present in the work by Murase et al.[19], and the expressions for partial pressure used to calculate the reaction rate using the Temkin equation are also not elaborated, with these oversights being corrected by Upreti and Deb [160], and later in more detail by Babu and Angira [143]. However, both works while presenting expressions for partial pressures of individual species, do not use a general form but rather expressions that only apply for the specific molar feed composition and operating pressure as presented in the works of Baddour [138] and Murase et al. [19], with these same formulations being used by Carvalho et al. [144]. These works also make mathematical simplifications, such as considering specific heat of gas and heat of reaction to be constant throughout the reactor, whereas in the physical sense they are affected by both gas temperature and reactor pressure. Khademi and Sabbaghi [161] while considering variable values for specific heat and heat of reaction, use plant data taken from the Murase work without correcting the typographical errors. The works of Suhan et al. [20] and Shamiri and Aliabadi [137] are more robust in their methodology, using general expressions and being devoid of typographical errors

to the best knowledge of the authors of this work. However, they limit their analysis to adiabatic reactors, and so the parametric analysis of non-adiabatic reactors, using more sophisticated mathematical formulation and thermodynamic libraries remains an important avenue for further study.

In this work, a mathematical model is developed to conduct parametric analyses on the ammonia production process considering both non-adiabatic and adiabatic ammonia reactors, and an optimization study is carried out using a Differential Evolution (DE) algorithm, in order to find out the optimal operating conditions and feed mixture compositions for both non-adiabatic and adiabatic ammonia reactors. The model results are initially compared with industrial data to validate the model. Different feed temperatures, or in the case of non-adiabatic reactors, top temperatures, are considered, as well as different operating pressures. The effect of different compositions of the reactant mixture is also studied.

4.3 **Methodology and Mathematical Model**

In the Haber-Bosch process [3], ammonia is produced through the reaction of elemental nitrogen and hydrogen, by the reaction;



This is the fundamental reaction by which ammonia is produced, regardless of the type of reactor being used to synthesize the ammonia. This reaction can be characterized as an equilibrium reaction, wherein the forward reaction, signifying the synthesis of ammonia from nitrogen and hydrogen, is exothermic, while the reverse reaction, denoting the decomposition of ammonia, is endothermic. Following Le Chatelier's principle [163], it can be inferred that the production of ammonia is favored by low temperatures and elevated pressures, with these conditions inducing a

rightward shift in the equilibrium position. However, under ambient conditions, this behavior is not observed.

The substantial energy requirement associated with the disruption of the $\text{N}\equiv\text{N}$ triple bond means that the required activation energy for the reaction to proceed in the gaseous phase is significantly elevated [11]. Attainment of this activation energy threshold is only feasible at temperatures approaching approximately 3000°C . However, at this extreme temperature range, the equilibrium position shifts towards the backward reaction, leading to a decrease in ammonia production, rather than its enhancement. The most significant achievement of the Haber-Bosch process was to solve this issue of high activation energy, with the use of iron catalyst and recirculation of the reactant stream, increasing the synthesis rate of ammonia and increasing the overall yield from reactants.

The ammonia production could be modelled numerically by deriving a system of differential equations describing the temperature, pressure, concentration behavior across the reactor through a mass and energy balance derivation under specific boundary and initial conditions.

Generally, ammonia reactors are categorized into two main categories based on the type of cooling system, shown in Fig. 1. Internal direct cooling reactor (IDCR), in which the catalyst bed is cooled by the feed gas carried in cooling tubes running through the bed. It can be thought of as a shell-and-tube exchanger in which the catalyst bed is packed within one side, and the cooling feed flows on the other side. The feed gas, which consists of the reactant feed mixture, is heated by the reaction gas and rises up to the top of the reactor, reaching the top temperature, T_o , prior to entering the catalyst bed. When considering the feed gas, this top temperature T_o is considered as a boundary condition and is referred to as feed temperature, T_f , and is labeled as such in Figure 4, with the true feed temperature at the bottom of the outlet being calculated by solution of the system of differential

equations. The feed gas then enters the catalyst bed, where the reaction progresses, is cooled by the feed gas in the cooling tubes, and then exits the reactor.

Adiabatic reactors on the other hand, have no cooling stream, and instead the feed gas is preheated to the feed temperature, T_f , and then enters the catalyst bed. Upon exiting the bed, the reaction gas is cooled down, either through use of a heat exchanger or by mixing with another feed stream. This cooled stream then enters another reactor bed, allowing the reaction to progress, as according to Le Chatelier's principle, the exothermic reaction is inhibited by high temperatures of the feed.

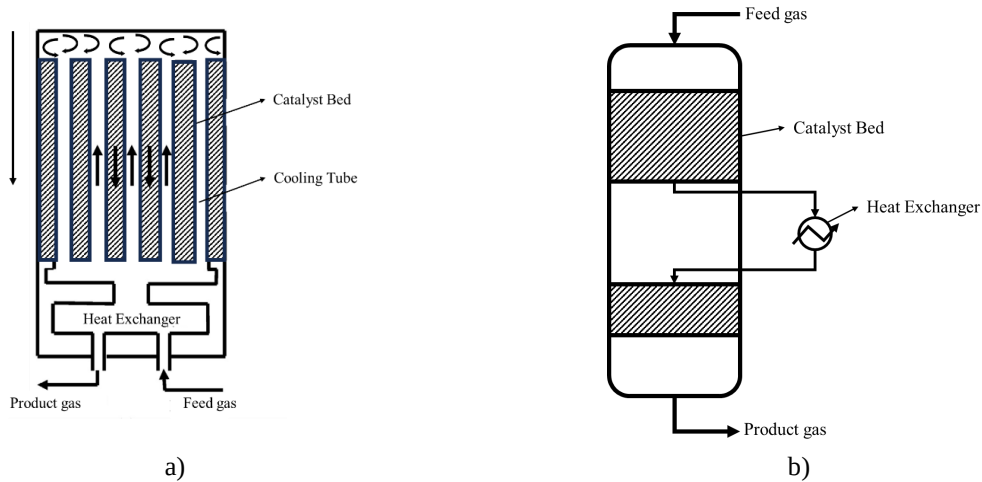


Figure 4 : Design of a) internal direct cooling reactor and b) adiabatic reactor for ammonia synthesis (redrawn from Khademi and Sabbaghi [161])

In general, the same principles and assumptions are used to develop the differential expressions, which are also of the same form, with the only necessary modifications being made to consider operation as either adiabatic or non-adiabatic. The control volume for each scheme is shown in Fig. 5, and the mathematical model is formulated based on the following assumptions:

1. The ammonia reactor is operating under steady-state conditions.
2. The heat transfer resistance between the gas and the catalyst particle is considered insignificant [164].

3. Minimal thermal and concentration gradients are observed in the radial direction [165], and thus they are neglected
4. Negligible pressure drop is noted along the reactor [138].
5. Due to the high gas velocities, there is minimal heat and mass dispersion in the longitudinal direction [166], [167], and thus it is neglected.

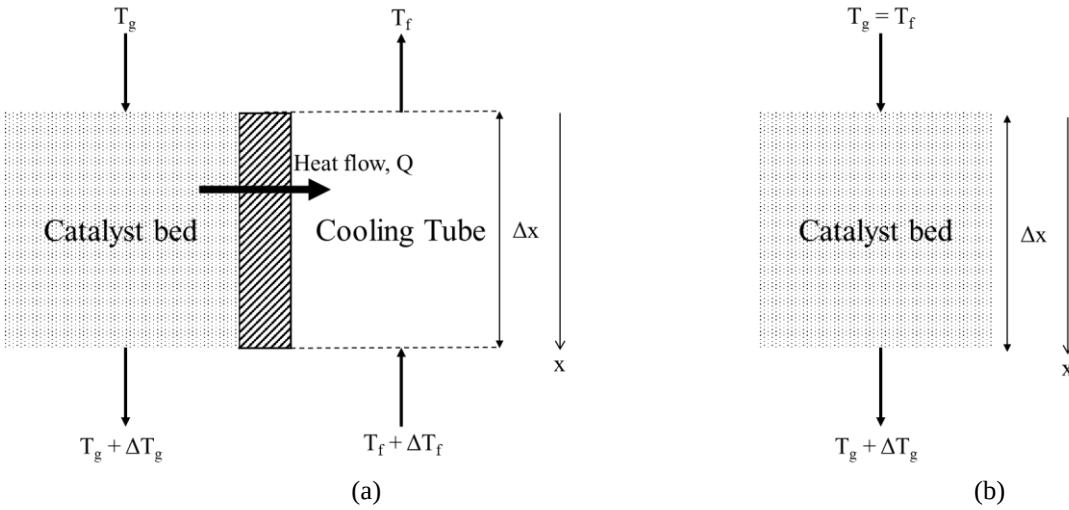


Figure 5: Control volume for (a) non-adiabatic and (b) adiabatic ammonia reactor

Molar conservation can be applied for N_2 flow in terms of kmole/hr over the control volume of the reactor bed only, as there is no flow apart from feed gas in cooling tubes, to gain the expression,

$$\begin{aligned} n_{N_2,V} - n_{N_2,V+\Delta V} - \Delta r_{N_2} &= 0 \\ \frac{dn_{N_2}}{dV} &= r_{N_2} = -\frac{1}{2}(r_{NH_3}) \end{aligned} \quad (4.2)$$

Thus, following stoichiometry, mole balance for hydrogen and ammonia can be expressed as,

$$\frac{dn_{H_2}}{dV} = -\frac{2}{3}(r_{NH_3}) \quad (4.3)$$

$$\frac{dn_{NH_3}}{dV} = (r_{NH_3}) \quad (4.4)$$

The most widely used method to model the rate of ammonia synthesis as found in the literature

[6], [10]-[14], [24] is the Temkin-Pyzhev equation [162], which expresses the rate of ammonia production as,

$$r_{N_2} = -f \times \left[k_A p_{N_2} \left(\frac{p_{H_2}^{1.5}}{p_{NH_3}} \right) - k_B \frac{p_{NH_3}}{p_{H_2}^{1.5}} \right] \quad (4.5)$$

Where, f is the catalyst activity, k_A is the forward rate of reaction, k_B is the backward rate of reaction, α is a kinetic parameter having value of 0.5, and p_{N_2} , p_{H_2} and p_{NH_3} are the partial pressures of N_2 , H_2 and NH_3 , respectively.

k_A and k_B are calculated using the Arrhenius equation [143], [161], and have the form,

$$k_A = 1.78954 \times 10^4 \exp \left(-\frac{87027}{RT_g} \right) \quad (4.6)$$

$$k_B = 2.5714 \times 10^{16} \exp \left(-\frac{198321}{RT_g} \right) \quad (4.7)$$

Where R is the universal gas constant having a value of 8.314 kJ/kmol.K, and T_g denotes the temperature of gases inside the reactor in Kelvin.

Dyson and Simon [140] suggested a modification of the Temkin-Pyzhev equation, considering equilibrium component activity instead of partial pressure, in order to more accurately capture the reaction behavior.

$$r_{NH_3} = k_B \left[K_a^2 a_{N_2} \left(\frac{a_{H_2}^3}{a_{NH_3}^2} \right)^\alpha - \left(\frac{a_{NH_3}^2}{a_{H_2}^3} \right)^{1-\alpha} \right] \quad (4.8)$$

Where a_{N_2} , a_{H_2} and a_{NH_3} are activities of N_2 , H_2 and NH_3 , respectively, and are functions of mole fractions, fugacity of the component and pressure. k_B is the backward reaction rates constant, and is given by

$$k_B = 1.7698 \times 10^{15} \exp \left(-\frac{170560}{RT_g} \right) \quad (4.9)$$

The activities are calculated as

$$a_i = \frac{f_i}{f_i^0} = \frac{f_i}{1} = y_i \phi_i P \quad (4.10)$$

Where, f_i is the fugacity of the species at the reaction condition, and f_i^0 is the reference fugacity at 1 atm pressure. The expression can thus be reduced to a function of the species mole fraction, y , the fugacity coefficient ϕ , and the operating pressure. Fugacity coefficients may be calculated using the correlations developed by Dyson and Simon[140],

$$\phi_{H_2} = \exp \left(\left(e^{(-3.8402(T^{0.125})+0.541)} \right) \times P - \left(e^{-0.1263(T^{0.5})-15.98(P^2)} \right) \right) + \left(300 \left(e^{-0.011901T-5.941} \left(\left(e^{-\frac{P}{300}} \right) - 1 \right) \right) \right) \right) \quad (4.11)$$

$$\phi_{N_2} = 0.93431797 + 0.3101804 \times 10^{-3}T + 0.295896 \times 10^{-3} \times P - 0.2707279 \times 10^{-6}T^2 + 0.4775207 \times 10^{-6}P^2 \quad (4.12)$$

$$\phi_{NH_3} = 0.1438996 + 0.2028538 \times 10^{-2}T - 0.4487672 \times 10^{-3}P - 0.1142945 \times 10^{-5}T^2 + 0.2761216 \times 10^{-6}P^2 \quad (4.13)$$

The use of activities for calculation of the rate accounts for the deviation from ideal gas behavior, however the equilibrium constant must also be calculated considering real gas behavior. This deviation was first observed by Gillespie and Beattie [168], who developed the correlation for finding equilibrium constant, and validated it against existing industrial reactor data.

$$\log_{10} K_a = -2.691122 \log_{10} T - 5.519265 \times 10^{-5} T + 1.848863 \times 10^{-7}T^2 + \frac{2001.6}{T} + 2.6899 \quad (4.14)$$

As r_{NH_3} is a function of the partial pressures in the general Temkin-Pyzhev equation form, they are also required to be calculated, and may be obtained from the expressions [20], [140],

$$p_{N_2} = y_{N_2} P = \frac{N_{N_2}^0 (1 - X_{N_2})}{1 - 2X_{N_2} N_{N_2}^0} P \quad (4.15)$$

$$p_{H_2} = y_{H_2} P = \frac{N_{H_2}^0 - 3X_{N_2} N_{N_2}^0}{1 - 2X_{N_2} N_{N_2}^0} P \quad (4.16)$$

$$p_{NH_3} = y_{NH_3} P = \frac{N_{NH_3}^0 + 2X_{N_2} N_{N_2}^0}{1 - 2X_{N_2} N_{N_2}^0} P \quad (4.17)$$

Where $N_{N_2}^0$ is the initial molar flow rate of N_2 in the feed, and X_{N_2} denotes the conversion of N_2 along the reactor bed and is given by the expression [19], [140],

$$X_{N_2} = \frac{\text{molar flow of } N_2 \text{ at inlet} - \text{molar flow of } N_2 \text{ across reactor section}}{\text{molar flow of } N_2 \text{ at inlet}} \quad (4.18)$$

For increased accuracy in calculation of the reaction rate, the interaction of kinetic and transport effects on the diffusion behavior of reaction gas on the surface of the catalyst must also be considered, and this is done through use of the effectiveness factor, ε , which can be defined as the rate at which reaction would occur if the concentration and temperature throughout the catalyst pellet was uniform.

$$\varepsilon = \frac{\text{molar flux of component across catalyst surface} \times \text{surface area of pellet}}{\text{volume of pellet} \times \text{rate of formation of component at surface}} \quad (4.19)$$

Dyson and Simon[140] developed the correlation to calculate the effectiveness factor for standard catalyst particle size in the range 6-10 mm, operating at pressures between 150-300 atm,

$$\varepsilon = b_0 + b_1 T_g + b_2 X_{N_2} + b_3 T_g^2 + b_4 X_{N_2}^2 + b_5 T_g^3 + b_6 X_{N_2}^3 \quad (4.20)$$

Where the values of b_i are correlation coefficients and the corresponding values for operating pressure are given in Table 9.

Table 9: Correlation coefficients for calculating effectiveness factor, ε

Pressure (atm)	b_0	b_1	b_2	b_3	b_4	b_5	b_6
150	-17.539096	0.07697849	6.900548	-1.082790×10^{-4}	-26.42469	4.927648×10^{-8}	38.93727
225	-8.2125534	0.03774149	6.190112	-5.354571×10^{-5}	-20.86963	2.379142×10^{-8}	27.88403
300	-4.6757259	0.02354872	4.687353	-3.463308×10^{-5}	-11.28031	1.540881×10^{-8}	10.46627

Applying energy balance can be applied for the control volume to gain the expressions for differential change in T_f and T_g .

The heat transfer across the cooling tube wall is given by the expression,

$$Q = UA\Delta T = US_1 dx(T_g - T_f) \quad (4.21)$$

Where S_1 is the outer surface area of the cooling tube per unit length of the reactor, and U is the overall heat transfer coefficient across the tube.

Considering the feed gas in cooling tubes and applying energy balance,

$$Energy_{in} = Energy_{out}$$

$$WC_{p_f}(T_f + dT_f) + US_1 dx(T_g - T_f) = WC_{p_f}T_f$$

$$WC_{p_f}dT_f = -US_1 dx(T_g - T_f)$$

$$\frac{dT_f}{dx} = -\frac{US_1(T_g - T_f)}{WC_{p_f}} \quad (4.22)$$

Where C_{p_f} is the specific heat capacity of the feed gas at constant pressure, W is the total mass flow rate of feed gas, and dT_f is the change in feed gas temperature.

Considering the reacting gas in catalyst bed,

$$Energy_{in} = Energy_{out}$$

$$WC_{p_g}T_g + \Delta Hr_{NH_3}S_2dx = WC_{p_g}(T_g + dT_g) + US_1dx(T_g - T_f)$$

$$WC_{p_g}dT_g = -US_1dx(T_g - T_f) + \Delta Hr_{NH_3}S_2dx$$

$$\frac{dT_g}{dx} = -\frac{US_1(T_g - T_f) + \Delta Hr_{NH_3}S_2}{WC_{p_g}}$$

Where S_2 is the cross-sectional area of the reactor bed, C_{p_g} is the specific heat capacity of the reacting gas at constant pressure, and dT_g is the change in reacting gas temperature.

As $\Delta H = -\Delta H_r$, as the heat of reaction of ammonia is exothermic,

$$\frac{dT_g}{dx} = -\frac{US_1(T_g - T_f) - \Delta H_r r_{NH_3} S_2}{WC_{p_g}} \quad (4.23)$$

For adiabatic reactors, there is no cooling stream, and thus no heat transfer across the cooling tube wall, so the temperature of feed gas undergoes no change. The energy balance can thus be expressed simply as,

$$\frac{dT_g}{dx} = -\frac{-\Delta H_r r_{NH_3} S_2}{WC_{p_f}}$$

The system of differential equations of Equations (1), (22) (23) can thus be solved to model the performance of the reactor bed.

The system of equations is solved for both adiabatic and non-adiabatic reactors boundary conditions. The parameter β can be used to differentiate between adiabatic and non-adiabatic

behavior, with the value being 1 for non-adiabatic, cooled reactors, and 0 for adiabatic reactors [161].

The values of C_{p_f} and C_{p_g} are calculated at each step of the solution from the mass fraction composition of reactor gas, using the CoolProp library. The value of the heat of reaction, ΔH_r is calculated from the correlation [20], [169]:

$$\Delta H_{r_{N_2}} = (2 \times 4.184) \left[- \left(0.54526 + \frac{846.609}{T} + \frac{459.734 \times 10^6}{T} \right) \times P - 5.34685 \times T - 0.2525 \times 10^{-3} \times T^2 + 1.69197 \times 10^{-6} \times T^3 - 9157.09 \right] \quad (4.24)$$

Parametric analysis of the reactor models in terms of change with different feed temperatures and operating pressures is considered. Feed temperature variation of 600 K to 750 K is considered, and the operating pressure of the reactors is varied from 129 atm to 300 atm. The effect of different feed compositions on the overall NH_3 production and reactor behavior is also studied. Nine different feed compositions are considered, including those currently used in industrial reactors, as well as theoretical compositions to simulate power-to-ammonia production with high purity H_2 and N_2 and minimal inerts and CH_4 , as well as feed compositions with limiting reactant quantity. The detailed molar compositions are given in Table 10.

Table 10: Molar compositions of studied feed cases

Case ID	Mole Fraction				
	N_2	H_2	NH_3	Ar	CH_4
1	0.2175	0.6525	0.0500	0.0400	0.0400
2	0.2173	0.6608	0.0380	0.0212	0.0626
3	0.2375	0.7125	0.0500	0.0000	0.0000
4	0.2475	0.7425	0.0100	0.0000	0.0000
5	0.3000	0.5700	0.0500	0.0400	0.0400
6	0.1700	0.7000	0.0500	0.0400	0.0400
7	0.1500	0.5500	0.1000	0.1000	0.1000
8	0.1750	0.5250	0.1000	0.1000	0.1000

Cases 1 and 2 are taken from industrial data [19], [20]. Cases 3 and 4 simulate a green power-to-ammonia reactor, with high purity reactants at a stoichiometric ration of 1:3, with no inerts. For Cases 5,6, and 7, the feed ratio of $N_2:H_2$ deviates from stoichiometric, with either excess N_2 (case 5) or excess H_2 (case 6 and 7). Finally, case 7 and 8 are considered to understand the effect of excess inerts in feed.

4.4 Reactor Model validation

The mathematical model has been developed using the Python 3 programming language, and the open-source scientific computing packages NumPy [170] and SciPy [171] have been used for ease of solution of differential equations and mathematical computation.

4.4.1 Validation of Adiabatic reactor model

The adiabatic model has been validated against the results from the work of Suhan et al. [20], who themselves validate their results against the industrial plant data for an adiabatic, intercooled reactor located in Bangladesh, operating at a pressure 129 atm. The mass flow rate is 231262.31 kg/h and the diameter of the reactor is 3 m, with the first reactor bed being 15 m in length, and the second 7.5 m. A Runge-Kutta 4th order solver is used to solve the system of equations, for the domain $0 \leq x \leq 22.5$, i.e the total length of the reactor beds, with the initial conditions being,

$$T_0 = T_f^0 = T_g^0 = 360 \text{ } ^\circ\text{C} = 633 \text{ K}$$

$$N_{N_2}^0 = 747.79 \frac{\text{kmol}}{\text{hm}^2}$$

The mixture is quenched to 650 K after exiting the first reactor bed, with no quenching occurring after the second bed.

The feed composition of the input gas is given in Table 11.

Table 11: Molar composition of feed gas

Component	Mole Fraction
N ₂	0.2173
H ₂	0.6608
NH ₃	0.0380
CH ₄	0.0212
Ar	0.0626

The validation results are summarized in Figure 6.

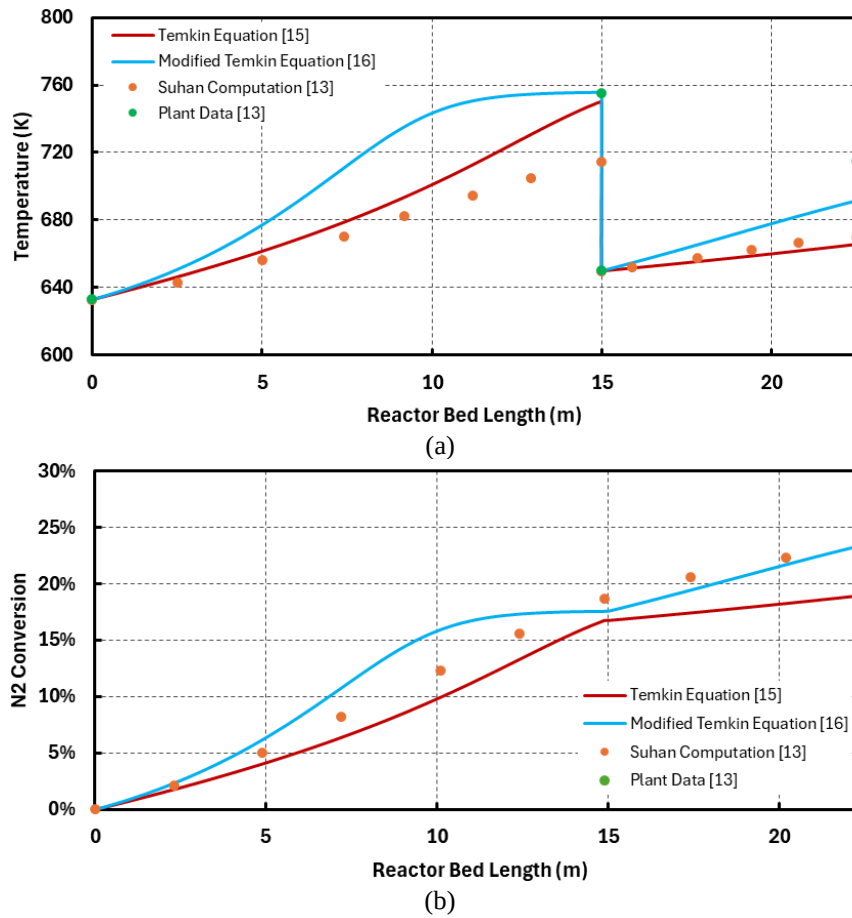


Figure 6: Validation of mathematical model for adiabatic reactor for a) reactor gas temperature and b) N₂ conversion along reactor bed length with different reaction equations [140], [162] compared with reference and plant data [20]

The validation study is carried out by computing the rate of reaction using both the general Temkin-Pyzhev equation [162], the modified equation proposed by Dyson and Simon [140]. It is observed that the Modified Dyson provides more accurate results. From the graphs, it can be seen

that both the Temkin and Modified Temkin equations underestimate the extent of reaction, especially in the second reactor bed, leading to underestimating both the outlet temperature and the overall conversion of N₂. This conclusion is further substantiated by comparing output mole fraction from the different calculations to the plant data, as shown in Table 12.

Table 12: Comparison of calculated result and industrial plant data

	Outlet N ₂ mole fraction	% deviation	Outlet Temperature (K)	% deviation
Plant Data	0.1847	-	715	-
Suhan[20]	0.1745	5.52%	670	6.29%
Temkin Equation	0.1919	3.90%	665.79	6.88%
Modified Temkin Equation	0.1852	0.27%	691.54	3.28%

4.4.2 Validation of non-adiabatic reactor model

The non-adiabatic model has been validated against the results from the work of Carvalho et al. [144] and Murase et al. [19], which themselves validate their results against the industrial plant data for a non-adiabatic, internal direct cooling reactor. A Runge-Kutta 4th order solver is used to solve the system of equations, for the domain $0 \leq x \leq 5.18$, i.e. the length of the reactor, with the initial conditions being,

$$T_0 = T_f^0 = T_g^0 = 421 \text{ } ^\circ\text{C} = 694 \text{ K}$$

$$N_{N_2}^0 = 701.2 \frac{\text{kmol}}{\text{hm}^2}$$

The feed composition of the input gas is given in Table 13.

Table 13: Molar composition of feed gas

Component	Mole Fraction
N ₂	0.2175
H ₂	0.6525
NH ₃	0.0500
CH ₄	0.0400
Ar	0.0400

The values of additional reactor parameters required for the differential solution are given below in Table 14.

Table 14: Operating parameters of non-adiabatic reactor model.

Parameter	Value	Units
Overall heat transfer coefficient, U	2090	$\text{kJ/hm}^2\text{K}$
Mass flow rate of feed, W	26400	kg/h
Surface area of cooling tubes per unit length reactor, S_1	10	m^2/m
Cross-sectional area of catalyst, S_2	0.78	m^2

The validation results are summarized in Fig. 7, with the Temkin equation having an average deviation compared to the plant data of 3.08%, and the modified equation having an average deviation of 3.54%, indicating that the general equation provides more accurate estimation for the non-adiabatic case.

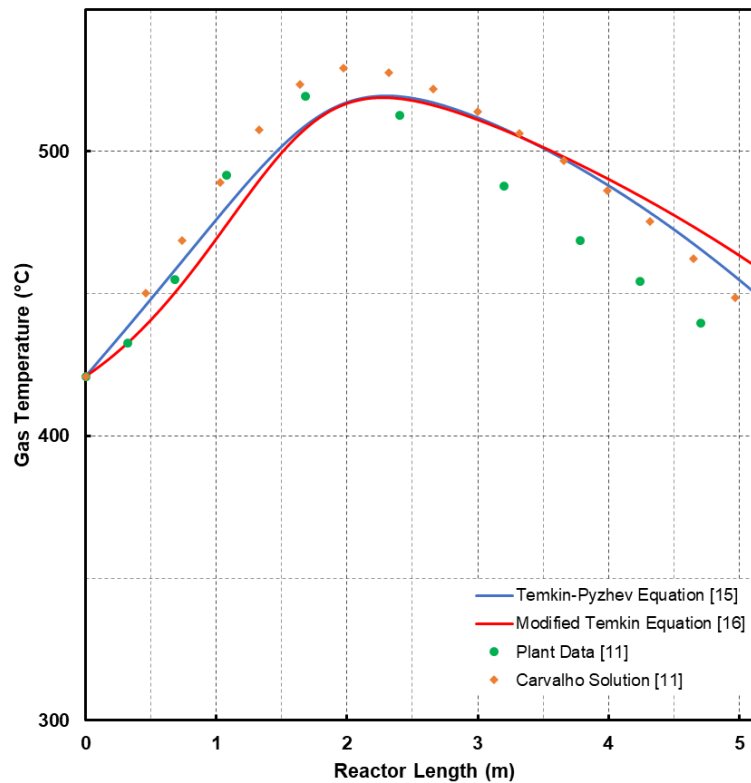


Figure 7: Validation of mathematical model for non-adiabatic reactor for reactor gas temperature along reactor bed length with different reaction equations [140], [162] compared with reference [144] and plant data [19]

The effect of using different equations to calculate rate of reaction is first considered, with Figure 7 showing the estimated results of reactor gas temperature along the length of the reactor against

the plant data for the TVA reactor [19]. It is observed that both equations overestimate the exit temperature of the reactor gas, with the average deviation being 1.97% for the Temkin-Pyzhev equation and 2.41% for the modified equation proposed by Dyson, with the deviation at the exit being 3.31% and 4.63% for the Temkin-Pyzhev equation and Dyson modification respectively. While both equations have deviation values of less than 5%, based on these results, it seems the general Temkin-Pyzhev equation provides greater accuracy, at least for non-adiabatic reactors.

4.5 RESULTS AND DISCUSSION

4.5.1 Adiabatic Reactor

Figure 8 shows the effect of pressure on the reactor gas temperature and N_2 consumption, which is an indication of the N_2 conversion and thus NH_3 production. The feed gas has molar composition as shown in Table 11, and the feed temperature is 633 K. The gas mixture is quenched to a temperature of 650 K at the end of the first bed, with no further cooling in the rest of the bed. The reactor consists of two beds, each of diameter 3 m, the first being of length 15 m, and the second of length 7.5 m, and the mass flow rate in all cases is 231262.31 kg/h, which are the reactor dimensions and mass flow rate in the industrial case that has been validated. The rate of reaction has been calculated by the Modified Temkin equation.

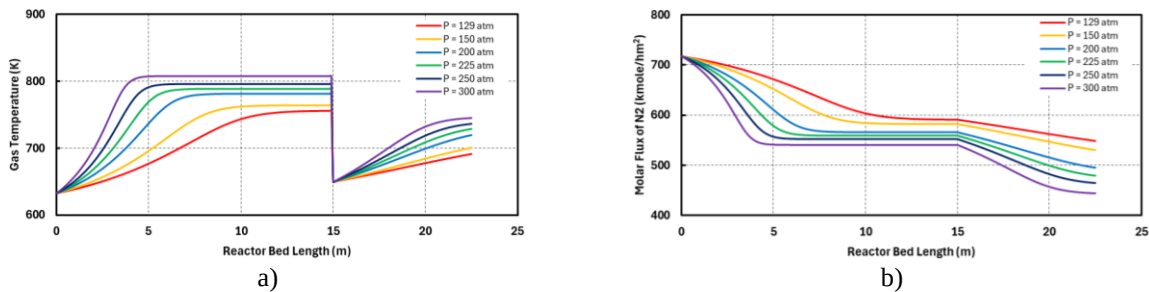


Figure 8: Effect of changing the operating pressure on a) reactor gas temperature, and b) molar flux of N_2

It can be seen that increasing pressure causes a rise in the rate of reaction, resulting in greater peak reactor gas temperatures and N_2 consumption, and thus an increase in the amount of NH_3 generated. As pressure increases, the peak temperature comes earlier in the bed length, reaching a high of 817 K at 300 atm pressure. The initial rate of N_2 consumption increases with pressure, with greater pressures having a higher initial rate of N_2 consumption. At higher pressures, reaction rates are higher, resulting in more N_2 consumption and NH_3 generation. It is noteworthy that both the temperature and N_2 molar flux values become constant after reaching the maximum and minimum values, respectively, for the specific reactor bed, indicating that the reaction stagnates in that condition. Quenching of the flow allows for the reaction to continue in subsequent beds, increasing overall N_2 conversion.

Figure 9 shows the effect of feed temperature on the reactor gas temperature and N_2 consumption. The feed gas has molar composition as shown in Table 11, and the operating pressure is 129 atm. Once again, the gas mixture is quenched to a temperature of 650 K at the end of the first bed.

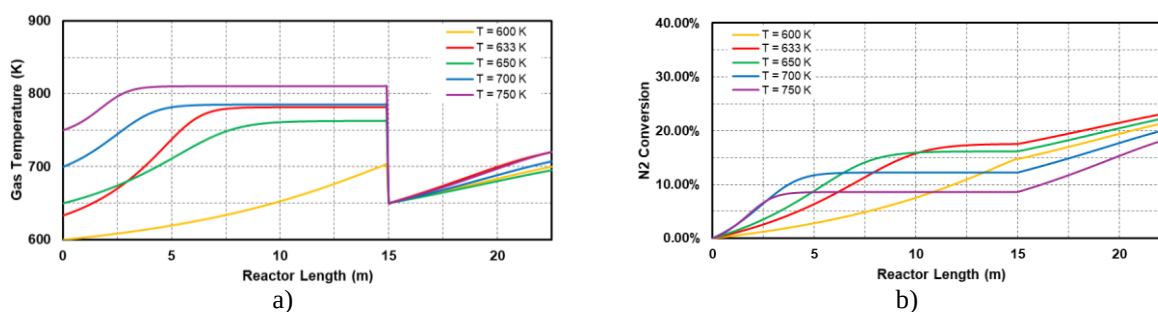


Figure 9: Effect of changing the feed temperature on a) reactor gas temperature, and b) N_2 conversion

When considering the effect of temperature on the reaction, it is important the conflicting effects that higher temperature has on the reaction rate and equilibrium, with the high temperature increasing reaction rate, while at the same time favoring the dissociation of ammonia, thereby inhibiting the synthesis reaction. It is observed that higher feed temperatures result in higher rates

of reaction at the initial stages of the reactor. However, the reaction then stagnates, due to the higher temperature inhibiting the production of ammonia and shifting the equilibrium towards its dissociation. At lower feed temperatures, while the reaction may progress relatively slower initially, regarding N_2 conversion, which is an indicator of the NH_3 production, at the exit of the reactors is higher at lower temperatures. This observation agrees with the industrial adoption of the lower feed temperature of 633 K, as it results in greater ammonia production while maintaining acceptable rate of reaction, with the temperature being high enough to allow for a high rate of reaction, and thus greater production of ammonia, while not favoring the shift of the equilibrium toward the endothermic decomposition of ammonia, which would inhibit ammonia production.

Figure 10 shows the effect of the different feed compositions, as detailed in Table 3, on adiabatic reactor behavior. Feed entering the reactor is at 633 K and is quenched to 650 K at the exit of the first catalyst bed, with no further quenching in subsequent beds and the operating pressure is 129 atm, for all cases. The length of the first bed is 15 m, and for the second bed is 7.5 m, as in the validated industrial case.

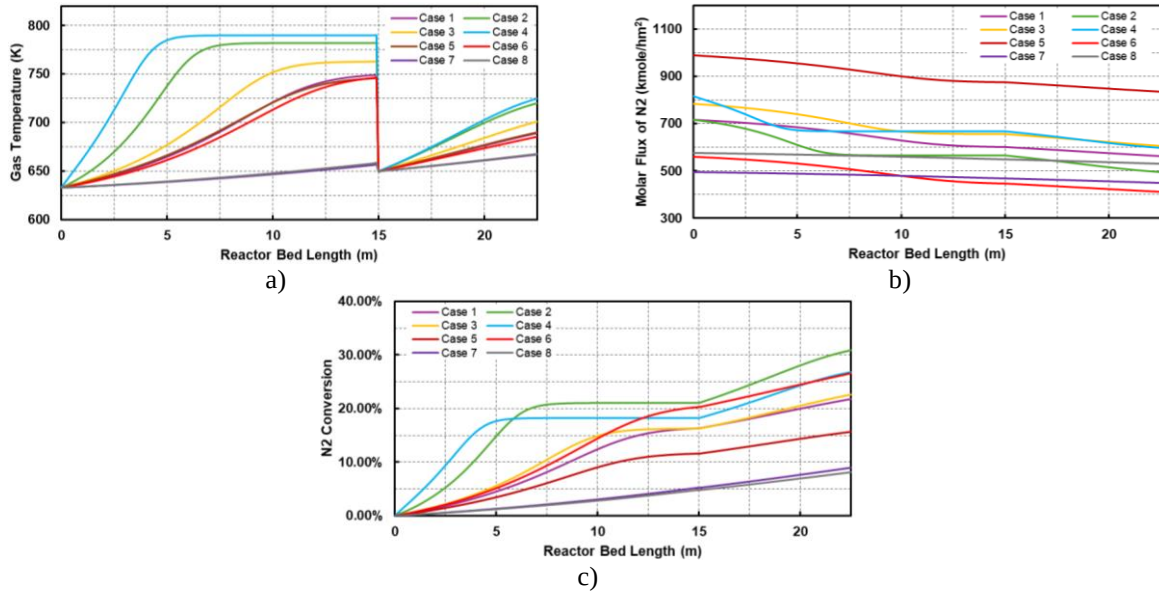


Figure 10: Effect different feed compositions on a) reactor gas temperature, b) molar flux of N₂, and c) N₂ conversion

Temperature, molar flux and conversion profiles for cases 1 and 2 are industrial cases taken from the literature. Case 2 achieves higher outlet temperature being about 715 K, compared to 688 K for Case 1. However, as the temperature and conversion profiles show, the reaction stagnates in the first bed before reaching the exit of the first catalyst bed for case 2, resulting in the flattening of the curves, prior to quenching, with the reaction once again progressing in the second bed. Regardless, Case 2 achieves the highest overall N₂ conversion of about 31%, while Case 1 achieves N₂ conversion of 21.8%.

Cases 3 and 4, have similar amounts of initial N₂ and H₂, and no inerts in the feed, but differ in the initial NH₃ amount. It is observed that Case 4 reaches the higher temperatures throughout the reactor length and at the exit, for all cases, as well as having the second highest N₂ conversion of 26.7%. Case 3 experiences lower overall conversion, about 22.6%, with the exit temperature also being lower by about 24 K.

Cases 5,6 and 7 are used to understand the effect of limiting reactant amount and deviation from stoichiometric composition on ammonia synthesis, with case 5 having insufficient H_2 , and 6 and 7 having insufficient N_2 . Case 6 achieves the second highest overall N_2 conversion, same as Case 4, of 26.6%, while Case 7 achieves the overall second lowest conversion, only 9%. The lack of available N_2 coupled with the high presence of inerts means that the overall conversion is low for Cases 7, and indeed the reaction is observed to progress very slowly and stagnate quite early, as is evident in the temperature profile. Interestingly, Case 6, while having similar initial feed compositions of N_2 and H_2 as Case 7 shows better overall performance, with the reaction progressing slowly in the first catalyst bed, demonstrated by the higher gradient of the temperature profile, likely due to the lower presence of inerts. Case 5, on the other hand, while having low presence of inerts, does not have sufficient amount of H_2 , and as a result while the reaction does progress, the overall conversion is lower than expected at 12.6%. Considering Case 8, which while having stoichiometric amounts of N_2 and H_2 achieves the lowest overall N_2 conversion of 8.1% and the lowest reactor outlet temperature of 667 K, the effect of initial NH_3 and inert amount in the feed on shifting the equilibria towards the backward reaction and inhibiting the forward NH_3 synthesis reaction becomes more apparent.

4.5.2 Non-Adiabatic Reactor

Figure 11 shows the variation of feed temperature, synthesis gas temperature and N_2 conversion with increase in pressure. T_0 is known as the top temperature and is the initial temperature of both feed gas after reaching the top of the reactor, and gas entering the reactor bed. In all cases, the top temperature and the mass flowrate remain constant at value of 694 K, and 26400 kg/h, respectively, with the reactor bed having a diameter of 1.1 m. Molar composition of the feed is detailed in Table 13.

It is observed that increasing pressure results in an increased rate of reaction leading to higher peak reactor gas temperatures, and N_2 consumption, which consequently means that the amount NH_3 produced is increased. The peak temperature also occurs at earlier stages as pressure increases, reaching a maximum value of 839 K at 500 atm pressure. Feed gas temperatures are observed to fall more rapidly as pressure increases. Likewise, the consumption of N_2 also increases with increase in pressure. It is also observed that the initial rate of N_2 consumption is higher at higher pressures. All these effects stem from the higher pressures resulting in higher rates of reaction, resulting in greater N_2 consumption and NH_3 production. Consequently, the heat generated in the catalyst bed is also increased, and so the overall heat transfer between the feed and reactor gas streams is increased.

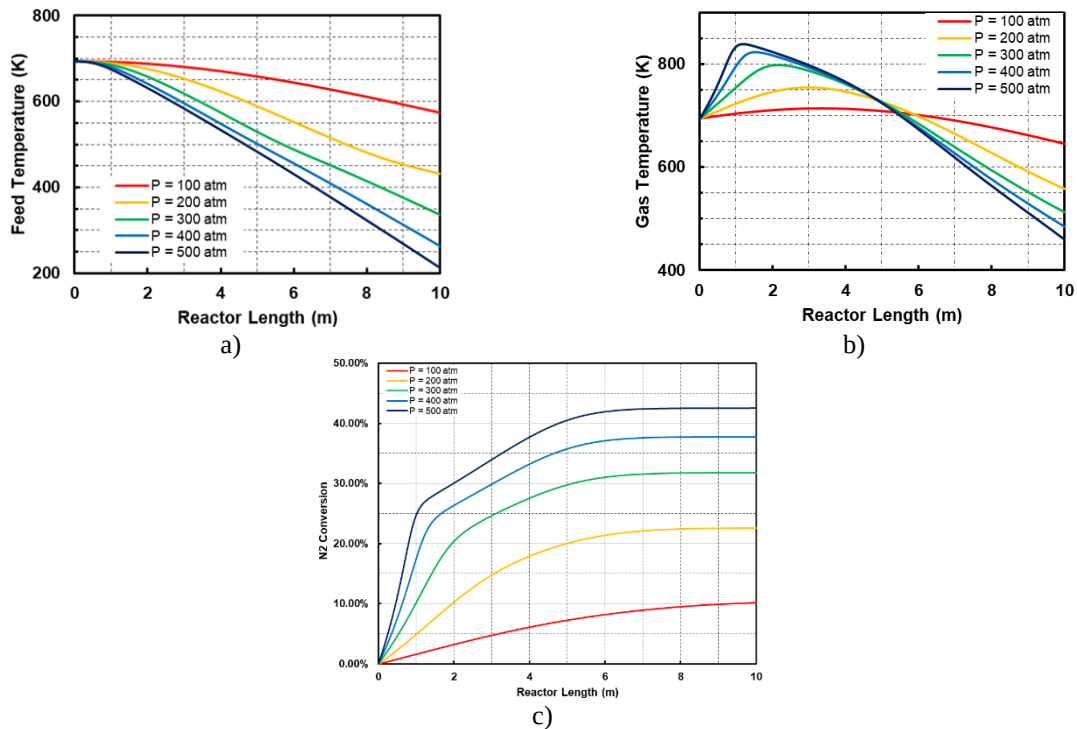


Figure 11: Effect of changing the operating pressure on a) feed temperature b) reactor gas, and c) N_2 conversion

Figure 12 shows the effect of the top temperature on non-adiabatic reactor performance. The reactor pressure is considered as 286 atm for all cases with mass flowrate of 26400 kg/h, and the feed

composition is that for case 2, as shown in Table 13. Similar to Figure 11, higher peak temperature of reactor gas is also observed, and the peak being reached at earlier reactor lengths as temperature increases. It is also observed that at 600 K the reaction does not progress significant amount due to the low kinetic energy of the molecules at lower temperatures [172]. With increase in temperature, we observe increase in the rate of reaction, and thus consequently higher peak temperatures of reactor gas, and higher N_2 consumption and NH_3 production. Worth noting regarding N_2 consumption, which predicts the NH_3 production, is that the exit condition of the reactors is similar for T_0 values above 700 K, however the behavior inside the reactor is more gradual at the lower temperature of 700 K than at higher values. This is likely why in the industrial setting the relatively lower top temperature of 694 K is preferred, as it results in ammonia production equal to higher temperature condition while having less thermal requirements.

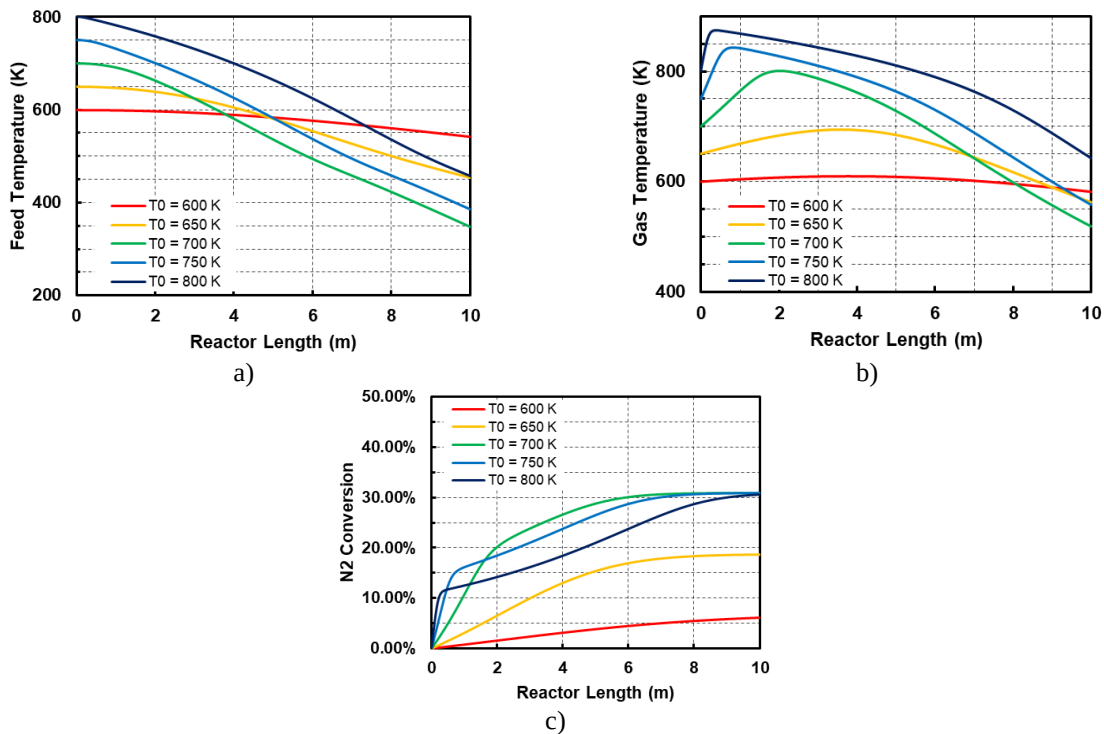


Figure 12: Effect of changing the top temperature on a) feed temperature b) reaction gas temperature, and c) N_2 conversion

Figure 13 shows the effect of different feed compositions on non-adiabatic reactor behavior, with the cases study being the same as those considered for adiabatic reactors. Feed entering the reactor is considered to be at 698 K and the operating pressure is 286 atm, for all cases.

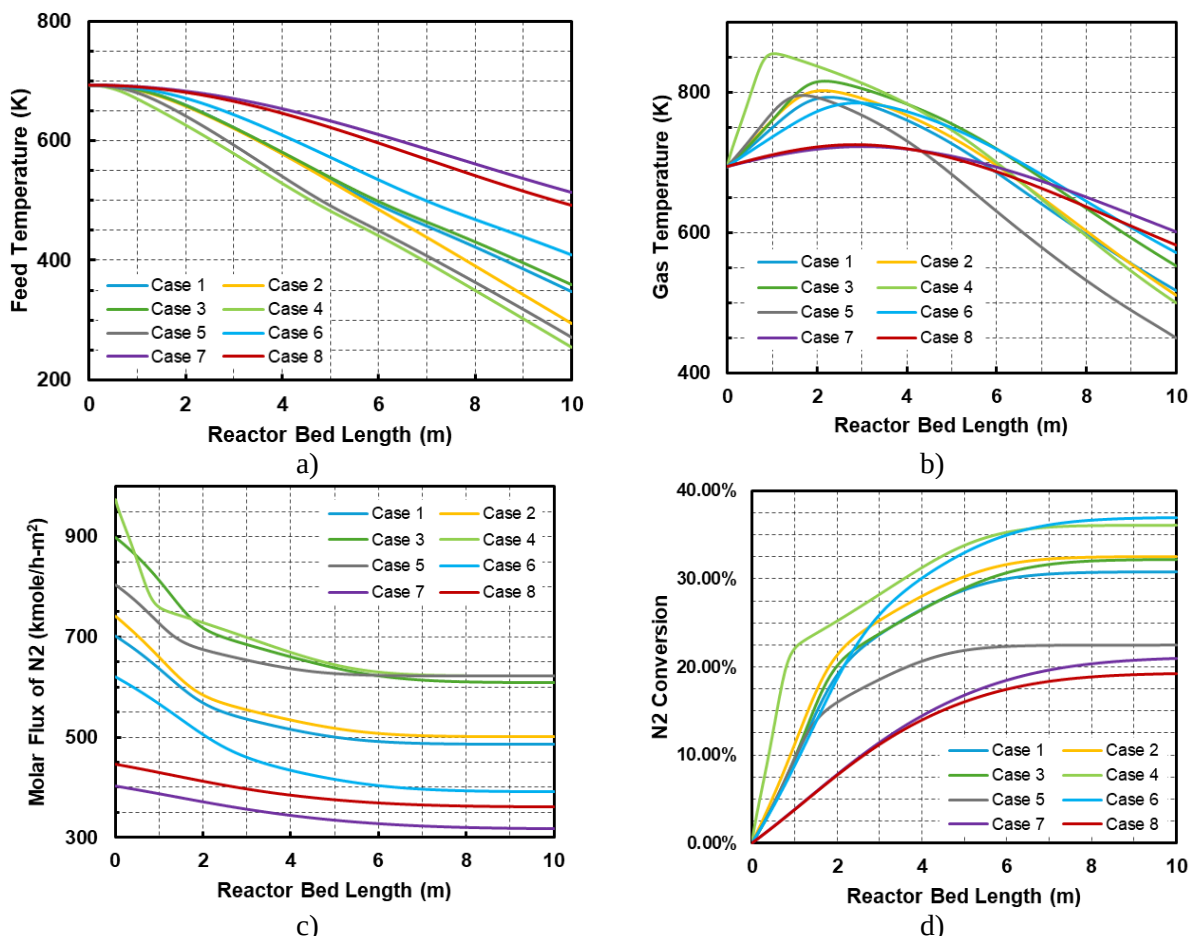


Figure 13: Effect of different feed composition on a) feed and b) reactor gas temperature, c) molar flux of N₂, and d) N₂ Conversion

Case 1 and 2 show similar behavior in terms of both feed and gas temperature profiles, with case 1 having higher feed temperature and lower reactor gas temperature throughout the reactor length. Notably, while Case 1 and 2 have similar temperature profiles, Case 2 has higher overall conversion than Case 1. This is most likely due to slight excess of H₂ in the feed composition of Case 2, but the lower NH₃ content in the feed may also have an effect, encouraging the forward synthesis reaction.

Cases 3 and 4 simulate a Generation 2 renewable power-to-ammonia synthesis scheme, having no inert gases present. Case 4 shows very high overall N_2 conversion, about 36%, and also achieves high peak temperatures in the reactor bed. However, the heat transfer along the reactor bed between the feed and reaction gas streams is also very efficient, with both exiting at lower temperatures than Case 3 which has lower initial feed amounts of N_2 and H_2 . In both cases, the overall conversion exceeds 30%, outperforming most currently deployed systems, which generally achieve single-pass conversions of around 20%.

Case 5, 6 and 7 are used to further study the effect of non-stoichiometric $N_2:H_2$ ratios in the feed composition. Comparing Case 5 and 6, with the former having insufficient amount of H_2 and the latter having excess H_2 , the latter case achieves overall conversion of almost 37%, the highest of all studied cases, whereas the former has a relatively low conversion of 22.5%. Temperature profile curves also show that the heat transfer along the reactor length for Case 6 is more gradual than for Case 5. Overall, this tends to indicate that introducing excess H_2 in the feed may lead to higher overall conversion in the case of non-adiabatic reactors. However, considering Case 7 which also has excess H_2 , similar to Case 6, but also an increased amount of inerts and NH_3 in the feed, the overall conversion is relatively low at about 21%. The temperature profiles also suggest that this feed composition undergoes the least change in temperature along the reactor length and the heat transfer is inhibited compared to other cases.

Comparing Case 7 and 8, the temperature profiles are nearly identical, with Case 8 having lower conversion than Case 7 despite having stoichiometric ratio for N_2 and H_2 and higher initial amount of N_2 . The slow progression of the reaction in these cases is most likely due to the higher NH_3 content in the feed shifting the equilibrium to the left, inhibiting the forward synthesis reaction, behavior that is also observed in the adiabatic case.

4.6 OPTIMIZATION OF AMMONIA REACTORS USING DIFFERENTIAL EVOLUTION (DE) ALGORITHM

Following on from the parametric study, optimization of operating parameters for ammonia reactors can also be considered. Previously, optimization has been carried out for economic cost return functions for non-adiabatic, indirectly cooled reactors [19], [143], [144], and on the basis of ammonia production for adiabatic reactors [173]. However, these works have considered only operating conditions of the reactor, i.e., the inlet temperature, inlet mass flow rate, operating pressures [173], or reactor design parameters such as the length of the reactors [19], [144] as decision variables for the optimization. Till now, to the best of the authors' knowledge, there has not been any optimization study done regarding optimal molar feed composition for performance improvement of ammonia reactors. Furthermore, for the case of adiabatic reactors, the optimal quench temperature is also a parameter worth studying.

In this work, we have considered the maximizing of ammonia production, through the control of parameters such as feed temperature (T_0), operating pressure (P), and the molar composition of the feed (y_{N_2} , y_{H_2} , y_{NH_3} , y_{Ar} , y_{CH_4}). In the case of adiabatic reactors, the quench temperature (T_q) has also been considered as control parameter for the overall optimization of ammonia production.

The optimization problem for non-adiabatic reactors can thus be summarized as,

$$\begin{aligned}
& \max NH_{3out}(T_f^0, P, y_{N_2}^0, y_{H_2}^0, y_{NH_3}^0, y_{Ar}^0, y_{CH_4}^0) \\
& \textbf{subject to} \\
& \frac{dm_{N_2}}{dV} = -\frac{1}{2}(r_{NH_3}) \\
& \frac{dT_g}{dx} = -\frac{US_1}{WC_{P_{gas}}}(T_g - T_f) - \frac{(-\Delta H_r)r_{NH_3}S_2}{WC_{P_{gas}}} \\
& \frac{dT_f}{dx} = -\frac{US_1}{WC_{P_{feed}}}(T_g - T_f) \\
& y_{N_2} + y_{H_2} + y_{NH_3} + y_{Ar} + y_{CH_4} = 1 \\
& 3y_{N_2} = y_{H_2} \\
& 600\text{ K} \leq T_f^0 \leq 800\text{ K}, \quad 129\text{ atm} \leq P \leq 300\text{ atm}, \\
& 0.1 \leq y_{N_2}, y_{H_2} \leq 1.0, \quad 0.01 \leq y_{NH_3}, y_{Ar}, y_{CH_4} \leq 0.1
\end{aligned}$$

For adiabatic reactors, it can be summarized as,

$$\begin{aligned}
& \max NH_{3out}(T_f^0, T_q^0, P, y_{N_2}^0, y_{H_2}^0, y_{NH_3}^0, y_{Ar}^0, y_{CH_4}^0) \\
& \textbf{subject to} \\
& \frac{dm_{N_2}}{dV} = -\frac{1}{2}(r_{NH_3}) \\
& \frac{dT_g}{dx} = -\frac{(-\Delta H_r)r_{NH_3}S_2}{WC_{P_{gas}}} \\
& y_{N_2}^0 + y_{H_2}^0 + y_{NH_3}^0 + y_{Ar}^0 + y_{CH_4}^0 = 1 \\
& 3y_{N_2} = y_{H_2} \\
& 600\text{ K} \leq T_f^0, T_q^0 \leq 800\text{ K}, \quad 129\text{ atm} \leq P \leq 300\text{ atm}, \\
& 0.1 \leq y_{N_2}^0, y_{H_2}^0 \leq 1.0, \quad 0.01 \leq y_{NH_3}^0, y_{Ar}^0, y_{CH_4}^0 \leq 0.1
\end{aligned}$$

The SciPy Python package [171] has been used for the optimization solution, with the chosen algorithm used being differential evolution [174]. Differential Evolution (DE) is a stochastic optimization technique that draws inspiration from the principles of biological evolution, and method is particularly effective for solving complex, multidimensional problems where the relationship between variables and outcomes is not easily defined. DE operates by maintaining a population of candidate solutions, which evolve over successive generations. The algorithm begins with a diverse set of potential solutions and iteratively refines them through processes analogous to genetic mutation and crossover. In each generation, new candidate solutions are created by combining existing ones, and the most promising solutions are selected to continue to the next

iteration. This process mimics natural selection, allowing the population to converge towards optimal solutions over time.

In the context of our reactor model optimization, DE proves to be a powerful tool. The algorithm is tasked with finding the optimal operating conditions for the reactor, including parameters such as temperature, pressure, and reactant concentrations. Each candidate solution in the DE population represents a specific configuration of these parameters. The optimization process begins with a set of random reactor conditions and progressively refines them. At each step, new potential configurations are generated by combining and modifying existing ones. These configurations are then evaluated using our reactor model to assess their performance. The best-performing setups are retained and used to inform the next generation of solutions. Over numerous iterations, the algorithm converges towards the set of reactor conditions that yield the best performance. The strength of using DE for this optimization lies in its ability to handle the non-linear nature of chemical reactions, its independence from detailed mathematical problem formulations, and its capacity to find robust solutions in complex, multidimensional spaces. This approach enables us to efficiently explore a vast range of possible reactor configurations and identify optimal operating conditions.

In this study, the current-to-best/1 mutation strategy [175] is used, which offers a middle ground between exploring the parameter space while utilizing the best current solution, allowing for faster solution of the overall optimization problem. The following parameters have been considered constant during the study, as shown in Table 15. It should be noted that for the adiabatic case, a three-bed reactor, with quenching at the exit of the first bed has been considered.

Table 15: Ammonia reactor parameters for optimization solutions

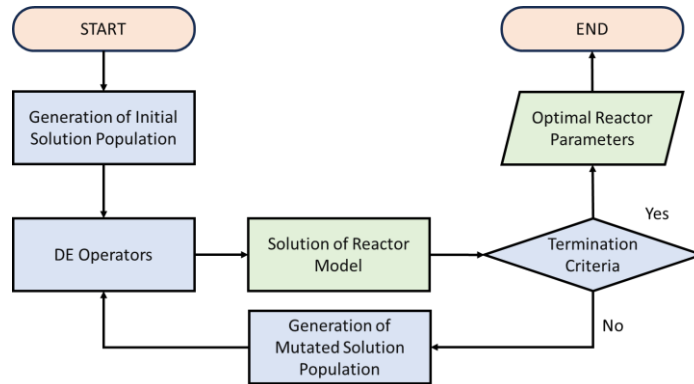
Parameter	Value		Unit
	Non-adiabatic	Adiabatic	
Heat transfer coefficient, U	2092	-	$\text{kJ/m}^2\text{hK}$
Surface area of cooling tube per unit length of reactor, S_1	10	-	m^2/m
Cross-sectional area of reactor bed, S_2	0.78	7.069	m^2
Mass flow rate of feed, W	26400	231262.31	kg/h
Length of reactor, L	10	22.5	m

The optimization algorithm parameters are detailed in Table 16.

Table 16: Differential Evolution Optimization parameters

Parameter	Value
Population Size	100
Maximum number of iterations	1000
Mutation constant	0.5
Recombination constant	0.6

The process flow for the DE optimization is shown in Figure 14.

**Figure 14: Process flow for optimization of reactor parameters using Differential Evolution algorithm**

4.6.1 Adiabatic Reactor

The optimum solution for the adiabatic reactor case with quenching at the exit of the first reactor bed is given in Table 17.

Table 17: Optimum Solution for adiabatic reactor

Objective		
Maximum flow of ammonia at outlet	745.2223	kmol/hm ²
Controlled Parameters		
Inlet Temperature	600.4986	K
Quench Temperature	674.8974	K
Reactor Operating Pressure	299.8535	atm
Molar Fractions		
N ₂	0.2267	
H ₂	0.6800	
NH ₃	0.0141	
Ar	0.0689	
CH ₄	0.0103	

The temperature and molar flow profiles for the optimum solution is given in Figure 15 and 16.

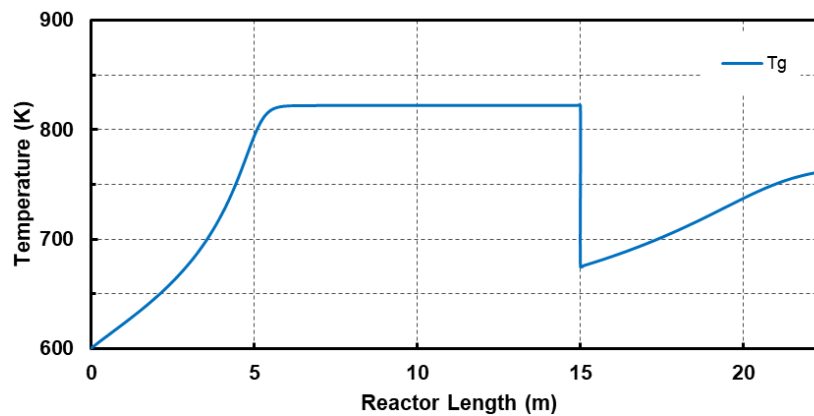


Figure 15: Temperature profile for feed gas stream and reactor gas stream along the length of the reactor for the optimum solution (adiabatic)

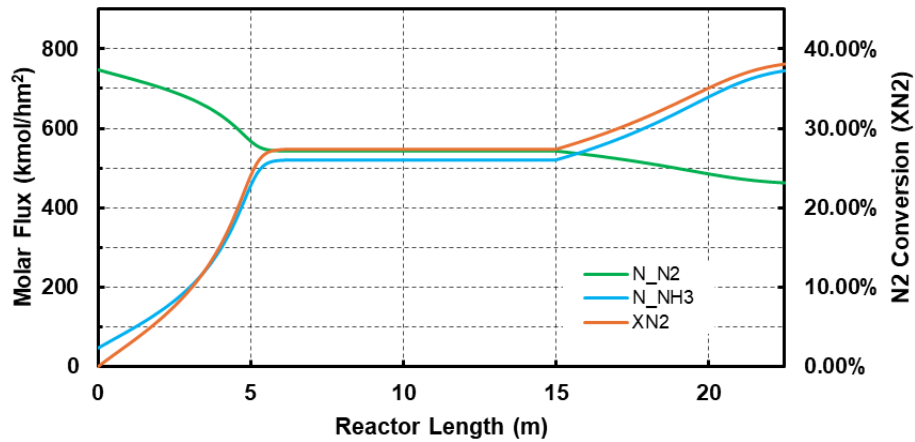


Figure 16: Molar flow profile for N₂ and NH₃, and conversion of N₂ along the length of the reactor for the optimum solution (adiabatic)

It can be seen that for adiabatic reactor, a lower initial NH₃ flow is required for the maximizing of product NH₃ at the outlet, with the overall N₂ conversion being 38.1%. Furthermore, lower inlet temperature of 600 K is used, while the quench temperature of 674 K is higher than the literature values of 640 K and 665 K, respectively. Higher pressures are still preferred, and the low presence of inerts is also similar to the optimum solution obtained for non-adiabatic reactors. Similar to the optimum solution for the non-adiabatic case, the peak temperature observed in the reactor, at the end of the first bed, is higher than that observed in industrial data, being about 822 K. It is also observed that the reaction progresses much faster in the first bed, and then the rate of reaction increasing in the second bed following quenching. From this, it can be assumed that by operating the reactor at higher pressure and using these feed conditions, the length of the first reactor bed can be significantly reduced, which would undoubtedly lead to reduction in overall plant costs.

Considering this point, the length of the first reactor bed can be reduced to 6 m, while operating under the same conditions and with same feed conditions, and still reach the same overall N₂ conversion, as shown in Figure 17 and 18.

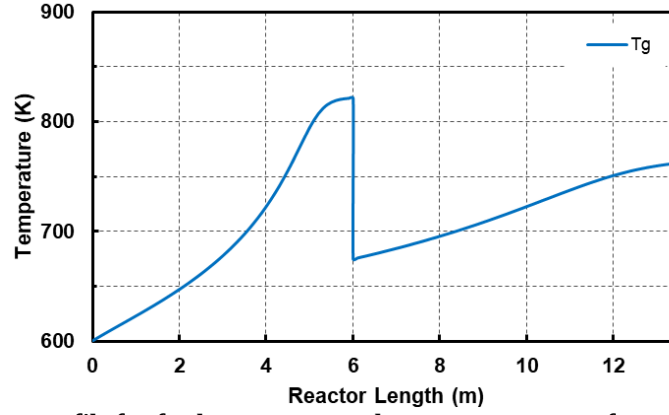


Figure 17: Temperature profile for feed gas stream and reactor gas stream for reduced reactor bed under optimum operating conditions (adiabatic)

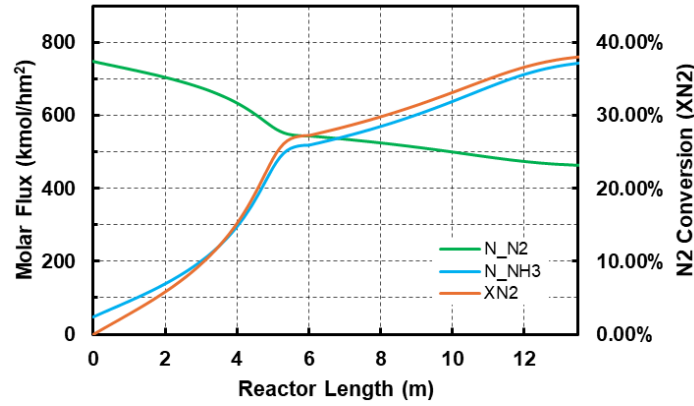


Figure 18: Molar flow profile for N₂ and NH₃, and conversion of N₂ for reduced reactor bed length under optimum operating conditions (adiabatic)

A rudimentary cost analysis can be carried out considering the capital costs involved in catalyst and reactor sizing based on the reduced reactor length under the optimal operating conditions. The cost of the reactor can be calculated using the method developed by Turton[176],

$$\log_{10} C_{P,reactor}^0 = 3.4974 + 0.4485 \log_{10} \lambda + 0.1074(\log_{10} \lambda)^2 \quad (4.25)$$

$$C_{BM,reactor} = C_{P,reactor}^0 \left(\frac{I_{2024}}{I_{2000}} \right) \times 59.89 \quad (4.26)$$

Where $C_{P,reactor}^0$ is the purchased cost of the reactor and λ is the capacity parameter, which is considered to be the volume of the reactor. I_{2024} and I_{2020} are the Chemical Engineering Plant Cost

Indices (CEPCI) for the year 2024 and 2000 respectively, having value 795 and 394 [177]. The cost of the catalyst is considered to be 21.63 \$/kg, and the density of the catalyst is 2300 kg/m³ [178].

It is seen that the catalyst volume and cost can be reduced by about 40%, while the cost of the reactor can be reduced by about 35%, with the overall capital investment decreasing by 37%. However, while cost savings due to reduced volume of reactor are observed, it is worth noting that the optimal case operates at higher pressure than the industrial case, meaning that considerable work, and thus cost, is involved in the compression of feed gas. The effect of this higher compressive work and thus the net savings of the system remains a point of further study. Furthermore, while it has not been considered in this study, pressure drop does occur along the length of the reactor, and thus reducing the length of the first reactor bed may lead to reduction in the pressure drop, further improving the performance of the overall reactor.

4.6.2 Non-adiabatic reactor

Considering the case of the non-adiabatic reactor, the optimum solution is summarized in Table 18.

Table 18: Optimum Solution for non-adiabatic reactor

Objective	Value	Unit
Maximum flow of ammonia at outlet	865.3770	kmol/hm ²
Controlled Parameters		
Inlet Temperature	707.9579	K
Reactor Operating Pressure	299.8736	atm
Molar Fractions		
N ₂	0.2302	
H ₂	0.6907	
NH ₃	0.0589	
Ar	0.0101	
CH ₄	0.0101	

The temperature and nitrogen flow profile for the reactor is given in Figure 19.

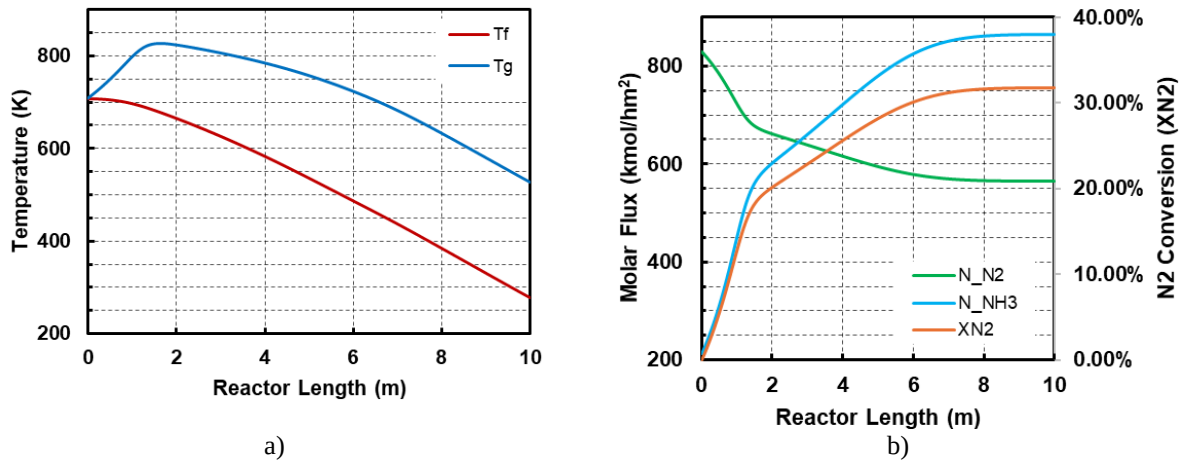


Figure 19: a) Temperature profile for feed gas stream, reactor gas stream, and b) molar flow profile for N₂, NH₃, and conversion of N₂ along the length of the reactor for the optimum solution (non-adiabatic)

Considering the optimum solution, we observe that higher operating pressure is preferred, as the optimum pressure value approaches the maximum limit of operable pressures, while low presence of inerts is preferred, with both Ar and CH₄ tending toward the minimum possible value. Interestingly, the amount of initial NH₃ in the optimum solution is slightly higher than in the industrial scenarios, being closer to 6% mole fraction than the 1-5% range that is commonly seen in the literature [19], [20]. Comparing the temperature and N₂ profiles in Figure 19 with the validated industrial case, it seems this results in a higher initial rate of reaction, which results in higher overall NH₃ production, with the overall N₂ conversion being 31.8%. Finally, the inlet temperature is about 708 K, which is close to the literature value of 694 K. This is expected, as equilibrium theory states that at high temperatures the reaction would shift toward the decomposition of NH₃ to N₂ and H₂, hindering the overall NH₃ production without providing substantial benefit in terms of rate of reaction, as can be seen in Figure 12. It is also worth noting that with the higher inlet temperature and operating pressures, the peak temperature observed within the reactor is also higher, being about 815 K, with the reaction progressing faster and to a greater extent, especially at lower reactor lengths.

4.7 Conclusions

A study of non-adiabatic and adiabatic industrial ammonia reactors has been carried out by developing a mathematical model in Python. The mathematical models have been validated against available literature and industrial data, and variation of reactor behavior with change in feed temperature, reactor operating pressure and different feed conditions has been studied. Several different cases have been devised for feed conditions, with the aim of studying the reactor behavior under industrial feed conditions, as well as to understand effect of initial ammonia fraction, deviation from stoichiometric condition, and effect of inert components. The main conclusions of the study are summarized below;

- For both adiabatic and non-adiabatic reactors, reaction gas temperature rises with increase in feed temperature. Overall N_2 conversion of the reactors is also observed to initially increase until reaching optimum reaction temperature, about 650 K for adiabatic reactor and 700 K for non-adiabatic reactor, with temperatures higher than this inhibiting forward ammonia synthesis reaction and resulting in lower N_2 conversion.
- For both reactor types, higher operating pressures result in higher N_2 conversion and reaction gas temperatures. This agrees with the equilibrium principle for exothermic reactions.
- For both reactor types, high presence of inert is seen to inhibit the reaction, most likely due to reducing reaction gas temperature and thus the forward rate of reaction. Similarly, increased N_2 conversion is observed for feed cases with reduced inerts, with the maximum conversion being observed when H_2 is in excess and amount of feed ammonia and inerts is low.

- Comparing behavior between the reactor types, non-adiabatic reactors achieve higher overall N₂ conversions while operating with similar temperature margins as adiabatic reactors. However, they require longer reactor lengths to achieve this improvement in performance, which may make adiabatic reactors preferable when dealing with material and dimensional costs and constraints.

CHAPTER 5

Technoeconomic Analysis and Optimization of Conventional and Cascaded Ammonia Reactor Arrangements

5.1 Introduction

The increasing importance of ammonia in the global hydrogen and energy economy, both as a vector for hydrogen and as a combustible fuel, has resulted in increased attention regarding the optimization and performance enhancement of ammonia reactors. The shift toward green ammonia production, using renewable resources not dependent on fossil fuels creates the obligation for the modeling and optimization of green ammonia reactors. The absence of inerts such as CH_4 , produced from the refining of natural gas for the production of H_2 in green ammonia reactors, lead to differences in reactor behavior relating to internal gas temperature and NH_3 production rates. As such is an important field of study as green ammonia plants gain more popularity.

Adiabatic quench reactors are popular in the industrial context. They operate by having the catalyst split into multiple beds, and the reactant mixture entering each reactor and being cooled at the exit of the reactor bed. At too high temperatures, the equilibrium of the reaction shifts toward reactant side and thus the synthesis of ammonia is inhibited. Generally, this is done by the use of quench coolers [161]. However, as shown in Figure 20, the ammonia reactors may also be arranged to allow for the use of split feeds having lower mass flow rate to each reactor, and the feed streams being used to cool products gas stream from a prior reactor bed via mixing of the two streams.

These differences in design may result in different performance of the overall reactor in terms of thermal efficiency, N_2 conversion and cost of production.

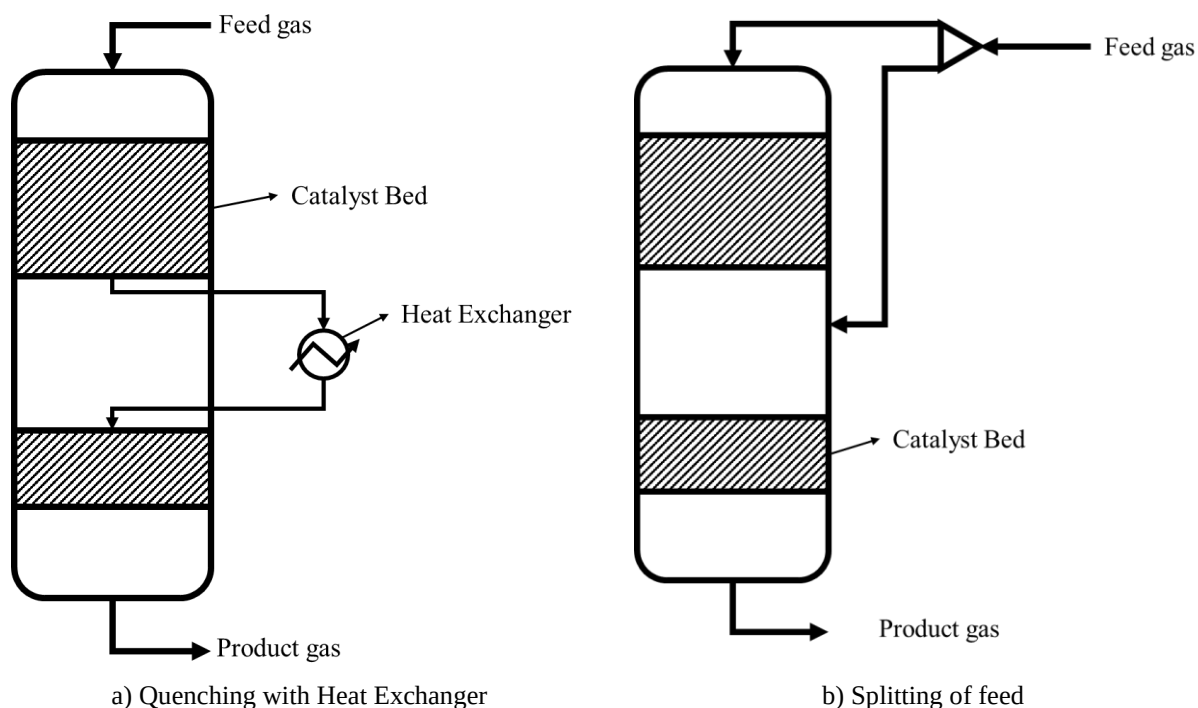


Figure 20: Adiabatic reactor with two reactor beds operating with a) quenching via heat exchanger and b) splitting of feed

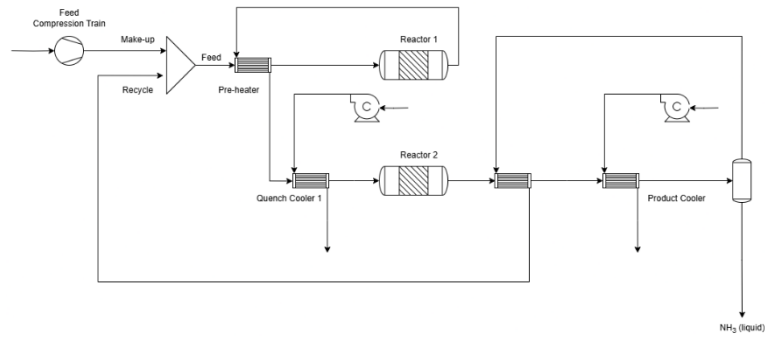
The reactor configurations as seen in the literature may be of two [1] - [4], or three [5] - [7] reactor beds. While a three-reactor bed design leads to higher NH_3 production, it also results in higher cost of production, due to the added investment of an additional reactor bed. Since green ammonia production has generally been found to be more economically viable when operating at smaller production scales [5], [8], [37], whether the benefit of higher production offsets the higher initial investment related to a three-bed configuration is a point of interest.

The process optimization of ammonia reactors has also been done extensively in the literature [3], [11] - [16]. However, these studies have either focused on non-adiabatic reactors, with the optimization being done for the maximization of production or overall plant value, or optimal temperature control of the plant. The optimization of ammonia synthesis loops for the minimization of the cost of production thus requires further study.

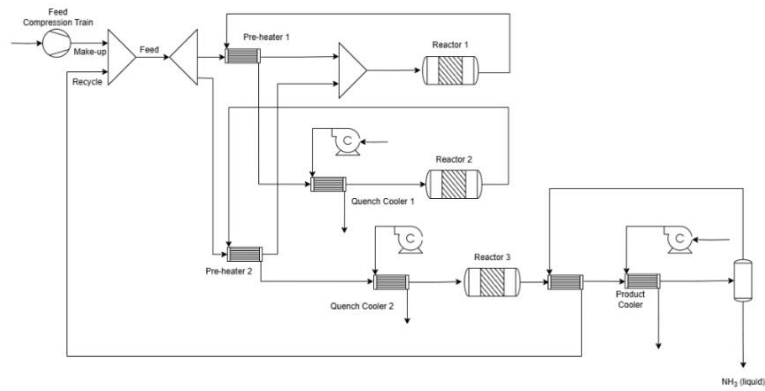
This work thus compares the behavior of conventional adiabatic reactor arrangements considering cooling both via quenching and mixing with feed splitting. Four reactor arrangements are considered, consisting of either two or three reactor beds. The arrangements are modeled in Aspen HYSYS, and their operation is considered in both low pressure (150 bar) and high pressure (300 bar) scenarios. The arrangements are optimized for minimization of the levelized cost of production of ammonia (LCOA) using a Differential Evolution algorithm, and their performance compared across both scenarios. Comparing optimized performance of the reactor arrangements may lead improvements in levelized cost of production compared to literature values, and provide insight as to whether operating in low pressure scenario provides enough cost saving from reduced compression work to offset higher reactor investment, or whether high-pressure production scenario is more favorable overall.

5.2 System Description

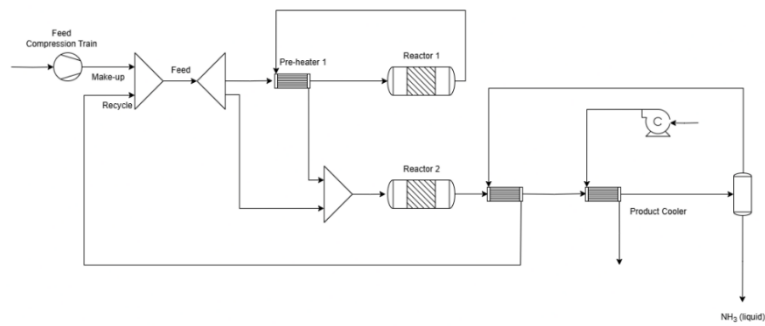
Figure 21 shows the different arrangements of reactors that have been studied. Each reactor bed has been considered as individual reactors. The effect of quenching after each reactor bed and prior to being fed into the subsequent reactor, as well as mixing with cooled feed stream to quench the flow is also considered.



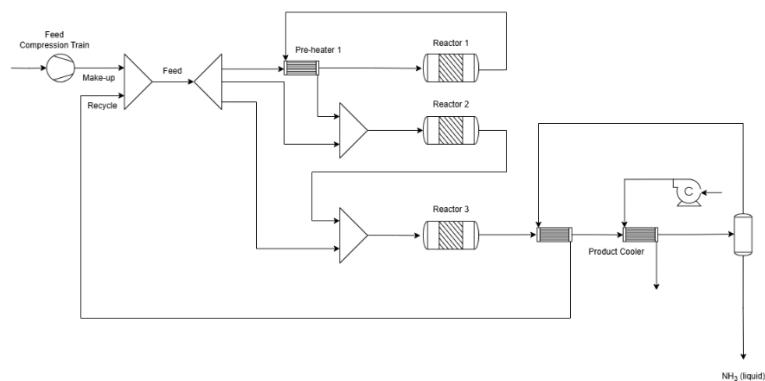
(a) Arrangement A



(b) Arrangement B



(c) Arrangement C



(d) Arrangement D

Figure 21: Schematic Diagram of different cascade generation arrangements showing a) two-reactor arrangement with quenching, b) three-reactor arrangement with quenching, c) two-reactor arrangement with splitting of feed, and d) three-reactor arrangement with splitting of feed

For arrangement (a) and (b), the entirety of the feed stream flows through each reactor, with quenching of the product gas to required temperature being done prior to feed to subsequent reactor. For arrangement (a), the product gas from the first reactor bed is used to heat the feed flow to the required temperature at reactor inlet, whereas in arrangement (b) the feed is split and preheated by the product flow of the first and second reactor bed, before being merged into the feed for the first reactor bed. For both these cases, the total mass flow in each reactor bed is equal.

For arrangements (c) and (d), the feed is equally split into two or three streams, respectively, prior to entering the first reactor bed. For arrangement (c), one of these streams is then preheated by the product gas from the first reactor bed, and the cooled product gas is then quenched by mixing with the other feed stream. The mixed stream is then fed into the second reactor bed. The configuration for arrangement (d) is similar, with the product gas of the first reactor bed preheating the feed entering the first reactor and then mixing with the feed entering the second reactor bed, and the product gas from the second reactor bed being mixed with the final feed stream and then being fed into the third reactor bed.

The product gases are cooled to ambient temperatures by cooling water for the separation of product ammonia as a liquid. The unreacted gases are then heated back to required temperature by recovering heat from the product gas stream of the final reactor and recycled back into the system, along with a makeup stream consisting of N_2 and H_2 in stoichiometric proportion.

5.3 Methodology

The analysis is carried out by considering each reactor bed as adiabatic and using the Temkin-Pyzhev equation to model the reaction kinetics [140], which has been elaborated in detail in the previous chapter and repeated here for clarity.

$$r_{N_2} = f \times \left[k_A p_{N_2} \left(\frac{p_{H_2}^{1.5}}{p_{NH_3}} \right) - k_B \frac{p_{NH_3}}{p_{H_2}^{1.5}} \right] \quad (4.5)$$

The initial feed mixture is at 326.85 °C and is heated to a temperature of 336.85 °C in the heat exchanger prior to entering the first reactor bed. For arrangements (a) and (b), the temperature after quenching is around 350 °C, similar to the industrial case studied by Suhan et al.[20]. Industrial KMR catalyst in the packed bed reactor has been considered [144]. Each reactor bed is of 3m diameter, with the total feed through each reactor arrangement being 23318 kmol/hr, as in the industrial case presented by Suhan et al.[20]. The composition of the makeup stream consists of nitrogen and hydrogen in a 3:1 stoichiometric ratio, with the composition of the feed entering the reactor being determined after mixing with recycle stream and is calculated by HYSYS. Tra

The modeling is carried out in Aspen HYSYS V14, using the Soave-Redlich-Kwong equations of state [182] being used to calculate the required stream properties at specified state condition.

The N_2 conversion, X_{N_2} has been calculated as,

$$X_{N_2} = \frac{\text{molar flow rate of } N_2 \text{ at inlet} - \text{molar flow rate of } N_2 \text{ at outlet}}{\text{molar flow rate of } N_2 \text{ at inlet}} \quad (4.18)$$

For the overall conversion of the arrangement, the molar flow rates at the inlet and at the overall system outlet can be considered when carrying out the calculation.

5.3.1 Economic assessment

Cost analysis has been carried out considering the levelized cost of ammonia for each of the reactor arrangements. The analysis is done considering a lifetime of 15 years, with the plant operating for 350 days per year. Additional economic parameters are detailed in Tables 19 and 20.

The capital cost of the reactor is estimated using the method developed by Turton et. al [176], and which has been previously used in the economic assessment of ammonia plants by Sousa et al. [45]. The base purchased cost of equipment, C_p^0 is calculated using the equation,

$$\log_{10} C_p^0 = K_1 + K_2 \log_{10} \lambda + K_3 (\log_{10} \lambda)^2 \quad (4.25)$$

Where K_1 , K_2 and K_3 are correlation constants for the specific equipment as calculated by Turton et al.[176] , and λ is the capacity parameter, with each equipment having different capacity variables, as detailed in Table 19.

For this analysis, only reactor beds, quench coolers and pumps have been considered in the calculation, the required economic parameters are given in Table 19. The reactor beds can be modeled as vertical process vessels, the quench coolers as floating head heat exchangers [45] having entirely stainless-steel construction to mitigate the corrosive properties of NH_3 , and the pumps are considered to be centrifugal pumps.

Table 19: Correlation constants and bare module factors for ammonia plant equipment

Equipment	K_1	K_2	K_3	Capacity, λ	Bare module factor, F_{BM}
Reactor Beds, Separator	3.4974	0.4485	0.1074	Volume (m^3)	59.89
Pump	3.3892	0.0536	0.1538	Power (kW)	1.89
Compressor	2.2897	1.3604	-0.1027	Power (kW)	2.89
Heat Exchangers	4.8306	-0.85	0.3187	Area (m^2)	7.73

Following this, the bare module cost, C_{BM} , which accounts for any indirect cost related to the equipment, is calculated as,

$$C_{BM} = C_P^0 \left(\frac{I_{2024}}{I_{2000}} \right) F_{BM} \quad (4.26)$$

Where I_{2024} and I_{2000} are the Chemical Engineering Plant Cost Indices (CEPCI) for the year 2024 and 2000, having value 795 and 394, respectively [177]. F_{BM} is the bare module factor and is specific to the equipment, which accounts for additional miscellaneous costs related to installation, such as concrete, piping, electrical, etc. for the specific piece of equipment [183].

The total equipment cost required can thus be calculated as the fixed capital investment of equipment, FCI. In addition to the module costs, the fixed capital investment also accounts for contingency fees and miscellaneous costs, using the equation,

$$FCI_{eq} = 1.18 \sum C_{BM} + 0.50 \sum C_{BM}^0 \quad (5.8)$$

In addition to the capital cost of equipment, the cost of catalyst has also been considered in the initial investment cost, and it is assumed that over the 15-year lifetime of the plant, new catalyst replenishment will not be required [124], [125]. The amount of catalyst required is calculated considering the volume capacity of each reactor bed, the bed voidage, density of catalyst material, and the number of reactor beds. The total cost of catalyst is calculated based on required mass amount.

Thus, the total initial investment, INV , can be expressed as,

$$Initial\ Investment, INV = FCI_{eq} + Cost_{catalyst, total} \quad (5.9)$$

The other economic parameters are summarized in Table 20.

Table 20: Economic parameters of the arrangements

Economic Data	Value	Reference
Ammonia price (\$/ton)	4000	[184]
Plant Lifetime (years)	15	[124], [125]
Cost of Hydrogen (\$/ton)	700	[185]
Cost of Nitrogen (\$/ton)	20	[186], [187]
Cost of Cooling Water (\$/GJ)	0.378	[176]
Reactor Catalyst Cost (\$/kg)	21.63	[178]
Operating days per year	350	
Operations Cost (% of initial investment)	1.5	[188]
Discount rate (%)	6.47	[189]
Pressure drop in condenser (bar)	0.7	[190]
Electricity cost (\$/kWh)	0.0533	[191]

The feasibility of each arrangement is carried out considering the levelized cost of ammonia, LCOA, which can be expressed as [26],

$$LCOA = \frac{f_{cr} \times INV + C_{O,ann} + C_{elec,ann} + C_{H_2,ann} + C_{N_2,ann} + C_{cooling\ water,ann}}{P_t} \quad (5.15)$$

Where f_{cr} is the fixed cost factor, calculated as

$$f_{cr} = \frac{i(1+i)^n}{(1+i)^n - 1} \quad (5.16)$$

5.3.2 Optimization Methodology

Each arrangement is optimized for the minimization of the levelized cost of ammonia, with the length of the reactor beds being the controlled variables of the problem. From our previous study, presented in Chapter 4, and Le Chatelier's principle, we know that for ammonia synthesis, higher pressure is favored. Low-pressure behavior is also considered in this study, as it is important to understand in the context of green hydrogen production, where lower pressure operation may be preferred due to the lower initial investment. Furthermore, it is important to determine if the reduction in compressive work results in overall cost reduction, or the lowered rate of production of NH_3 leads to increase in overall cost of production. The composition in this study considers only the N_2 , H_2 and NH_3 , as CH_4 as an inert is not present for the case of green hydrogen, and thus

green ammonia, production, and Ar can be neglected as both are inert that do not participate in the reaction and for ease of modeling. From the study carried out in Chapter 4, we know that at higher temperatures, the reaction is inhibited, and that quenching the flow to low temperatures allows for the reaction to progress. Varying the length of the reactors varies the extent to which the reaction occurs in each reactor bed, and thereby varies the rate of ammonia production, required makeup flow and thus the overall performance and cost of production.

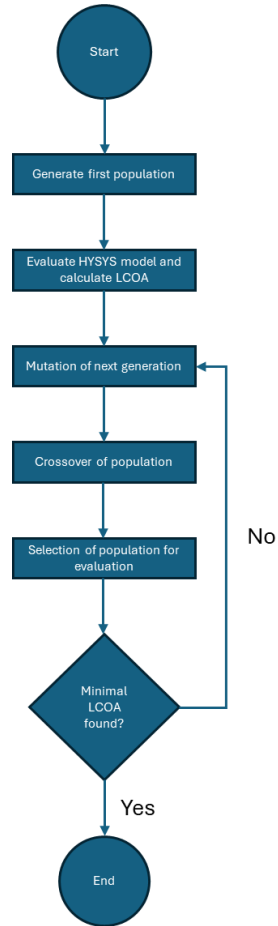
A differential evolution algorithm is used to optimize the arrangements [174], [175]. The optimization routine was developed and implemented using MATLAB, which communicates with HYSYS, to evaluate each of the length vectors for each arrangement and the result data then used to evaluate the objective function, i.e LCOA.

The differential evolution process creates an initial population of possible length combinations for the reactor beds, and each of these combinations, or length vectors, are evaluated and the combination having the least LCOA, i.e best solution, is identified. Following this, the next generation of length vectors are generated, and a mutation phase is carried out, where each new vector of the new generation undergoes comparison with previous solutions, with inferior solutions being discarded in favor of retaining their predecessors. The length vectors resulting from this selection process are used to calculate new LCOA values, with the minimum value from the current generation compared against the previously established best solution. This process continues until the best possible length vector resulting in least possible LCOA value is identified.

The optimization algorithm parameters are detailed in Table 21, and the process flow is shown in Figure 22.

Table 21: Differential Evolution Optimization parameters

Parameter	Value
Population Size	100
Maximum number of iterations	500
Mutation factor	0.5
Crossover factor	0.9

**Figure 22: Process flow for optimization of reactor arrangements using Differential Evolution algorithm**

5.4 Results and Discussion

Figure 23 shows the variation of the objective function with number of generations during the differential evolution optimization process for each arrangement operating at 300 bar reactor pressure. It is generally observed that the solutions converge in under 200 generations, and it is

worth noting that the arrangements with split feed achieve lower LCOA values when operating at their respective optimal reactor lengths.

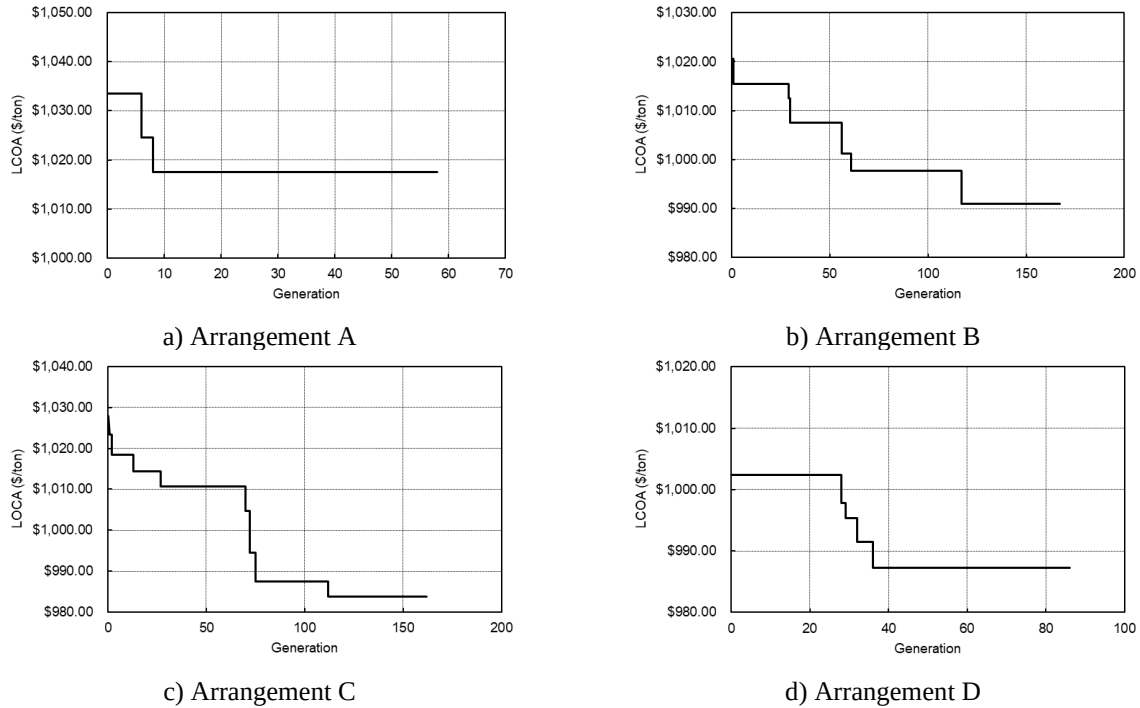


Figure 23: Levelized cost of ammonia obtained during differential evolution optimization for each arrangement at 300 bar reactor pressure

Table 22 details the optimal reactor lengths and LCOA values for the reactor arrangements operating at 300 bar reactor pressure, while Table 23 details the reactor outlet conditions. As is expected, the high operating pressure means that the initial rate of reaction is very high, and thus the optimal reactor lengths are relatively small. For arrangement (a) and (b), without splitting of feed and quenching of reaction gas stream, it is generally observed that the bulk amount of NH_3 produced is in the first reactor, with the production reducing in subsequent reactors.

Table 22: Optimal reactor bed lengths for each reactor arrangement operating at 300 bar reactor pressure

Arrangement	A	B	C	D
L_1 (m)	2	3	2	3
L_2 (m)	1	4	4.65	4
L_3 (m)		3.26		3.28
Total Reactor Bed Lengths (m)	3	10.26	6.65	10.28
Levelized Cost of Ammonia (\$/ton)	1,017.50	991.02	983.85	987.24

For arrangements c) and d), it is seen that significant amounts of NH_3 is produced in each reactor, and the overall production scale is larger than corresponding arrangement without splitting of feed.

Table 23: Reactor outlet conditions for optimal configuration of each arrangement operating at 300 bar reactor pressure

Arrangement	Temperature at R1 outlet (°C)	Temperature at R2 outlet (°C)	Temperature at R3 outlet (°C)	NH_3 at R1 outlet (kmol/h)	NH_3 at R2 outlet (kmol/h)	NH_3 at R3 outlet (kmol/h)	Liquid NH_3 produced (kmol/h)
A	354.25	343.66	-	1669.37	1759.24	-	327.17
B	369.21	368.05	354.14	1757.40	2173.52	2402.44	1074.20
C	377.84	403.44	-	903.95	2279.18	-	1003.50
D	545.95	542.29	542.28	1271.67	2597.83	3935.83	2828.85

Figure 24 summarizes the results of the optimal solutions for each reactor arrangement operating at 300 bar. It is observed that for high-pressure systems, arrangement C yields the lowest LCOA value of 983.85 \$/ton, at a production rate of 1003.50 kmol/hr, while arrangement A has the highest LCOA value of 1017.50 \$/ton, while operating at the lowest production rate of 327.17 kmol/hr. Considering three reactor arrangements B and D, the LCOA is lower for the arrangement with splitting of feed, i.e arrangement D, at 987.24 \$/ton compared to arrangement B having no splitting of feed at 991.02 \$/ton, with the production rate for arrangement D also being the highest at 2828.85 kmol/hr. Overall, this seems to indicate that splitting of the feed, while resulting in initial increase in reactor investment, leads to improvement in production and thus lowers the overall LCOA values.

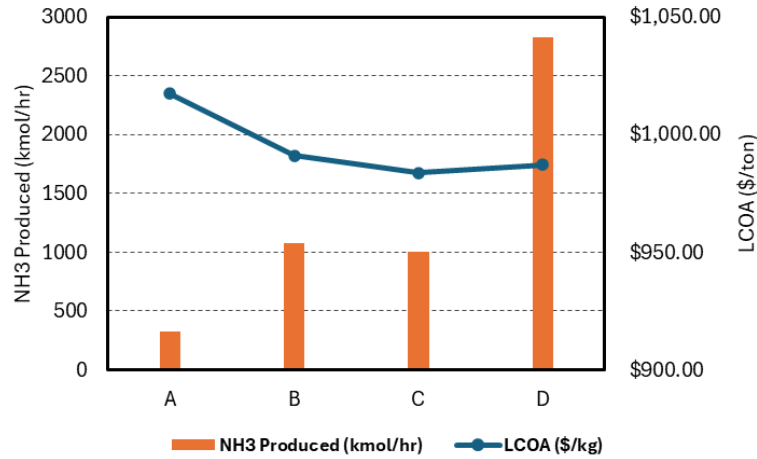


Figure 24: Variation in NH₃ production and LCOA for reactor arrangements at 300 bar reactor pressure

Figure 25 shows the variation of the objective function with number of generations during the differential evolution optimization process for each arrangement operating at 150 bar. Compared to the high-pressure scenario, the optimal solution is found much faster in under 100 generations for each arrangement.

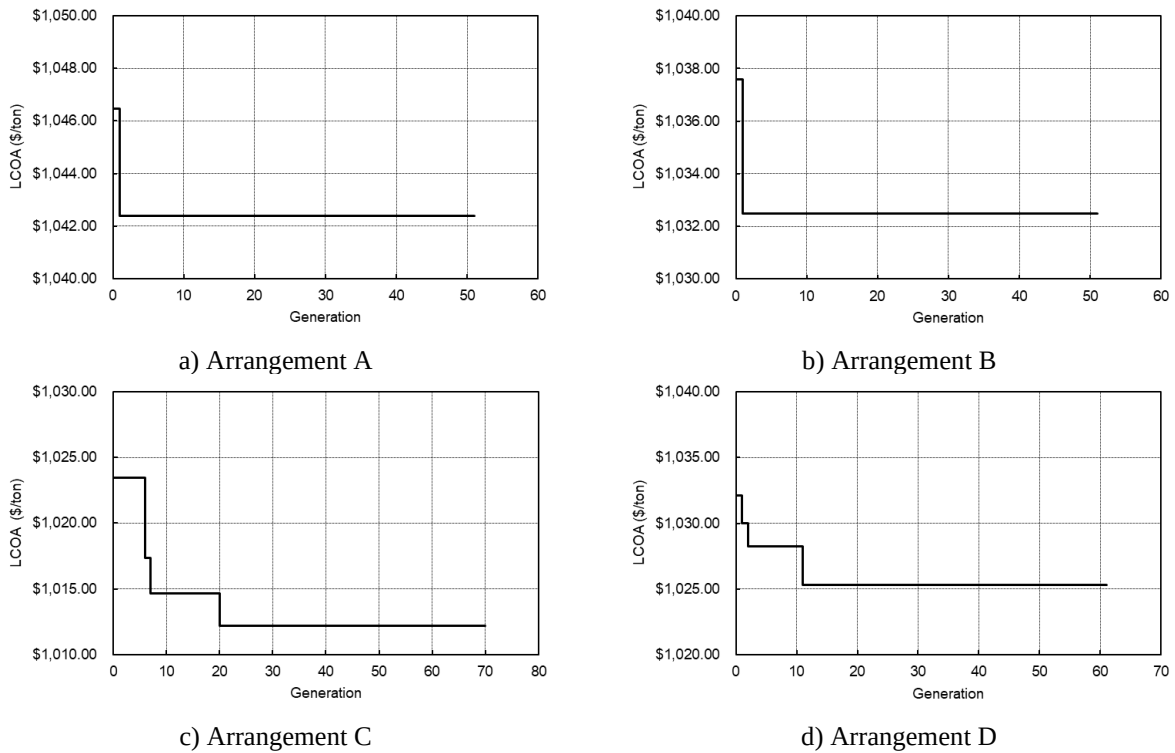


Figure 25: Levelized cost of ammonia obtained during differential evolution optimization for each arrangement at 150 bar reactor pressure

Table 24 shows the optimal reactor lengths for the reactor arrangements in the low-pressure scenario. Due to the lower operating pressure, the optimal reactor lengths are found to be higher, to allow for the reaction to reach completion in each reactor bed, and this leads to increase in the initial investment, and thus an overall increase in LCOA is observed for all arrangements.

Table 24: Optimal reactor bed lengths for each reactor arrangement operating at 150 bar reactor pressure

Arrangement	A	B	C	D
L ₁ (m)	9.24	11.05	8.87	7.70
L ₂ (m)	7.56	5.24	6.93	8.62
L ₃ (m)		5.70		4.62
Total Reactor Bed Lengths (m)	16.80	22.00	15.8	20.93
Levelized Cost of Ammonia (\$/ton)	1,042.40	1,032.50	1,012.20	1,025.30

Table 25 details the reactor outlet conditions for each arrangement operating in optimal configuration at 150 bar reactor pressure. In conjunction with the decrease in pressure, a decrease in the overall production rate for all the arrangements is also observed. This is expected, as the rate of reaction is lower at the lower pressure, leading to reduced production despite the increase in reactor lengths. This decrease in production combined with the higher investment requirements lead to the overall increase in LCOA for all the arrangements operating at this lower reactor pressure.

Table 25: Reactor outlet conditions for optimal configuration of each arrangement operating at 150 bar reactor pressure

Arrangement	Temperature at R1 outlet (°C)	Temperature at R2 outlet (°C)	Temperature at R3 outlet (°C)	NH ₃ at R1 outlet (kmol/h)	NH ₃ at R2 outlet (kmol/h)	NH ₃ at R3 outlet (kmol/h)	Liquid NH ₃ produced (kmol/h)
A	349.87	346.13	-	2378.17	2505.57	-	375.94
B	357.21	344.13	344.36	2523.01	2623.53	2727.03	486.29
C	345.51	335.10	-	1180.63	2355.82	-	442.68
D	382.66	374.66	367.26	918.53	1855.50	2710.40	874.39

Figure 26 summarizes the results of the optimal solutions for each reactor arrangement operating at 150 bar. In low-pressure systems, all arrangements show increased LCOA values due to increased total reactor lengths. Arrangement C is the most economically favorable configuration, achieving the lowest overall LCOA of 1012.20 \$/ton, at a NH_3 production rate of 442.68 kmol/hr. Similar to the results for high pressure scenario, arrangement A has the highest LCOA and lowest production rate at 1042.40 \$/ton and 375.95 kmol/hr, respectively.

Overall, there is a reduction in the production rate compared to the high-pressure scenario, and an increase in the range of 30-40 \$/ton in LCOA across all the arrangements. While there is reduction in compressor work, and required feed flow, the lower production rates at lower pressures ultimately lead to increase in overall cost of production. The LCOA of the arrangements is a function of the production rate of NH_3 , and as such, we can conclude that for green ammonia plants, it is generally more profitable to improved production scales, in order to minimize the cost of production and thus improve overall economic feasibility.

The differential evolution algorithm also demonstrates a tendency to minimize reactor length, in order to minimize reactor construction costs, which have a large impact on overall plant economics, which may be more significant than the resulting reduction in ammonia production, especially in the high-pressure scenario.

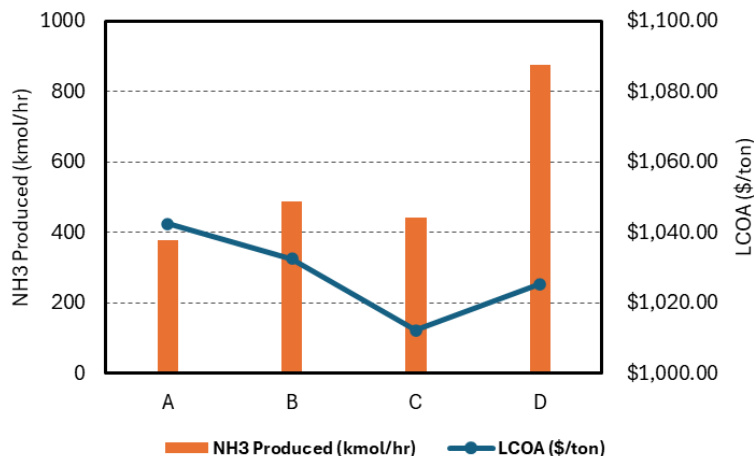


Figure 26: Variation in NH₃ production and LCOA for reactor arrangements at 150 bar reactor pressure

5.5 Conclusions

An analysis of ammonia generation systems using cascade ammonia reactors with different arrangements of reactor beds and the use of split feed streams is carried out. It is found that number of reactor beds and split-streams significantly impact the overall system performance in terms of ammonia production, and levelized cost of ammonia production. The primary conclusions from the study are;

- The comparison between conventional once-through and cascaded split-feed arrangements reveals that reactor configuration significantly impacts both production capacity and economic viability. Optimal configuration varies depending on operating conditions, with the two-bed conventional arrangement proving most economical in high-pressure scenarios, while the two-bed split-feed arrangement excels in low-pressure applications.
- For high-pressure systems, the two-bed arrangement with splitting (Arrangement C) yields the lowest LCOA at 983.85 \$/ton, at a production rate of 1003.50 kmol/hr. In contrast, the two-bed conventional configuration (Arrangement A) demonstrates the highest LCOA at

1017.50 \$/ton, while operating at the lowest production rate of 327.17 kmol/hr. Split-feed arrangements generally show improved economic performance, with Arrangement D achieving the highest ammonia production rate at 2826.74 kmol/hr while having a reduced LCOA of 987.24 \$/ton compared to its conventional counterpart.

- Under low-pressure conditions, all arrangements exhibit increased LCOA values due to increased reactor lengths, with the two-bed split-feed configuration still remaining the most economically favorable at 1012.20 \$/ton.
- A relationship between production scale and LCOA is observed, with improvements in production rate leading to improvements in LCOA for the arrangement.
- The cost of production is dominated by costs associated with the reactor investment, and feed, which is more pronounced due to the use of green hydrogen as feedstock. The dominance of feedstock costs in the overall economic equation suggests that smaller-scale production may be more financially viable for green ammonia plants.
- The optimization methodology employing differential evolution algorithms successfully identified reactor bed lengths that minimize the levelized cost of ammonia production across all configurations. This approach revealed a consistent tendency toward minimizing reactor dimensions, as capital costs associated with reactor construction may exert a greater influence on overall economics than the corresponding reduction in ammonia production capacity.

CHAPTER 6

Performance Analysis of a Green Ammonia Generation System with Energy

Recovery by Integrated Steam Rankine Cycle

6.1 Introduction

The global shift toward renewable energy resources has seen an upsurge in interest regarding ammonia. While ammonia has consistently been one of the most important industrially produced chemicals of the past century, ever since the methodology for its mass manufacturing was devised by Fritz Haber and Carl Bosch [11], the new interest in its production has added dimensionalities. Ammonia is traditionally produced using H_2 produced from steam methane reforming, and nitrogen produced from air separation. Steam methane reforming is a process where H_2 is produced from natural gas, while air separation processes require energy which is mostly produced from fossil fuel-based technologies [9].

In recent times, however, as interest has turned towards renewable energy and harnessing renewable resources, there have been proposals to reduce the dependency of ammonia production on fossil fuels, and to reduce the overall environmental impact of ammonia production, which currently accounts for 1% of global CO_2 emissions [192]. These include the implementation of carbon capture technologies into existing NH_3 production plants, which is known as Generation 1 Ammonia Technology, the use of entirely renewable resources, such as air and water, and renewable energy, such as solar and wind, to produce the required feed for ammonia production, known as Generation 2 Ammonia Technology, and the production of ammonia from the electroreduction of N_2 gas using renewable energy, which is known as Generation 3 Ammonia

Technology [29]. The production of ammonia without the use of any non-renewable resources is known as Green Ammonia, and as such both Generation 2 and Generation 3 technologies can be categorized as Green Ammonia Technologies. While Generation 3 is still in research at the lab scale, Generation 2 technologies have already been deployed as pilot projects, and have gained popularity in both industry and literature [8].

Ammonia's role in the global economy extends far beyond its traditional application as a fertilizer feedstock. As the world transitions toward renewable energy systems, ammonia has emerged as a promising energy carrier, particularly for hydrogen storage and transport [193]. Its relatively high hydrogen content (17.8% by weight) and established global transportation infrastructure make it an attractive vector for hydrogen delivery. Unlike pure hydrogen, ammonia can be liquefied at moderate pressures and temperatures (-33°C at atmospheric pressure), significantly simplifying storage and transportation logistics.

Furthermore, ammonia's potential as a direct fuel source has garnered increasing attention [194]. Its combustion produces nitrogen and water vapor without carbon emissions, making it an attractive alternative for maritime applications and industrial furnaces [195], [196]. Recent developments in fuel cell technology have also demonstrated ammonia's viability in direct ammonia fuel cells, though challenges remain in catalyst development and system optimization [43], [125], [181]. The maritime sector has shown particular interest in ammonia as a bunker fuel, with several major shipping companies investing in ammonia-powered vessel development.

The transition to green ammonia production faces several technical and economic challenges. The large capital investment for electrolyzer installation and operation, coupled with the intermittent nature of renewable energy sources, necessitates careful system design and potentially hybrid

approaches to ensure continuous operation of the Haber-Bosch process. However, rapidly declining renewable energy costs and improving electrolyzer technologies are enhancing the economic viability of green ammonia production [39], [41]. Several demonstration projects worldwide are showcasing the feasibility of integrated renewable-powered ammonia production facilities, with capacities ranging from pilot scale to commercial production [37], [197].

As the world progresses toward a carbon-neutral economy, ammonia's versatility positions it as a crucial component of the future energy landscape due to its dual role as both a chemical feedstock and energy carrier in the developing hydrogen economy. The established global ammonia infrastructure, combined with emerging technologies in production and utilization, suggests that ammonia will play an increasingly important role in the transition to sustainable energy systems.

Generation 2 technologies, which use nitrogen and hydrogen feedstock produced from renewable resources and using renewable energy have enjoyed particularly high interest. In general, the nitrogen used in Generation 2 technologies is produced from air via processes such as pressure swing adsorption or cryogenic separation [198], [199], while the hydrogen is most commonly produced from water electrolysis, either alkaline water electrolysis (AWE), or proton exchange membrane (PEM) electrolysis [200], [201]. While solid oxide electrolysis (SOE) has great promise in terms of efficiency and more favorable operating conditions, it has still not yet left the lab environment. Similarly, while PEM electrolysis has been deployed in real-world applications, it is still at the pilot stage and is at the current stage not suitable for large amount of H_2 production. In this regard, AWE technologies are preferable, with the technology being mature and industrially adopted for the production of green H_2 .

In both current industrial and green ammonia processes, the nitrogen required is produced by separation from the air, either via pressure swing adsorption or cryogenic separation processes. The distinction in this regard lies in how the work required for air separation is produced, with it being considered a green technology if the electricity required for the process is produced from renewable sources such as solar or wind.

Pressure Swing Adsorption (PSA) exploits the differential adsorption characteristics of gas molecules under pressure. The process utilizes molecular sieves, typically zeolites, which preferentially adsorb nitrogen over oxygen at elevated pressures. The technology operates through cyclical pressurization and depressurization phases, where compressed air is passed through adsorbent beds [202]. During depressurization, the concentrated product gas (typically oxygen or nitrogen) is released while the adsorbent is regenerated for subsequent cycles. PSA generally requires lower capital investment compared to cryogenic systems, while having faster start-up and shutdown capabilities and lower energy consumption for small to medium-scale operations. However, the production capacity is limited, and the specific energy consumption being high at larger production scales.

Cryogenic separation leverages the different boiling points of atmospheric gases (N_2 : -196°C , O_2 : -183°C) through a complex distillation process. The process involves multi-stage compression, purification, and heat exchange, followed by separation in distillation columns operating at cryogenic temperatures. Modern cryogenic ASUs typically employ double-column distillation configurations with integrated reboiler-condensers. This allows for the purity of the produced N_2 and O_2 to be very high ($>99.5\%$), with the specific energy consumption also being relatively low at large production scales. However, cryogenic separation plants do tend to require larger initial investment and might be less efficient at smaller scales of production. Regardless, due to the higher

purity of products, it remains the preferred method of nitrogen production in large-scale chemical production and industry, with PSA systems primarily being deployed at small and large-scale, particularly in medical oxygen generation and industrial applications requiring moderate purity levels [199].

The Haber-Bosch process operates at high temperatures (400-450°C) and pressures (150-300 bar), via catalytic process combining nitrogen and hydrogen over an iron catalyst to produce ammonia. Traditionally, hydrogen feedstock has been derived from natural gas through steam methane reforming, while nitrogen is separated from air via cryogenic distillation. This conventional process accounts for approximately 1-2% of global energy consumption and generates significant CO₂ emissions, estimated at 1.8 tonnes of CO₂ per tonne of ammonia produced.

Recent years have witnessed a paradigm shift toward sustainable ammonia production, driven by climate change concerns and the increasing availability of renewable energy sources. This transition to "green ammonia" maintains the core Haber-Bosch synthesis technology but revolutionizes the feedstock production methods. Hydrogen production through water electrolysis powered by renewable electricity eliminates the carbon footprint associated with steam methane reforming. The integration of renewable energy sources, primarily wind and solar power [37], [129], [203], with electrolysis technology presents new challenges in process control and optimization, particularly regarding the intermittent nature of renewable power generation.

Recent research has demonstrated the viability of small-scale ammonia production at significantly reduced pressures, ranging from 20 to 60 bar, while maintaining production efficiency comparable to industrial-scale operations. Cussler et al. [37], [50], [51], [75] developed a pilot plant utilizing nitrogen from air separation units and electrolysis-derived hydrogen, with wind turbines providing

the power requirements for all processes. The key innovation lies in the substitution of traditional condensers with absorbent materials, specifically magnesium chloride, for ammonia extraction from the synthesis loop. However, the widespread implementation of this technology faces limitations regarding the stability and availability of suitable absorbent materials, with high-performing absorbents often lacking the durability required for industrial-scale applications. Subsequent optimization studies [52], [53] revealed that while absorption enables more efficient ammonia removal compared to condensation at equivalent pressures, this advantage diminishes as operating pressures increase.

Similarly, a detailed technoeconomic analysis of a green ammonia facility integrating PEM electrolysis with conventional Haber-Bosch synthesis has been conducted by Sousa et al. [45], drawing from experimental data. The facility employed a three-bed adiabatic reactor, achieving an overall ammonia conversion rate of 26%. The analysis determined a levelized cost of ammonia production at approximately 1250 €/MT_{NH₃}, approximately triple the cost of conventional production methods. However, the economic viability is projected to improve substantially with the continued expansion of renewable energy infrastructure, declining electricity costs, and strategic site selection for optimal resource utilization.

Ishaq et al. [41], [42] developed and tested a cascaded ammonia synthesis reactor operating at reduced conditions of 310-390°C temperature and 6-12 bar pressure, utilizing industrial KMR catalyst. The system employs two ammonia reactors containing activated catalyst, with the output stream from the first reactor feeding the second, and an ammonia trap positioned after the second reactor. Their research demonstrated that temperature and pressure variations significantly impact ammonia conversion rates in the cascaded system. Increasing temperature from 310°C to 370°C

at 12 bar pressure resulted in higher ammonia conversion rates in both synthesis reactors, while pressure elevation from 6 to 12 bar at 370°C similarly improved conversion ratios.

Siddiqui et al. [42] conducted experimental investigations on a direct synthesis ammonia reactor powered by photovoltaic solar energy. The system utilized green hydrogen produced via a proton exchange membrane electrolyzer powered by solar photovoltaic cells. The setup employed a tubular reactor containing 50 grams of iron oxide industrial catalyst, activated by hydrogen gas flow at 16.7 cm³/s for 7 hours at 300°C, with controlled temperature ramping of 10°C per minute. Under steady-state conditions at 300°C and 10 bar, the system achieved an ammonia synthesis rate of 0.016 mmol/s, resulting in overall energy and exergetic efficiencies of 1.9% and 1.8% respectively. The solar-to-hydrogen component demonstrated higher efficiencies of 2.4% (energy) and 2.1% (exergy), while the PEM electrolysis subsystem achieved energy and exergy efficiencies of 19% and 15.3% respectively.

Integrated systems combining ammonia synthesis with fuel cell technology have been developed for solar photovoltaic applications [39]. These systems utilize excess solar power for ammonia production, which can later be used as fuel during periods of low solar availability, effectively storing surplus energy as NH₃. Peak production rates achieve 97.2 mol/s for H₂ and 64.8 mol/s for NH₃, with overall energy and exergy efficiencies of 15.83% and 16.67% respectively, and maximum energy discharge capacity of 7924.2 kWh. Furthermore, photovoltaic-driven ammonia production systems using PEM electrolyzers demonstrated energy and exergy efficiencies of 26.08% and 30.17% respectively at minimum solar irradiation (200 W/cm²). Efficiency decreased with increasing solar irradiation at constant air flow due to low energy and exergy output despite higher radiation levels. The system achieved nitrogen and hydrogen production rates of 10.58 mol/s and 2.35 mol/s respectively, resulting in ammonia production of 12.9 mol/s.

While these theoretical studies have preferred PEM electrolysis, the practical application of this technology has not yet been done at industrial scales due to difficulties relating to the high component costs and durability of materials [200]. As such, till now, alkaline electrolysis has seen more popularity and has also been shown to be more economically viable [201] and, when operating at higher pressures, more efficient [204]. The technology presents significant advantages for industrial-scale deployment, primarily due to its economic viability. The system employs simpler design configurations, resulting in lower capital expenditure compared to PEM systems. With over a century of industrial implementation, alkaline electrolysis benefits from mature supply chains, established maintenance protocols, and proven scalability in large installations exceeding 100 MW. The technology demonstrates remarkable durability, achieving operational lifespans of 60,000-90,000 hours with well-understood degradation mechanisms.

This work aims to model a green ammonia production plant operating at industrial scales, consisting of a cryogenic air separator for production of nitrogen, an alkaline electrolysis stack for the production of green hydrogen, a Haber-Bosch loop for the production of green ammonia, and a refrigeration cycle to provide cooling required for the separation of ammonia from product gas. The production capacity of the system is comparable to modern fuel-reforming based NH_3 production plants at 1 kmol/s or 3600 kg/hr. The system is evaluated with and without the inclusion of a steam turbine to generate power from heat recovered in the ammonia reactor beds and, and the effect of its presence on the overall plant performance is assessed. The system features a novel design for a heat exchanger in the ammonia synthesis loop which uses the cold recycle stream to cool down the product gas and recovers heat from cooling water used to cool compressors throughout the system to provide pre-heating of nitrogen vapor, and nitrogen-hydrogen feed mixture. The entire system is powered by renewable energy sources, making it a Generation 2

green ammonia plant, and is entirely modeled within the process flow modeling software ASPEN HYSYS [205]. The ammonia generation systems can be powered by solar energy using solar photovoltaic cells to generate electrical power required electrical power for the compressors and the AWE water electrolyzer, with the required solar photovoltaic are being estimate by System Advisor Model (SAM) [206].

6.2 System Description

The proposed system is designed to produce green ammonia from entirely renewable sources, at a production rate of 1 kmol/s. In conjunction with ammonia, the system also produces oxygen and can thus be classified as a multigeneration system. The system, as detailed in Figure 27 and 28, consists of air compression, cryogenic air separation, N_2 compression cycle, alkaline electrolyzer, feed compression train, and ammonia loop with integrated Rankine cycle for energy recovery. The entire system is powered by solar photovoltaic cells. Air enters the system and is compressed, and then N_2 is separated by cryogenic air separation in a separator column. The N_2 exits the separator column as saturated liquid, and is heated to gaseous phase using cooling water, and then the product N_2 is compressed to feed pressure. The air separation column also produces O_2 as a liquid, which is removed from the system as a product. Concurrently, an AWE stack, utilizing renewable solar or wind energy, is used to produce H_2 , which is then compressed to the NH_3 reactor pressure. The N_2 and H_2 streams are then mixed and fed into the ammonia synthesis loop, which consists of three ammonia reactor beds, as commonly observed in the literature and industrial context [125], [144], [179], with the product gas being cooled after exiting each reactor bed. The product gas is then used to partially pre-heat the feed mixture entering the NH_3 synthesis loop, before being cooled down to ambient temperatures by water, and then further cooled by a refrigeration cycle using R717 refrigerant, to separate the product NH_3 from the product gas mixture. The unreacted

N_2 and H_2 , which remains as the recycle stream, is then used to cool down the product streams from the ammonia reactor beds in a combined heat exchanger, while being simultaneously heated up to the required feed temperature. This unreacted N_2 and H_2 stream is then combined with the feed stream as a recycle stream, improving the overall plant performance.

The cryogenic air separation process begins with ambient air intake (1 bar). The air then undergoes compression with multiple compressors, with intercoolers (by utilizing cooling water) to reduce the temperature of the air prior to further compression, eventually elevating pressure to 33 bar at 50°C .

An expander unit then expands the pressure to 4.5 bar and reduces the temperature to -72.27°C [199], following which a heat exchanger uses the cold saturated liquid N_2 to cool the air to a temperature of -173°C [207] before entering the distillation tower. The cryogenic distillation process, further expands the air, reducing the temperature to approximately -196°C and the pressure to 1 bar, separating the air components based on their respective boiling points, producing liquid nitrogen and liquid oxygen as primary products. The produced nitrogen is then passed through the heat exchanger to cool down the air, and then compressed to the ammonia reactor operating pressure, while the liquid oxygen is removed from the system directly as a product output.

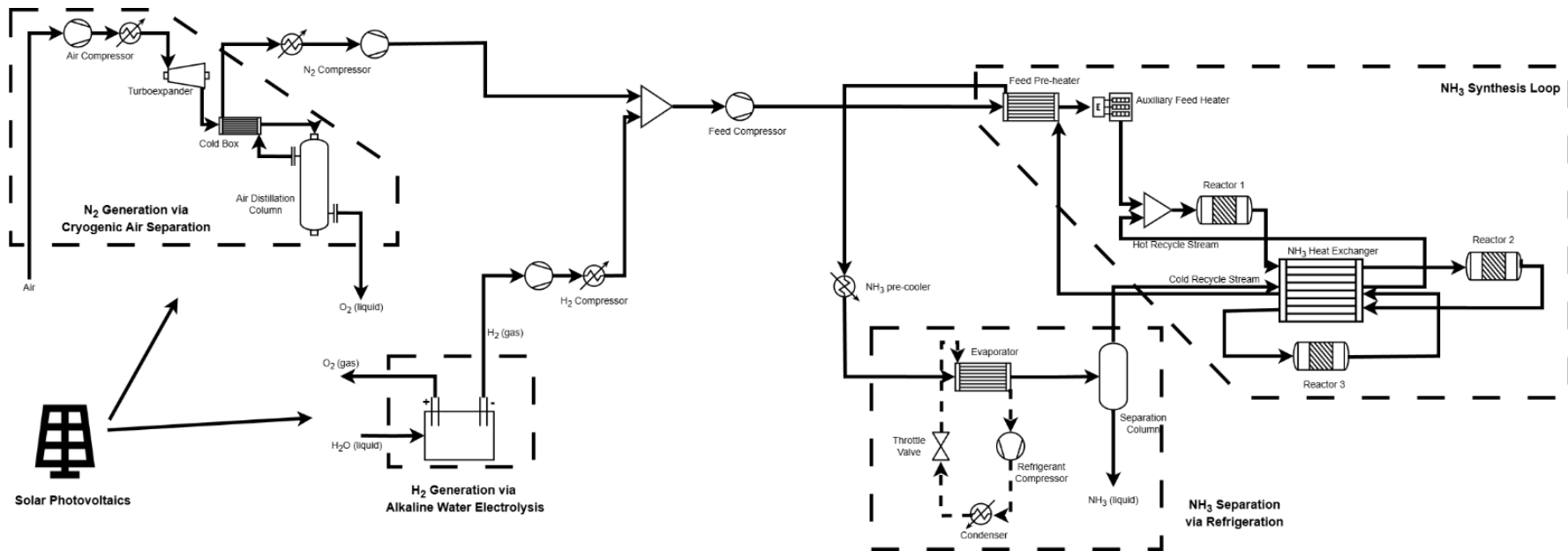


Figure 27: Schematic Diagram of the Ammonia Generation System without any energy recovery (configuration a)

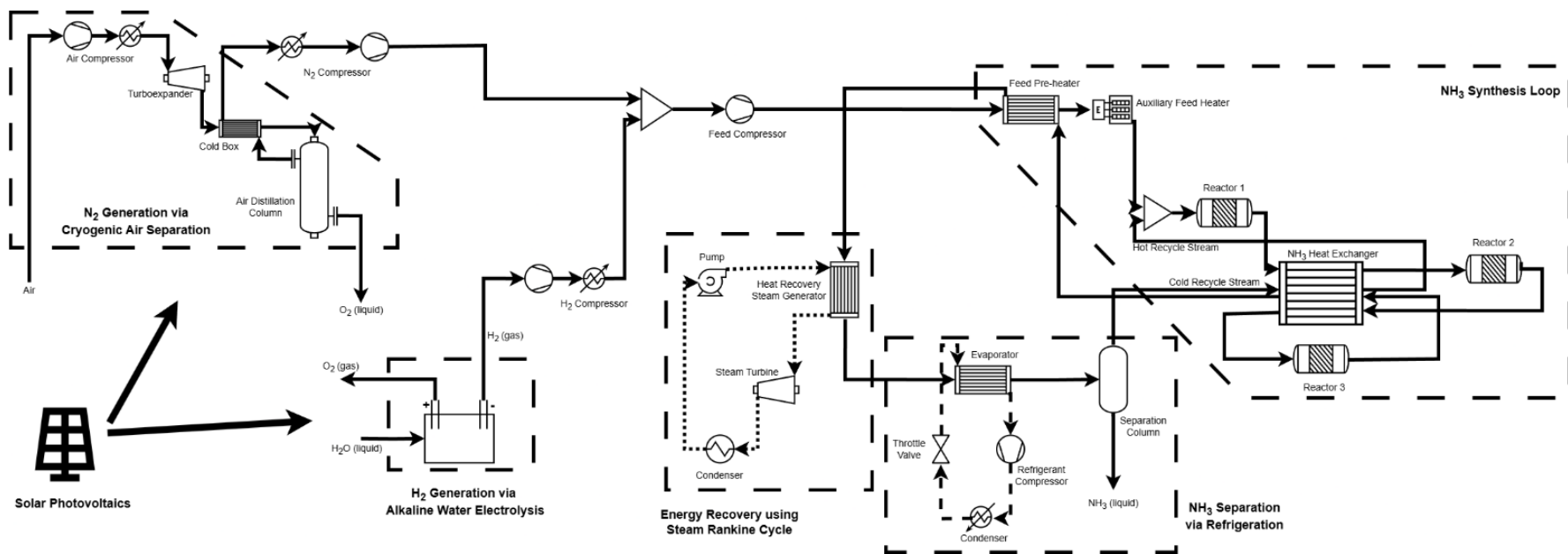


Figure 28: Schematic Diagram of the Ammonia Generation System with energy recovery via steam turbine (configuration b)

The alkaline water electrolyzer splits water, producing gaseous oxygen and hydrogen. Alkaline electrolysis operates through a liquid electrolyte medium, typically 20-30% KOH or NaOH. The process involves two half-reactions: at the cathode, water reduction produces hydrogen and hydroxide ions ($2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$), while at the anode, hydroxide oxidation generates oxygen ($2\text{OH}^- \rightarrow \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^-$). The overall reaction ($\text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2}\text{O}_2$) is facilitated by hydroxide ions acting as charge carriers through the electrolyte. Water is heated from 25 °C to the electrolyzer operating temperature of 80 °C. The electrolyzer operates at a pressure of 30 bar [204], and the produced oxygen and hydrogen are separated from the anode and cathode, respectively. The oxygen produced is removed as end product, and the hydrogen is compressed to the operating pressure of the ammonia reactor.

The ammonia synthesis loop is a traditional Haber-Bosch process configuration, consisting of three reactor beds, arranged one after the other, similar to the designs observed in the literature and industry[45], [125], [179], with cooling of the flow occurring at the end of each reactor bed in a combined heat exchanger. At the outlet of the third reactor bed, the product gas is used to pre-heat the feed stream of N_2 and H_2 and is then cooled down to the ambient temperature of 25 °C by cooling water. It is then further cooled down to -10 °C by a vapor-compression refrigeration cycle using R717 or ammonia refrigerant in order to separate the product ammonia as liquid. The cold unreacted N_2 and H_2 is then used as the coolant stream for the combined heat exchanger for the outlet gas from each reactor bed and is then mixed with the incoming feed stream at the start of the loop.

Cooling water is used to cool the produced NH_3 to the ambient temperature and can be used to recover energy from the system. A pump and turbine can be added to the ammonia synthesis loop, and the cooling water heated to superheated state, and then expanded to ambient pressure in the

turbine, thus producing power that can be used to drive the components involved in the rest of the system.

6.3 Methodology

The system is modeled in Aspen HYSYS V14 [205], as shown in Figure 29. Aspen HYSYS has been used extensively in the literature for modeling power generation, chemical generation and petrochemical applications [4 - 9].

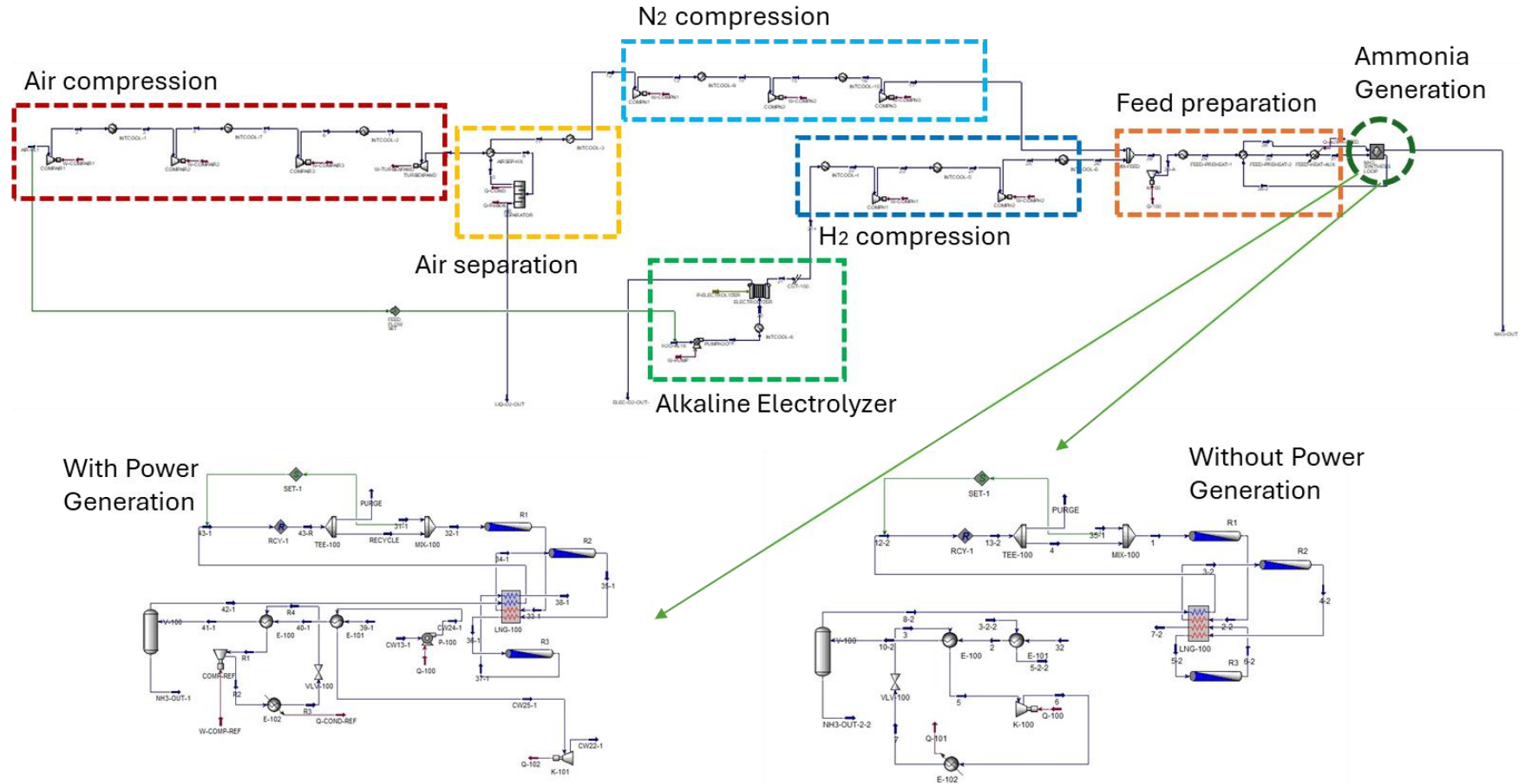


Figure 29: Aspen HYSYS Process Flow diagram for the system

6.3.1 Alkaline Water Electrolyzer (AWE)

The AWE electrolyzer, as shown in Figure 30, is modeled as an electrolyzer module consisting of the electrolyzer stack and gas separators, using the built-in AWE electrolyzer reactor component in HYSYS [205], and the required thermodynamic parameters for this specific component are calculated using the ElecNRTL property package in HYSYS. This simplified model considers only the components of H₂, O₂, and H₂O, with the electrolyte KOH being considered inert and not accumulating within the electrolyzer. The water stream is pumped from ambient condition to 30 bar and heated to 80 °C, i.e the operating condition of the electrolyzer cell. The purity of outlet H₂ and O₂ is fixed as 99.99% and 99.9%, respectively, with total electrolyzer module having 64 stacks and each stack having 4000000 cells. The overall Faradaic efficiency is 95%, and the voltage efficiency is 85%.

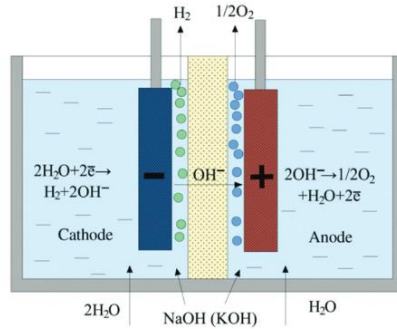


Figure 30: Schematic diagram of alkaline electrolysis cell [210], [211]

The hydrogen and oxygen production at the cathode and anode, respectively, can be expressed as,

$$\dot{N}_{H_2}^{cathode} = \frac{I_{cell}}{2F_c} \times n \quad (6.1)$$

$$\dot{N}_{O_2}^{anode} = \frac{I_{cell}}{4F_c} \times n \quad (6.2)$$

Where N is the rate of production of species in kmol/h, I_{cell} is the cell current, F_c is the Faraday constant and n is the number of total electrolyzer cells.

To meet the required NH_3 production rate of 3600 kmol/hr, the required rate of production for H_2 is found to be 5382 kmol/hr, which requires 5384 kmol/hr of water to be electrolyzed in the electrolyzer, equivalent to 97000 kg/hr.

The total power required by the module is calculated considering the control volume of the AWE module as,

$$P_{\text{electrolyzer}} = \dot{N}_{\text{H}_2}^{\text{cathode}} h_{\text{H}_2} + \dot{N}_{\text{O}_2}^{\text{anode}} h_{\text{O}_2} - \dot{N}_{\text{H}_2\text{O}}^{\text{electrolyzer}} h_{\text{H}_2\text{O}} \quad (6.3)$$

The AWE efficiency can thus be written in terms of the hydrogen production as,

$$\eta_{\text{LHV}} = \frac{\dot{N}_{\text{H}_2}^{\text{cathode}} \text{LHV}_{\text{H}_2}}{P_{\text{electrolyzer}}} \quad (6.4)$$

6.3.2 Cryogenic Air Separation System

The cryogenic air separation system, shown in Figure 31, is modeled as a simple distillation column integrating both the condenser and reboiler portions with the column calculations being done using the Fenske-Underwood method [212].

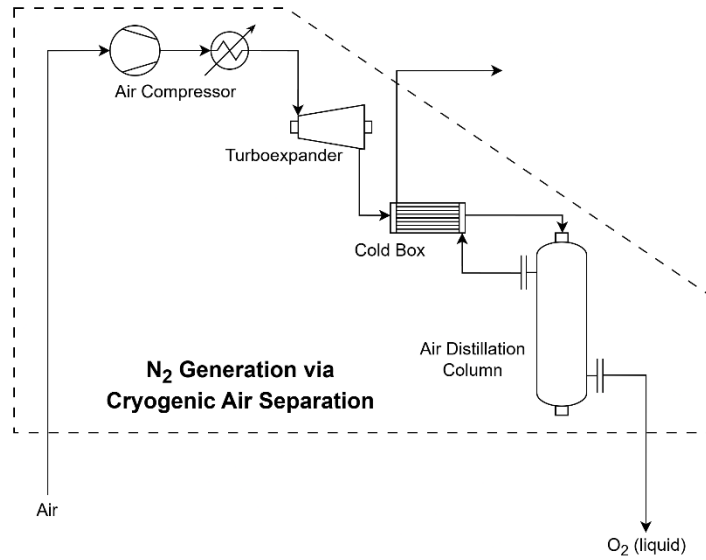


Figure 31: Schematic for Cryogenic Air Separation system

The number of stages for the column is calculated using the Fenske equation, as

$$N_m = \frac{\log \left[\left(\frac{\gamma_{N_2}}{\gamma_{O_2}} \right)_d \times \left(\frac{\gamma_{N_2}}{\gamma_{O_2}} \right)_b \right]}{\log(\gamma_{N_2})} \quad (6.4)$$

Where N_m is the number of stages, subscripts d and b refer to distillate and bottoms, i.e liquid extracted from top of the column and from bottom of the column, respectively, and γ_{N_2} is the volatility of nitrogen.

N₂ is separated out as liquid distillate, which is then heated up from saturated liquid state to vapor and then compressed to the operating pressure of the ammonia reactor. Liquid O₂ is also produced, which is removed from the system in the liquid state.

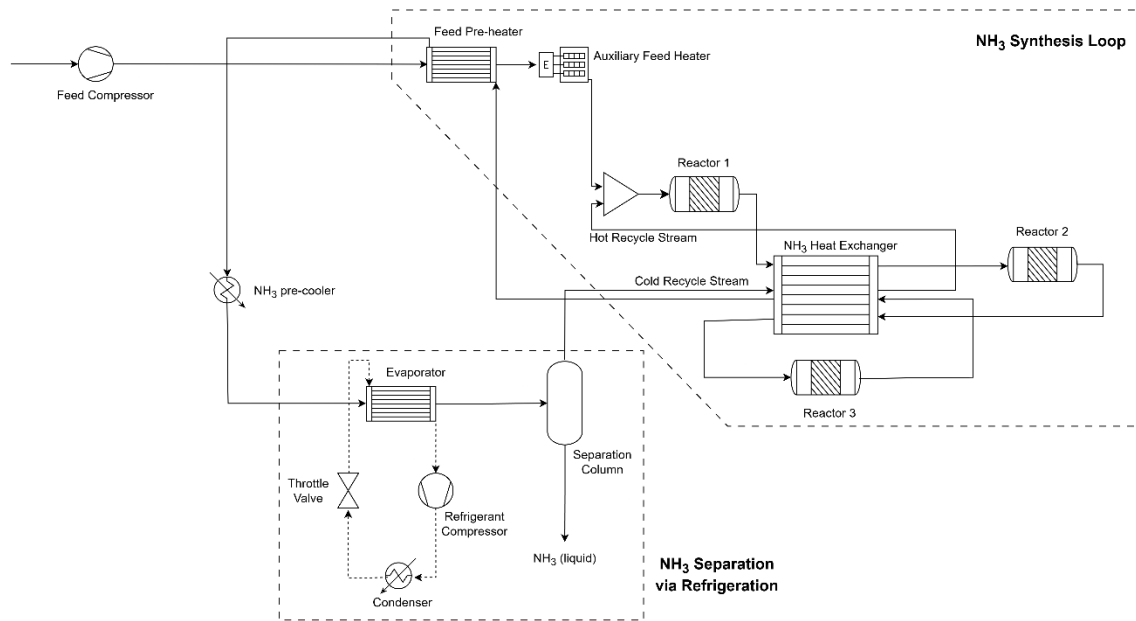
Air enters the separation column following compression and then subsequent expansion in the turboexpander, and further cooling via produced liquid N₂ at a temperature of -176.1 °C and pressure of 4.5 bar. It is then expanded further to 1 bar in the separator column, with N₂ being

separated out as distillate at a temperature of $-195.8\text{ }^{\circ}\text{C}$, with 1% mol of O_2 remaining in the liquid distillate. To meet the target NH_3 production rate of 3600 kmol/hr, the required flow rate for air entering the air separation system is set as 2300 kmol/hr, equivalent to 66630 kg/hr. The column reflux ratio is set as 0.7, and number of trays in the column is found to be 36.

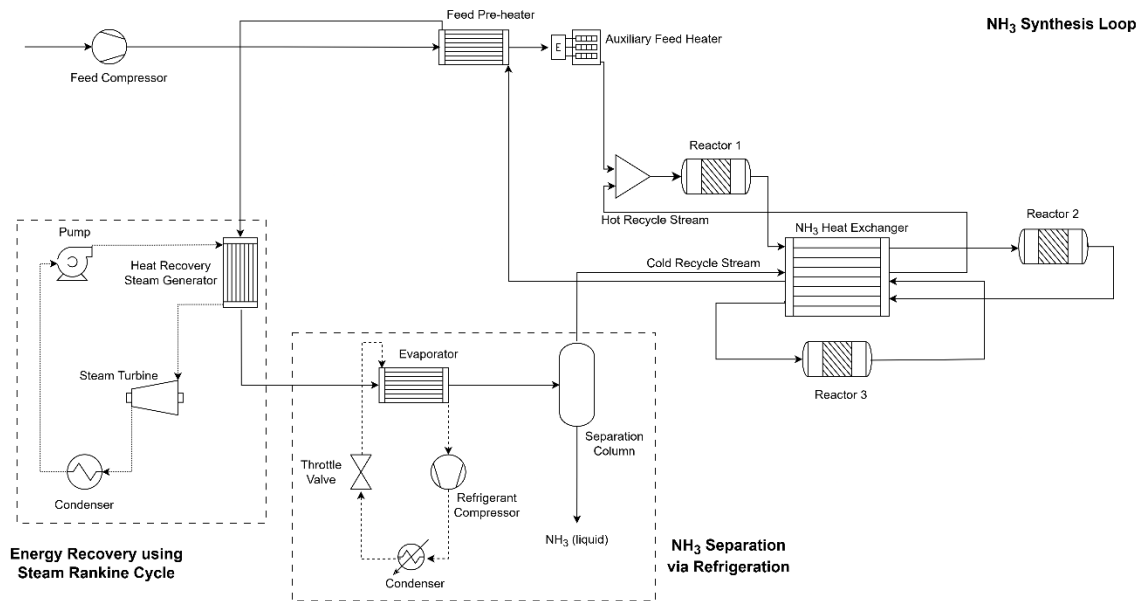
Produced gaseous N_2 is then mixed with the hydrogen stream to create the required feed stream for the ammonia reactor and is then preheated using both heat recovered by cooling water used to cool the compressor trains, as well as the product stream from the final reactor bed. It is then heated to the required inlet temperature using an auxiliary heater.

6.3.3 Ammonia Synthesis Loop

The ammonia reactors, as shown in Figure 32, are modeled as plug flow reactors, of diameter 3 m, with the length of the first reactor bed being 5 m, and the second and third bed being 20 m. NH_3 enters the first reactor at $336.9\text{ }^{\circ}\text{C}$, or 610 K, and is quenched at the reactor outlet to $356.9\text{ }^{\circ}\text{C}$, or 630 K, and fed to the second reactor. The product flow from the second reactor is also quenched to $356.9\text{ }^{\circ}\text{C}$, and the product flow from the final reactor is cooled and used to pre-heat the feed entering the loop, before being cooled using the refrigeration cycle to separate NH_3 as liquid. The quenching of the flows is done by exchanging heat with the cold recycle stream, and all of the reactor product streams and the cold recycle stream exchange heat in a combined heat exchanger.



a)



b)

Figure 32: Ammonia synthesis loop a) without energy recovery and b) with energy recovery

While most recent literature using process modeling software for the modeling of ammonia synthesis generally model ammonia synthesis as an equilibrium process [4 - 5], [11 - 13], this

approach is an idealization of the Haber-Bosch process and assumes that equilibrium will be reached over an infinite period of operation. Instead, in this work, ammonia reactors are modeled as adiabatic reactors, with the Temkin equation being used to model the reaction kinetics[162], [213], as detailed in Chapter 4 and repeated here for clarity.

$$r_{N_2} = -f \times \left[k_A p_{N_2} \left(\frac{p_{H_2}^{1.5}}{p_{NH_3}} \right) - k_B \frac{p_{NH_3}}{p_{H_2}^{1.5}} \right] \quad (4.5)$$

$$k_A = 1.78954 \times 10^4 \exp \left(-\frac{87027}{RT_g} \right) \quad (4.6)$$

$$k_B = 2.5714 \times 10^{16} \exp \left(-\frac{198321}{RT_g} \right) \quad (4.7)$$

The steam Rankine Cycle in configuration (b) recovers waste heat that is available in the product NH_3 stream after pre-heating of the feed. The inlet pressure of the steam turbine is set considering the saturation pressure of water at the temperature of product NH_3 , and with increase in reactor pressure, there is an observed increase in the temperature of the product NH_3 . This allows for higher turbine inlet pressure, and thus greater energy recovery. Table 26 summarizes the operating conditions for the steam turbine at the different reactor operating pressures.

Table 26: Operating parameters of steam turbine for energy recovery in configuration (b)

Reactor Operating Pressure (bar)	Temperature of NH_3 entering steam generator ($^{\circ}C$)	Inlet Pressure for steam turbine (bar)
130	238.51	28
140	253.34	36
150	267.38	46
160	283.34	58
170	302.62	78
180	331.27	110
190	343.85	130
200	398.07	248

The system uses multiple heat exchangers for recovering heat from the ammonia synthesis loop. For ease of modeling, these are modeled as simple shell and tube heat exchangers, being of TEMA

type AFL [214], i.e having two-pass shell with removable stationary head and fixed tube sheet rear head.

6.3.4 Overall System Analysis

For the analysis of the systems, it is assumed that it is operating at steady state conditions. The compressors and turbines are assumed to have isentropic efficiencies of 85%. All component properties and thermodynamic parameters other than those related to the electrolyzer are calculated using the Soave-Redlich-Kwong equations of state [8 - 10].

The systems may be evaluated on the basis of overall energy efficiency, which may be defined for ammonia production in the form,

$$\eta_{th} = \frac{m_{\dot{NH}_3} \times LHV_{NH_3}}{\dot{W}_{compressor\ work,in} + \dot{W}_{electrolyzer\ work,in} + \dot{Q}_{heating,in} - \dot{W}_{air\ expander,out} - \dot{W}_{turbine,out}} \quad (6.5)$$

Where $m_{\dot{NH}_3}$ is the production rate of ammonia in kg/s, LHV_{NH_3} is the lower heating value of ammonia in MJ/kg, taken as 18.6 MJ/kg [194], $\dot{W}_{compressor\ work,in}$ is the total compressor power involved in compression of air, N₂, H₂ and refrigerant, $\dot{W}_{electrolyzer\ work,in}$ is the power required for the alkaline electrolyzer, $\dot{Q}_{heating,in}$ is the auxiliary heating required to heat the reactant feed to required reactor inlet temperature, $\dot{W}_{air\ expander,out}$ is the power produced in the air expander used in the air separation process, and $\dot{W}_{turbine,out}$ is the power recovered in the steam turbine in the ammonia synthesis loop.

The input parameters for the system model are summarized in Table 27, with additional parameters for the steam turbine in configuration (b) being previously provided in Table 26.

Table 27: Input parameters for NH₃ generation system model

Parameter	Value	Unit
Air Intake Temperature	24	°C
Air Intake Pressure	1	bar
Air Intake Flow Rate	2300	kmol/h
Water Intake Temperature	24	°C
Water Intake Pressure	1	bar
Water Intake Flow Rate	5384	kmol/h
Compressor Efficiency	85	%
Compressor Pressure Ratio	4	
Pump Efficiency	85	%
Electrolyzer Temperature	80	°C
Electrolyzer Voltage Efficiency	85	%
Electrolyzer Faraday Efficiency	95	%
Electrolyzer Number of Stack	64	
Electrolyzer Number of Cells	4000000	
Electrolyzer H ₂ Purity	99.99	%
Electrolyzer O ₂ Purity	99.90	%
Turboexpander Input Pressure	33	bar
Air Separator Column Reflux Ratio	0.7	
Air Separator Input Pressure	4.5	bar
Air Separator Output Pressure	1	bar
Fraction of N ₂ in bottoms	0.01	
Fraction of H ₂ in distillate	0.001	
Reactor Input Temperature	336.85	°C
Reactor Quench Temperature	356.85	°C
Refrigerant	R717	
Refrigerant compressor output pressure	13.6	bar
Refrigerant evaporator temperature	-10	°C
Refrigerant condenser temperature	25	°C
Liquid NH ₃ temperature	-10	°C

6.4 Results and Discussion

Table 28 summarizes the outlet conditions of each reactor and the amount of NH₃ that is produced as liquid and recycled as vapor. A correlation between pressure and recycled NH₃ is observed here, with the recycle flow reducing at higher pressures. This is expected, as higher conversion means that less of the feed remains unreacted and thus less needs to be recycled. A decrease in the total NH₃ produced with increase in operating pressure is also observed, with the production in the first reactor increasing while later reactors producing less. This is due to the high fraction of NH₃ in the reactant stream entering reactors 2 and 3, which shifts the equilibrium of the overall reaction

toward the decomposition of NH_3 to N_2 and H_2 , inhibiting the forward production reaction of N_2 and H_2 combining to NH_3 .

Table 28 : Summary of reactor outlet conditions with change in operating pressure

Reactor Operating Pressure (bar)	Temperature at R1 outlet (°C)	Temperature at R2 outlet (°C)	Temperature at R3 outlet (°C)	NH_3 at R1 outlet (kmol/h)	NH_3 at R2 outlet (kmol/h)	NH_3 at R3 outlet (kmol/h)	Liquid NH_3 produced (kmol/h)	Vapor NH_3 in recycle (kmol/h)
130	358.00	506.30	382.23	1230.82	3986.80	4442.74	3631.00	811.73
140	365.40	510.61	386.99	1214.38	3847.70	4353.45	3647.63	705.82
150	373.40	512.74	392.14	1234.13	3742.00	4295.85	3675.62	620.24
160	385.30	513.11	398.68	1275.18	3580.99	4182.51	3649.38	533.12
170	401.80	511.26	405.01	1346.83	3408.28	4034.52	3582.16	452.36
180	425.80	506.71	409.65	1497.56	3315.48	3939.16	3554.08	385.08
190	467.90	496.13	408.74	1794.18	3309.80	3860.28	3538.51	321.76
200	537.20	477.44	403.42	2230.65	3375.76	3807.99	3551.83	256.15

The model in system configuration (a) with no energy recovery is initially run at a base case configuration considering an initial operating pressure of 130 bar, and a reactor inlet temperature of 337 °C or 610 K, without the use of a steam turbine for energy recovery. The reactor feed gas is pre-heated using heat recovered by cooling water from cooling of air, N_2 and H_2 in their respective compression trains, as well as by the product gas from the reactor outlet. An auxiliary amount of heat is still required, which heats up the reactant mixture to the required temperature of 610 K.

The system running at these conditions achieves a thermal efficiency of 55.04%, with the single-pass conversion in the reactor loop being 26.12%. Figure 33 shows the distribution of the different power requirements of the system, and it can be easily seen that the electrolyzer work accounts for 93% of the system's energy requirements.

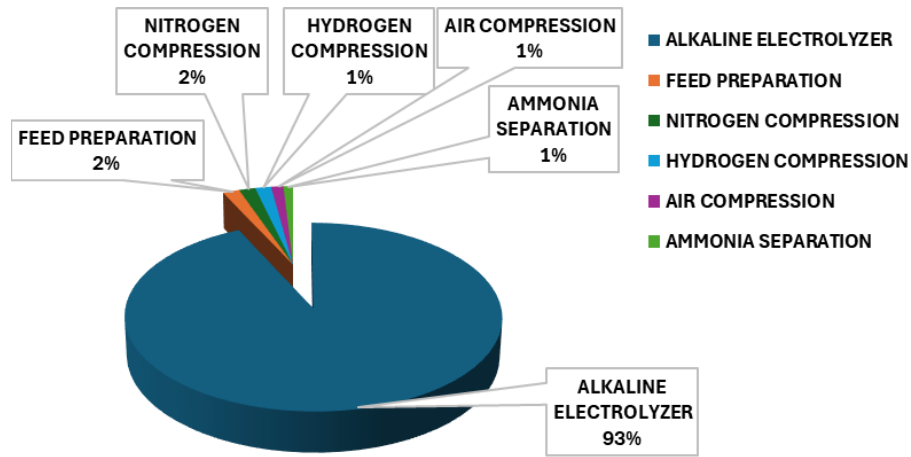


Figure 33 : Breakdown of power requirements for the base system without steam turbines

The high energy requirement of the electrolyzer relative to the rest of the system is consistent with other electrolyzer-based ammonia generation systems from the literature, with Lin et al. [40], [45] observing their alkaline electrolyzer to consume 91.8% of the overall system energy requirements when operating with condensation separation, and 95.1% of the system energy requirements when operating with absorption separation, and Sousa et al. [45] observing 88.5% system energy consumption for their PEM electrolyzer system. These large energy demands further illustrate the need for improvements in electrolyzer technology in terms of efficiency and production capacity, as it would lead to reduction in system energy demands and cost savings.

Figure 34 shows the variation of thermal efficiency and single pass conversion with change in pressure. The thermal efficiency is observed to vary more significantly with change in pressure, reaching a maximum value of 58.03% at 150 bar. It is also observed that the single pass conversion of N_2 increases with increase in operating pressure, with the conversion being 36.3% at 200 bar, with the corresponding thermal efficiency being 56.4%.

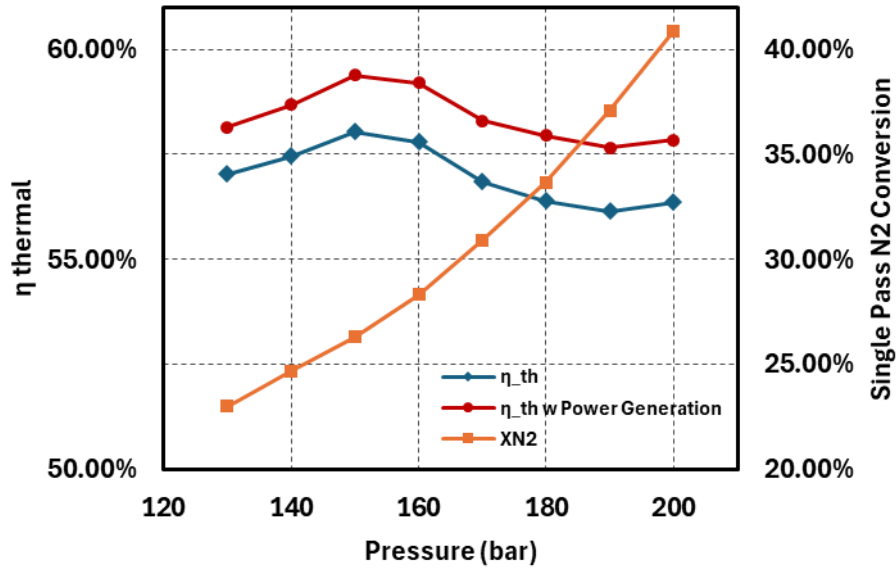


Figure 34 : Variation of thermal efficiency, N₂ conversion at different operating pressures, with and without steam Rankine cycle

With the inclusion of the steam Rankine cycle for energy recovery from the product gas, it is observed that an average of 13.5 MW of energy can be recovered from the system across all operating pressures, with the lowest recovery being 10.7 MW at 130 bar reactor pressure and the maximum being 15.1 MW at 180 bar reactor pressure, with more energy being available at higher operating pressures. The use of the steam turbine also contributes to a larger average improvement in the system thermal efficiency, about 1.39%. Given that thermal efficiency is a function of the ammonia production rate, with the inclusion of the steam Rankine cycle, it is still observed that the system's maximum thermal efficiency is achieved at 150 bar operating pressure, at which the rate of production is also highest. An overall peak thermal efficiency of 59.38% is observed for the system operating at 150 bar with the steam Rankine cycle.

Considering the required power requirement for the system, which is about 560 MW without the use of a turbine for energy recovery and about 545 MW with energy recovery, the required solar photovoltaic panel can be estimated using the System Advisor Model (SAM) software package by

NREL [206]. For the considered deployment location of Dhahran, Saudi Arabia, the relevant location and solar energy parameters are detailed in Table 29.

Table 29: Location and System Parameters for solar photovoltaic deployment location of Dhahran, Saudi Arabia

Location and System Parameters for solar photovoltaic array	Value	Units
Latitude	26.33	°
Longitude	50.14	°
Annual Average Global Horizontal Solar Intensity	5.88	kWh/m ² /day
Annual Average Direct Normal Solar Intensity	4.88	kWh/m ² /day
Annual Average Diffuse Horizontal Solar Intensity	2.54	kWh/m ² /day

Considering REC Solar Pro XL monocrystalline silicon photovoltaic panels with rated standard power output of 739.4 W and nominal efficiency of 22.20%, and SunGrow inverters having efficiency 98%, the complete photovoltaic generation array can be designed. The array has a total of 850,000 photovoltaic modules, with each string having 20 photovoltaic modules in series, and all the strings connected in parallel to generate the required power, and 225 inverters being required to invert the produced DC current to AC. The total photovoltaic module area for the array is found to be 2,830,500 m², and the corresponding land area is 2331.44 acres. The installed equipment cost totals \$413,930,000 for the system with no energy recovery, i.e configuration (a). With energy recovery via steam Rankine cycle, i.e configuration (b), the energy requirements reduce to 545 MW, resulting in a reduction in required total photovoltaic number to 830,000, and the number of required inverters reducing to 218. The required photovoltaic module area for configuration (b) thus reduces to 2,763,900 m² area, with the corresponding required land area being 2276.58 acres, and installed equipment cost reduces to \$404,190,000, which corresponds to a 2.35% decrease in land area and equipment cost.

Comparing the proposed system with similar systems from the literature [40], [43], [45] the performance of the system in terms of power per kg_{NH_3} produced is on par with other systems, or better if energy recovery is applied. The systems proposed by Lin et al.[40] operating at 150 bar with condensation separation, and at 20 bar with absorption separation, respectively, having net power per kg_{NH_3} values of 9.7 and 9.36 $\text{kWh/kg}_{\text{NH}_3}$, respectively. Similarly, the system based on PEM electrolyzer studied by Sousa et al.[45] operates at 10.98 $\text{kWh/kg}_{\text{NH}_3}$, while the system proposed and analysed in this work operates at an average of 9.22 $\text{kWh/kg}_{\text{NH}_3}$ without energy recovery, with the requirement reducing further to an average of 9.00 $\text{kWh/kg}_{\text{NH}_3}$ with energy recovery. It is worth noting that these values are achieved at a larger production scale, with the proposed system operating at a production rate of about 1 kmol/s compared to 0.65 kmol/s for Lin et al. [40] system and 0.05 kmol/s for Sousa et al. [45]

6.5 Conclusions

A Generation 2 ammonia plant based on alkaline electrolyzer, and cryogenic air separation technology operating at industrial production scale has been designed and evaluated in terms of its thermodynamic performance and compared with other systems based on similar technology from the literature. It is found that;

- The base system configuration (129 bar, 337°C inlet temperature) with no energy recovery achieved 57.04% thermal efficiency. Electrolyzer work accounts for the majority of total energy requirements at 93%.

- With no energy recovery, the thermal efficiency reaches a maximum value of 58.03% at 150 bar. With energy recovery, the thermal efficiency can be further improved to 59.38% at 150 bar.
- Higher operating pressures reduce the amount of recycle flow due to higher conversion rates. At higher pressures it is also necessary to shorten reactor bed lengths in order to maintain temperatures below 500°C. Above 170 bar, heat recovery from product gas is high enough to eliminate auxiliary heating requirements for ammonia reactor feed.
- Integration of steam Rankine cycle results in a recovery of at least 10 MW energy, and an average improvement of 1.39% in system thermal efficiency.
- System power requirements of 560 MW (without energy recovery) and 545 MW (with energy recovery) translate to PV module area requirements of 2.83 and 2.76 million m² respectively, with corresponding equipment costs of \$413.9M and \$404.2M.
- The proposed system has better thermal efficiency compared to literature systems, achieving 9.22 kWh/kgNH₃ without energy recovery and 9.00 kWh/kgNH₃ with recovery, while operating at larger production scale of 1 kmol_{NH3}/s

CHAPTER 7

Conclusions and Recommendations for Future Work

7.1 Conclusions

Considering the overall work, the most important insights that have been gained are;

- The Temkin-Pyzhev equation and its modified form offer more accurate estimation of the reaction characteristics of catalyzed ammonia synthesis than simple equilibrium calculations.
- Higher pressures are preferable for increased ammonia production, whereas temperatures are more sensitive with the positive effect of higher temperatures on rates of reaction needing to be balanced with its negative effect on the equilibrium of the ammonia synthesis process.
- Optimization of reaction parameters for both adiabatic and non-adiabatic ammonia reactors shows that lower presence of inerts such as CH_4 and Ar is preferred, as they tend to inhibit the reaction, both by reducing the amount of available reactants as well as having high specific heat that does not allow for the reaction temperature to be in a suitable range for maintaining high rate of reaction.
- Ammonia reactors can be configured in different arrangements, both with and without the splitting of feed flow. Overall, it is observed that arrangements without splitting have better performance in terms of both thermal efficiency and economics.

- Generation 2 green ammonia plants using water electrolysis and air separation powered by renewable energy operating at production scales of around 1 kmol/s consume around 9.00 kWh/kg_{NH3}
- The integration of a steam Rankine cycle for energy recovery increases the already respectable thermal efficiency of about 55% by about 1.4% to 57.1%

7.2 **Recommendations**

Future work regarding this topic can be focused on the following areas;

- Sensitivity analysis of the sale price of ammonia on the economic feasibility of different reactor configurations
- Optimization of reactor configurations based on economic feasibility and using differential evolution algorithms
- Simulation of low pressure Haber-Bosch synthesis utilizing different catalyst and rate equations
- Cost and exergy analysis of full Generation 2 Green Ammonia production plant

References

- [1] J. W. Erisman, M. A. Sutton, J. Galloway, Z. Klimont, and W. Winiwarter, 'How a century of ammonia synthesis changed the world', *Nat Geosci*, vol. 1, no. 10, pp. 636–639, Oct. 2008, doi: 10.1038/ngeo325.
- [2] S. Chen, S. Perathoner, C. Ampelli, and G. Centi, 'Electrochemical Dinitrogen Activation: To Find a Sustainable Way to Produce Ammonia', in *Studies in Surface Science and Catalysis*, vol. 178, Elsevier Inc., 2019, pp. 31–46. doi: 10.1016/B978-0-444-64127-4.00002-1.
- [3] F. Haber, 'The synthesis of ammonia from its elements Nobel Lecture, June 2, 1920', *Resonance*, vol. 7, no. 9, pp. 86–94, Sep. 2002, doi: 10.1007/BF02836189.
- [4] M. Aziz, A. T. Wijayanta, and A. B. D. Nandiyanto, 'Ammonia as Effective Hydrogen Storage: A Review on Production, Storage and Utilization', *Energies (Basel)*, vol. 13, no. 12, p. 3062, Jun. 2020, doi: 10.3390/en13123062.
- [5] N. Salmon and R. Bañares-Alcántara, 'Green ammonia as a spatial energy vector: A review', Jun. 07, 2021, *Royal Society of Chemistry*. doi: 10.1039/d1se00345c.
- [6] I. Dincer, 'Green methods for hydrogen production', in *International Journal of Hydrogen Energy*, Jan. 2012, pp. 1954–1971. doi: 10.1016/j.ijhydene.2011.03.173.
- [7] A. G. Olabi *et al.*, 'Recent progress in Green Ammonia: Production, applications, assessment; barriers, and its role in achieving the sustainable development goals', *Energy Convers Manag*, vol. 277, p. 116594, Feb. 2023, doi: 10.1016/j.enconman.2022.116594.
- [8] O. A. Ojelade, S. F. Zaman, and B. J. Ni, 'Green ammonia production technologies: A review of practical progress', Sep. 15, 2023, *Academic Press*. doi: 10.1016/j.jenvman.2023.118348.
- [9] E. M. A. Mokheimer, M. R. Shakeel, A. Harale, S. Paglieri, and R. Ben Mansour, 'Fuel reforming processes for hydrogen production', *Fuel*, vol. 359, p. 130427, Mar. 2024, doi: 10.1016/j.fuel.2023.130427.
- [10] S. Shiva Kumar and H. Lim, 'An overview of water electrolysis technologies for green hydrogen production', Nov. 01, 2022, *Elsevier Ltd*. doi: 10.1016/j.egyrs.2022.10.127.
- [11] J. M. Modak, 'Haber process for ammonia synthesis', *Resonance*, vol. 7, no. 9, pp. 69–77, Sep. 2002, doi: 10.1007/BF02836187.
- [12] C. Smith, A. K. Hill, and L. Torrente-Murciano, 'Current and future role of Haber-Bosch ammonia in a carbon-free energy landscape', *Energy Environ Sci*, vol. 13, no. 2, pp. 331–344, Feb. 2020, doi: 10.1039/c9ee02873k.
- [13] H. Liu, *Ammonia Synthesis Catalysts*. WORLD SCIENTIFIC / CHEMICAL INDUSTRY PRESS, CHINA, 2013. doi: 10.1142/8199.
- [14] J. Humphreys, R. Lan, and S. Tao, 'Development and Recent Progress on Ammonia Synthesis Catalysts for Haber–Bosch Process', *Advanced Energy and Sustainability Research*, vol. 2, no. 1, p. 2000043, Jan. 2021, doi: 10.1002/aesr.202000043.
- [15] L. RUDNITSKY, M. G. BERENGARTEN, and A. M. ALEKSEJEV, 'On the mechanism of promoting ammonia synthesis catalysts by an alkali', *J Catal*, vol. 30, no. 3, pp. 444–450, Sep. 1973, doi: 10.1016/0021-9517(73)90162-0.
- [16] T. Ogawa, 'Ammonia as a carrier of renewable energy: Recent progress of ammonia synthesis by homogeneous catalysts, heterogeneous catalysts, and electrochemical method', in *Emerging Trends to Approaching Zero Waste*, Elsevier, 2022, pp. 265–291. doi: 10.1016/B978-0-323-85403-0.00010-4.
- [17] A. Nielsen, J. Kjaer, and B. Hansen, 'Rate equation and mechanism of ammonia synthesis at industrial conditions', *J Catal*, vol. 3, no. 1, 1964, doi: 10.1016/0021-9517(64)90094-6.
- [18] M. El-Shafie, 'A comprehensive assessment of ammonia synthesis reaction kinetics and rate equations', *Int J Hydrogen Energy*, 2023, doi: 10.1016/j.ijhydene.2023.06.011.

- [19] A. Murase, H. L. Roberts, and A. O. Converse, 'Optimal Thermal Design of an Autothermal Ammonia Synthesis Reactor', *Industrial & Engineering Chemistry Process Design and Development*, vol. 9, no. 4, pp. 503–513, Oct. 1970, doi: 10.1021/i260036a003.
- [20] Md. Burhan Kabir Suhan, Md. Naimur Rahman Hemal, M. A. A. Shoukat Choudhury, Md. Ali Akkas Mazumder, and M. Islam, 'Optimal Design of Ammonia Synthesis Reactor for a Process Industry', *Journal of King Saud University - Engineering Sciences*, vol. 34, no. 1, pp. 23–30, Jan. 2022, doi: 10.1016/j.jksues.2020.08.004.
- [21] A. Yapicioglu and I. Dincer, 'A review on clean ammonia as a potential fuel for power generators', *Renewable and Sustainable Energy Reviews*, vol. 103, pp. 96–108, Apr. 2019, doi: 10.1016/j.rser.2018.12.023.
- [22] G. Mallouppas, C. Ioannou, and E. Ar. Yfantis, 'A Review of the Latest Trends in the Use of Green Ammonia as an Energy Carrier in Maritime Industry', *Energies (Basel)*, vol. 15, no. 4, p. 1453, Feb. 2022, doi: 10.3390/en15041453.
- [23] P. Butterworth, 'Green ammonia fuel faces three big challenges'. Accessed: Apr. 27, 2024. [Online]. Available: <https://sustainability.crugroup.com/article/green-ammonia-fuel-faces-three-big-challenges>
- [24] J. Armijo and C. Philibert, 'Flexible production of green hydrogen and ammonia from variable solar and wind energy: Case study of Chile and Argentina', *Int J Hydrogen Energy*, vol. 45, no. 3, pp. 1541–1558, Jan. 2020, doi: 10.1016/j.ijhydene.2019.11.028.
- [25] N. Salmon and R. Bañares-Alcántara, 'A global, spatially granular techno-economic analysis of offshore green ammonia production', *J Clean Prod*, vol. 367, p. 133045, Sep. 2022, doi: 10.1016/j.jclepro.2022.133045.
- [26] R. M. Nayak-Luke and R. Bañares-Alcántara, 'Techno-economic viability of islanded green ammonia as a carbon-free energy vector and as a substitute for conventional production', *Energy Environ Sci*, vol. 13, no. 9, pp. 2957–2966, 2020, doi: 10.1039/D0EE01707H.
- [27] B. Lee, D. Lim, H. Lee, and H. Lim, 'Which water electrolysis technology is appropriate?: Critical insights of potential water electrolysis for green ammonia production', *Renewable and Sustainable Energy Reviews*, vol. 143, p. 110963, Jun. 2021, doi: 10.1016/j.rser.2021.110963.
- [28] J. Cha *et al.*, 'An efficient process for sustainable and scalable hydrogen production from green ammonia', *Renewable and Sustainable Energy Reviews*, vol. 152, p. 111562, Dec. 2021, doi: 10.1016/j.rser.2021.111562.
- [29] D. R. MacFarlane *et al.*, 'A Roadmap to the Ammonia Economy', *Joule*, vol. 4, no. 6, pp. 1186–1205, Jun. 2020, doi: 10.1016/j.joule.2020.04.004.
- [30] I. Wilkinson, 'Green Ammonia – a significant contributor to a low-carbon energy system?' Accessed: Dec. 13, 2023. [Online]. Available: <https://blog.siemens.com/2018/05/green-ammonia-a-significant-contributor-to-a-low-carbon-energy-system/>
- [31] H.-L. Du *et al.*, 'Electroreduction of nitrogen with almost 100% current-to-ammonia efficiency', *Nature*, vol. 609, no. 7928, pp. 722–727, Sep. 2022, doi: 10.1038/s41586-022-05108-y.
- [32] D. Wen and M. Aziz, 'Design and analysis of biomass-to-ammonia-to-power as an energy storage method in a renewable multi-generation system', *Energy Convers Manag*, vol. 261, p. 115611, Jun. 2022, doi: 10.1016/j.enconman.2022.115611.
- [33] M. Byun *et al.*, 'Economically feasible decarbonization of the Haber-Bosch process through supercritical CO₂ Allam cycle integration', *Appl Energy*, vol. 307, p. 118183, Feb. 2022, doi: 10.1016/j.apenergy.2021.118183.
- [34] P. Cui *et al.*, 'Thermodynamic and Economic Analysis of an Ammonia Synthesis Process Integrating Liquefied Natural Gas Cold Energy with Carbon Capture and Storage', *ACS Sustain Chem Eng*, vol. 11, no. 7, pp. 3052–3064, Feb. 2023, doi: 10.1021/acssuschemeng.2c06841.

- [35] F. Yilmaz, M. Ozturk, and R. Selbas, ‘Thermodynamic performance analysis and environmental impact assessment of an integrated system for hydrogen and ammonia generation’, *Int J Hydrogen Energy*, vol. 46, no. 57, pp. 29663–29679, Aug. 2021, doi: 10.1016/j.ijhydene.2020.10.255.
- [36] V. Kyriakou, I. Garagounis, A. Vourros, E. Vasileiou, and M. Stoukides, ‘An Electrochemical Haber-Bosch Process’, *Joule*, vol. 4, no. 1, pp. 142–158, Jan. 2020, doi: 10.1016/j.joule.2019.10.006.
- [37] E. Cussler, A. McCormick, M. Reese, and M. Malmali, ‘Ammonia Synthesis at Low Pressure’, *Journal of Visualized Experiments*, no. 126, Aug. 2017, doi: 10.3791/55691.
- [38] K. H. M. Al-Hamed and I. Dincer, ‘Analysis and economic evaluation of a unique carbon capturing system with ammonia for producing ammonium bicarbonate’, *Energy Convers Manag*, vol. 252, p. 115062, Jan. 2022, doi: 10.1016/j.enconman.2021.115062.
- [39] M. Ozturk and I. Dincer, ‘An integrated system for ammonia production from renewable hydrogen: A case study’, *Int J Hydrogen Energy*, vol. 46, no. 8, pp. 5918–5925, Jan. 2021, doi: 10.1016/j.ijhydene.2019.12.127.
- [40] B. Lin, T. Wiesner, and M. Malmali, ‘Performance of a Small-Scale Haber Process: A Techno-Economic Analysis’, *ACS Sustain Chem Eng*, vol. 8, no. 41, pp. 15517–15531, Oct. 2020, doi: 10.1021/acssuschemeng.0c04313.
- [41] H. Ishaq and I. Dincer, ‘Design and simulation of a new cascaded ammonia synthesis system driven by renewables’, *Sustainable Energy Technologies and Assessments*, vol. 40, Aug. 2020, doi: 10.1016/j.seta.2020.100725.
- [42] O. Siddiqui, H. Ishaq, G. Chehade, and I. Dincer, ‘Experimental investigation of an integrated solar powered clean hydrogen to ammonia synthesis system’, *Appl Therm Eng*, vol. 176, Jul. 2020, doi: 10.1016/j.applthermaleng.2020.115443.
- [43] A. Sánchez and M. Martín, ‘Optimal renewable production of ammonia from water and air’, *J Clean Prod*, vol. 178, pp. 325–342, Mar. 2018, doi: 10.1016/j.jclepro.2017.12.279.
- [44] C. Fúnez Guerra, L. Reyes-Bozo, E. Vyhmeister, M. Jaén Caparrós, J. L. Salazar, and C. Clemente-Jul, ‘Technical-economic analysis for a green ammonia production plant in Chile and its subsequent transport to Japan’, *Renew Energy*, vol. 157, pp. 404–414, Sep. 2020, doi: 10.1016/j.renene.2020.05.041.
- [45] J. Sousa, W. Waiblinger, and K. A. Friedrich, ‘Techno-economic Study of an Electrolysis-Based Green Ammonia Production Plant’, *Ind Eng Chem Res*, vol. 61, no. 39, pp. 14515–14530, Oct. 2022, doi: 10.1021/acs.iecr.2c00383.
- [46] R. Lan, J. T. S. Irvine, and S. Tao, ‘Synthesis of ammonia directly from air and water at ambient temperature and pressure’, *Sci Rep*, vol. 3, no. 1, p. 1145, Jan. 2013, doi: 10.1038/srep01145.
- [47] H. Ishaq, O. Siddiqui, and I. Dincer, ‘Experimental and theoretical investigations of a new cascaded reactor for ammonia as a renewable fuel’, *Fuel Processing Technology*, vol. 217, Jun. 2021, doi: 10.1016/j.fuproc.2021.106780.
- [48] K. Wagner *et al.*, ‘Column absorption for reproducible cyclic separation in small scale ammonia synthesis’, *AIChE Journal*, vol. 63, no. 7, pp. 3058–3068, Jul. 2017, doi: 10.1002/aic.15685.
- [49] C. Smith, A. V. McCormick, and E. L. Cussler, ‘Optimizing the Conditions for Ammonia Production Using Absorption’, *ACS Sustain Chem Eng*, vol. 7, no. 4, pp. 4019–4029, Feb. 2019, doi: 10.1021/acssuschemeng.8b05395.
- [50] M. Malmali, Y. Wei, A. McCormick, and E. L. Cussler, ‘Ammonia Synthesis at Reduced Pressure via Reactive Separation’, *Ind Eng Chem Res*, vol. 55, no. 33, pp. 8922–8932, Aug. 2016, doi: 10.1021/acs.iecr.6b01880.
- [51] M. Malmali, M. Reese, A. V. McCormick, and E. L. Cussler, ‘Converting Wind Energy to Ammonia at Lower Pressure’, *ACS Sustain Chem Eng*, vol. 6, no. 1, pp. 827–834, Jan. 2018, doi: 10.1021/acssuschemeng.7b03159.

- [52] D. J. Hrtus, F. H. Nowrin, A. Lomas, Y. Fotsa, and M. Malmali, 'Achieving +95% Ammonia Purity by Optimizing the Absorption and Desorption Conditions of Supported Metal Halides', *ACS Sustain Chem Eng*, vol. 10, no. 1, pp. 204–212, Jan. 2022, doi: 10.1021/acssuschemeng.1c05668.
- [53] F. H. Nowrin and M. Malmali, 'Optimizing Reaction-Absorption Process for Lower Pressure Ammonia Production', *ACS Sustain Chem Eng*, vol. 10, no. 37, pp. 12319–12328, Sep. 2022, doi: 10.1021/acssuschemeng.2c03554.
- [54] T. Murakami, T. Nishikiori, T. Nohira, and Y. Ito, 'Electrolytic Synthesis of Ammonia in Molten Salts under Atmospheric Pressure', *J Am Chem Soc*, vol. 125, no. 2, pp. 334–335, Jan. 2003, doi: 10.1021/ja028891t.
- [55] Y. Bicer and I. Dincer, 'Performance assessment of electrochemical ammonia synthesis using photoelectrochemically produced hydrogen', *Int J Energy Res*, vol. 41, no. 14, pp. 1987–2000, Nov. 2017, doi: 10.1002/er.3756.
- [56] R. Lan, J. T. S. Irvine, and S. Tao, 'Ammonia and related chemicals as potential indirect hydrogen storage materials', *Int J Hydrogen Energy*, vol. 37, no. 2, pp. 1482–1494, Jan. 2012, doi: 10.1016/j.ijhydene.2011.10.004.
- [57] J. R. Gomez, J. Baca, and F. Garzon, 'Techno-economic analysis and life cycle assessment for electrochemical ammonia production using proton conducting membrane', *Int J Hydrogen Energy*, vol. 45, no. 1, pp. 721–737, Jan. 2020, doi: 10.1016/j.ijhydene.2019.10.174.
- [58] Y. Bicer and I. Dincer, 'Assessment of a Sustainable Electrochemical Ammonia Production System Using Photoelectrochemically Produced Hydrogen under Concentrated Sunlight', *ACS Sustain Chem Eng*, vol. 5, no. 9, pp. 8035–8043, Sep. 2017, doi: 10.1021/acssuschemeng.7b01638.
- [59] S. Anwar, F. Khan, Y. Zhang, and A. Djire, 'Recent development in electrocatalysts for hydrogen production through water electrolysis', *Int J Hydrogen Energy*, vol. 46, no. 63, pp. 32284–32317, Sep. 2021, doi: 10.1016/j.ijhydene.2021.06.191.
- [60] L. Klaas, D. Guban, M. Roeb, and C. Sattler, 'Recent progress towards solar energy integration into low-pressure green ammonia production technologies', *Int J Hydrogen Energy*, vol. 46, no. 49, pp. 25121–25136, Jul. 2021, doi: 10.1016/j.ijhydene.2021.05.063.
- [61] R. Zhao *et al.*, 'Recent progress in the electrochemical ammonia synthesis under ambient conditions', *EnergyChem*, vol. 1, no. 2, p. 100011, Sep. 2019, doi: 10.1016/j.enchem.2019.100011.
- [62] Y. Wei, W. Jiang, Y. Liu, X. Bai, D. Hao, and B.-J. Ni, 'Recent advances in photocatalytic nitrogen fixation and beyond', *Nanoscale*, vol. 14, no. 8, pp. 2990–2997, 2022, doi: 10.1039/D2NR00198E.
- [63] A. O. Gezerman, 'A Critical Assessment of Green Ammonia Production and Ammonia Production Technologies', *Kemija u industriji*, no. 1–2, Jan. 2022, doi: 10.15255/KUI.2021.013.
- [64] M. El-Shafie, 'Hydrogen production by water electrolysis technologies: A review', *Results in Engineering*, p. 101426, Dec. 2023, doi: 10.1016/j.rineng.2023.101426.
- [65] F. Hussin and M. K. Aroua, 'Recent trends in the development of adsorption technologies for carbon dioxide capture: A brief literature and patent reviews (2014–2018)', *J Clean Prod*, vol. 253, p. 119707, Apr. 2020, doi: 10.1016/j.jclepro.2019.119707.
- [66] G. Chehade and I. Dincer, 'Progress in green ammonia production as potential carbon-free fuel', Sep. 01, 2021, *Elsevier Ltd*. doi: 10.1016/j.fuel.2021.120845.
- [67] M. A. Abdelkareem *et al.*, 'Fuel cells for carbon capture applications', *Science of The Total Environment*, vol. 769, p. 144243, May 2021, doi: 10.1016/j.scitotenv.2020.144243.
- [68] M. Wang, Z. Wang, S. Zhao, J. Wang, and S. Wang, 'Recent advances on mixed matrix membranes for CO₂ separation', *Chin J Chem Eng*, vol. 25, no. 11, pp. 1581–1597, Nov. 2017, doi: 10.1016/j.cjche.2017.07.006.
- [69] H. Wang, M. Liu, H. Kong, and Y. Hao, 'Thermodynamic analysis on mid/low temperature solar methane steam reforming with hydrogen permeation membrane reactors', *Appl Therm Eng*, vol. 152, pp. 925–936, Apr. 2019, doi: 10.1016/j.applthermaleng.2018.03.030.

- [70] A. E. Yüzbaşıoğlu, A. H. Tatarhan, and A. O. Gezerman, 'Decarbonization in ammonia production, new technological methods in industrial scale ammonia production and critical evaluations', *Heliyon*, vol. 7, no. 10, p. e08257, Oct. 2021, doi: 10.1016/j.heliyon.2021.e08257.
- [71] S. Tang, D. Tang, J. Tang, S. Tao, H. Xu, and Y. Geng, 'Controlling factors of coalbed methane well productivity of multiple superposed coalbed methane systems: A case study on the Songhe mine field, Guizhou, China', *Energy Exploration & Exploitation*, vol. 35, no. 6, pp. 665–684, Nov. 2017, doi: 10.1177/0144598717711122.
- [72] L. Wang *et al.*, 'Advances in improved/enhanced oil recovery technologies for tight and shale reservoirs', *Fuel*, vol. 210, pp. 425–445, Dec. 2017, doi: 10.1016/j.fuel.2017.08.095.
- [73] A. Tripodi, F. Conte, and I. Rossetti, 'Carbon Dioxide Methanation: Design of a Fully Integrated Plant', *Energy & Fuels*, vol. 34, no. 6, pp. 7242–7256, Jun. 2020, doi: 10.1021/acs.energyfuels.0c00580.
- [74] D. Schmider, L. Maier, and O. Deutschmann, 'Reaction Kinetics of CO and CO₂ Methanation over Nickel', *Ind Eng Chem Res*, vol. 60, no. 16, pp. 5792–5805, Apr. 2021, doi: 10.1021/acs.iecr.1c00389.
- [75] M. Reese *et al.*, 'Performance of a Small-Scale Haber Process', *Ind Eng Chem Res*, vol. 55, no. 13, pp. 3742–3750, Apr. 2016, doi: 10.1021/acs.iecr.5b04909.
- [76] A. Allman, P. Daoutidis, D. Tiffany, and S. Kelley, 'A framework for ammonia supply chain optimization incorporating conventional and renewable generation', *AIChE Journal*, vol. 63, no. 10, pp. 4390–4402, Oct. 2017, doi: 10.1002/aic.15838.
- [77] S. Ardo *et al.*, 'Pathways to electrochemical solar-hydrogen technologies', *Energy Environ Sci*, vol. 11, no. 10, pp. 2768–2783, Oct. 2018, doi: 10.1039/c7ee03639f.
- [78] M. El-Shafie and S. Kambara, 'Recent advances in ammonia synthesis technologies: Toward future zero carbon emissions', *Int J Hydrogen Energy*, vol. 48, no. 30, pp. 11237–11273, Apr. 2023, doi: 10.1016/j.ijhydene.2022.09.061.
- [79] D. Lim *et al.*, 'Impact of voltage degradation in water electrolyzers on sustainability of synthetic natural gas production: Energy, economic, and environmental analysis', *Energy Convers Manag*, vol. 245, p. 114516, Oct. 2021, doi: 10.1016/j.enconman.2021.114516.
- [80] S. Shiva Kumar and V. Himabindu, 'Hydrogen production by PEM water electrolysis – A review', *Mater Sci Energy Technol*, vol. 2, no. 3, pp. 442–454, Dec. 2019, doi: 10.1016/j.mset.2019.03.002.
- [81] B. Yang, R. Zhang, Z. Shao, and C. Zhang, 'The economic analysis for hydrogen production cost towards electrolyzer technologies: Current and future competitiveness', *Int J Hydrogen Energy*, vol. 48, no. 37, pp. 13767–13779, Apr. 2023, doi: 10.1016/j.ijhydene.2022.12.204.
- [82] S. Shiva Kumar, S. U. B. Ramakrishna, S. V. Krishna, K. Srilatha, B. R. Devi, and V. Himabindu, 'Synthesis of titanium (IV) oxide composite membrane for hydrogen production through alkaline water electrolysis', *S Afr J Chem Eng*, vol. 25, pp. 54–61, Jun. 2018, doi: 10.1016/j.sajce.2017.12.004.
- [83] S. Shiva Kumar, S. U. B. Ramakrishna, B. Rama Devi, and V. Himabindu, 'Phosphorus-doped graphene supported palladium (Pd/PG) electrocatalyst for the hydrogen evolution reaction in PEM water electrolysis', *Int J Green Energy*, vol. 15, no. 10, pp. 558–567, Aug. 2018, doi: 10.1080/15435075.2018.1508468.
- [84] S. Shiva Kumar, S. U. B. Ramakrishna, B. Rama Devi, and V. Himabindu, 'Phosphorus-doped carbon nanoparticles supported palladium electrocatalyst for the hydrogen evolution reaction (HER) in PEM water electrolysis', *Ionics (Kiel)*, vol. 24, no. 10, pp. 3113–3121, Oct. 2018, doi: 10.1007/s11581-018-2471-0.
- [85] S. Shiva Kumar, S. U. B. Ramakrishna, D. Bhagawan, and V. Himabindu, 'Preparation of Ru/Pd1-xO2 electrocatalysts for the oxygen evolution reaction (OER) in PEM water electrolysis', *Ionics (Kiel)*, vol. 24, no. 8, pp. 2411–2419, Aug. 2018, doi: 10.1007/s11581-017-2359-4.
- [86] B. Lee *et al.*, 'Integrative techno-economic and environmental assessment for green H₂ production by alkaline water electrolysis based on experimental data', *J Environ Chem Eng*, vol. 9, no. 6, p. 106349, Dec. 2021, doi: 10.1016/j.jece.2021.106349.

- [87] N. Du, C. Roy, R. Peach, M. Turnbull, S. Thiele, and C. Bock, ‘Anion-Exchange Membrane Water Electrolyzers’, *Chem Rev*, vol. 122, no. 13, pp. 11830–11895, Jul. 2022, doi: 10.1021/acs.chemrev.1c00854.
- [88] International Energy Agency, ‘Global Hydrogen Review 2021’, Paris, 2021. Accessed: Oct. 08, 2023. [Online]. Available: <https://www.iea.org/reports/global-hydrogen-review-2021>
- [89] T. International Renewable Energy Agency, *GREEN HYDROGEN COST REDUCTION SCALING UP ELECTROLYSERS TO MEET THE 1.5°C CLIMATE GOAL H 2 O 2*. 2020. [Online]. Available: www.irena.org/publications
- [90] M. David, C. Ocampo-Martínez, and R. Sánchez-Peña, ‘Advances in alkaline water electrolyzers: A review’, *J Energy Storage*, vol. 23, pp. 392–403, Jun. 2019, doi: 10.1016/j.est.2019.03.001.
- [91] I. IRENA, ‘Green hydrogen cost reduction: scaling up electrolyzers to meet the 1.5 C climate goal’, *Abu Dhabi: International Renewable Energy Agency*, 2020.
- [92] A. Buttler and H. Spliethoff, ‘Current status of water electrolysis for energy storage, grid balancing and sector coupling via power-to-gas and power-to-liquids: A review’, *Renewable and Sustainable Energy Reviews*, vol. 82, pp. 2440–2454, Feb. 2018, doi: 10.1016/j.rser.2017.09.003.
- [93] A. Erdogan Karaca and I. Dincer, ‘A newly developed experimental green hydrogen generator: Analysis and assessment’, *Fuel*, vol. 328, Nov. 2022, doi: 10.1016/j.fuel.2022.125301.
- [94] A. E. Karaca and I. Dincer, ‘Development of a new photoelectrochemical system for clean hydrogen production and a comparative environmental impact assessment with other production methods’, *Chemosphere*, vol. 337, Oct. 2023, doi: 10.1016/j.chemosphere.2023.139367.
- [95] M. Appl, *Ammonia*. Wiley, 1999. doi: 10.1002/9783527613885.
- [96] L. Shi *et al.*, ‘Rigorous and reliable operations for electrocatalytic nitrogen reduction’, *Appl Catal B*, vol. 278, p. 119325, Dec. 2020, doi: 10.1016/j.apcatb.2020.119325.
- [97] A. J. Martín, T. Shinagawa, and J. Pérez-Ramírez, ‘Electrocatalytic Reduction of Nitrogen: From Haber-Bosch to Ammonia Artificial Leaf’, *Chem*, vol. 5, no. 2, pp. 263–283, Feb. 2019, doi: 10.1016/j.chempr.2018.10.010.
- [98] W. B. Wang, J. W. Liu, Y. D. Li, H. T. Wang, F. Zhang, and G. L. Ma, ‘Microstructures and proton conduction behaviors of Dy-doped BaCeO₃ ceramics at intermediate temperature’, *Solid State Ion*, vol. 181, no. 15–16, pp. 667–671, Jun. 2010, doi: 10.1016/j.ssi.2010.04.008.
- [99] W. B. Wang, X. B. Cao, W. J. Gao, F. Zhang, H. T. Wang, and G. L. Ma, ‘Ammonia synthesis at atmospheric pressure using a reactor with thin solid electrolyte BaCe_{0.85}Y_{0.15}O_{3-α} membrane’, *J Memb Sci*, vol. 360, no. 1–2, pp. 397–403, Sep. 2010, doi: 10.1016/j.memsci.2010.05.038.
- [100] T. H. Rod, A. Logadottir, and J. K. Nørskov, ‘Ammonia synthesis at low temperatures’, *J Chem Phys*, vol. 112, no. 12, pp. 5343–5347, Mar. 2000, doi: 10.1063/1.481103.
- [101] G. Marnellos and M. Stoukides, ‘Ammonia Synthesis at Atmospheric Pressure’, *Science (1979)*, vol. 282, no. 5386, pp. 98–100, Oct. 1998, doi: 10.1126/science.282.5386.98.
- [102] M. Hattori, S. Iijima, T. Nakao, H. Hosono, and M. Hara, ‘Solid solution for catalytic ammonia synthesis from nitrogen and hydrogen gases at 50 °C’, *Nat Commun*, vol. 11, no. 1, Dec. 2020, doi: 10.1038/s41467-020-15868-8.
- [103] M. Hattori, N. Okuyama, H. Kurosawa, and M. Hara, ‘Low-Temperature Ammonia Synthesis on Iron Catalyst with an Electron Donor’, *J Am Chem Soc*, vol. 145, no. 14, pp. 7888–7897, Apr. 2023, doi: 10.1021/jacs.2c13015.
- [104] S. Singh, A. K. Mohammed, A. A. AlHammadi, D. Shetty, and K. Polychronopoulou, ‘Hypes and hopes on the materials development strategies to produce ammonia at mild conditions’, *Int J Hydrogen Energy*, vol. 48, no. 89, pp. 34700–34739, Nov. 2023, doi: 10.1016/j.ijhydene.2023.05.206.

- [105] V. A. Borisov *et al.*, ‘Effect of high-temperature treatment of on the activity of Ru-Cs(Ba)/Sibunit catalysts in ammonia synthesis and their resistance to methanation’, *Diam Relat Mater*, vol. 108, p. 107986, Oct. 2020, doi: 10.1016/j.diamond.2020.107986.
- [106] C. Karakaya *et al.*, ‘Development, characterization, and modeling of a high-performance Ru/B2CA catalyst for ammonia synthesis’, *Chem Eng Sci*, vol. 247, p. 116902, Jan. 2022, doi: 10.1016/j.ces.2021.116902.
- [107] Y. Wang *et al.*, ‘Differential transformation mechanisms of exotic Cr(VI) in agricultural soils with contrasting physio-chemical and biological properties’, *Chemosphere*, vol. 279, p. 130546, Sep. 2021, doi: 10.1016/j.chemosphere.2021.130546.
- [108] X. Wei, D. Vogel, L. Keller, S. Kriescher, and M. Wessling, ‘Microtubular Gas Diffusion Electrode Based on Ruthenium-Carbon Nanotubes for Ambient Electrochemical Nitrogen Reduction to Ammonia’, *ChemElectroChem*, vol. 7, no. 22, pp. 4679–4684, Nov. 2020, doi: 10.1002/celec.202001370.
- [109] J. Ni *et al.*, ‘Enhanced catalytic performance of the carbon-supported Ru ammonia synthesis catalyst by an introduction of oxygen functional groups via gas-phase oxidation’, *J Catal*, vol. 409, pp. 78–86, May 2022, doi: 10.1016/j.jcat.2022.03.026.
- [110] X. Peng *et al.*, ‘Size-dependent activity of supported Ru catalysts for ammonia synthesis at mild conditions’, *J Catal*, vol. 408, pp. 98–108, Apr. 2022, doi: 10.1016/j.jcat.2022.02.024.
- [111] J. Huang *et al.*, ‘Cs-Promoted ruthenium catalyst supported on Ba₅Ta₄O₁₅ with abundant oxygen vacancies for ammonia synthesis’, *Appl Catal A Gen*, vol. 615, p. 118058, Apr. 2021, doi: 10.1016/j.apcata.2021.118058.
- [112] B. Lin *et al.*, ‘Effects of Using Carbon-Coated Alumina as Support for Ba-Promoted Ru Catalyst in Ammonia Synthesis’, *Ind Eng Chem Res*, vol. 58, no. 24, pp. 10285–10295, Jun. 2019, doi: 10.1021/acs.iecr.9b01610.
- [113] Y. Inoue *et al.*, ‘Direct Activation of Cobalt Catalyst by 12CaO·7Al₂O₃ Electride for Ammonia Synthesis’, *ACS Catal*, vol. 9, no. 3, pp. 1670–1679, Mar. 2019, doi: 10.1021/acscatal.8b03650.
- [114] M. Hara, M. Kitano, and H. Hosono, ‘Ru-Loaded C12A7:e⁻ Electride as a Catalyst for Ammonia Synthesis’, *ACS Catal*, vol. 7, no. 4, pp. 2313–2324, Apr. 2017, doi: 10.1021/acscatal.6b03357.
- [115] Y. Wang *et al.*, ‘Plasma-Enhanced Catalytic Synthesis of Ammonia over a Ni/Al₂O₃ Catalyst at Near-Room Temperature: Insights into the Importance of the Catalyst Surface on the Reaction Mechanism’, *ACS Catal*, vol. 9, no. 12, pp. 10780–10793, Dec. 2019, doi: 10.1021/acscatal.9b02538.
- [116] K. Chu, Y. Liu, Y. Li, H. Zhang, and Y. Tian, ‘Efficient electrocatalytic N₂ reduction on CoO quantum dots’, *J Mater Chem A Mater*, vol. 7, no. 9, pp. 4389–4394, 2019, doi: 10.1039/C9TA00016J.
- [117] H. Chen *et al.*, ‘Plasma-etched Ti₂O₃ with oxygen vacancies for enhanced NH₃ electrosynthesis and Zn–N₂ batteries’, *Inorg Chem Front*, vol. 9, no. 18, pp. 4608–4613, 2022, doi: 10.1039/D2QI01173E.
- [118] H. Chen *et al.*, ‘Ambient electrochemical N₂-to-NH₃ conversion catalyzed by TiO₂ decorated juncus effusus-derived carbon microtubes’, *Inorg Chem Front*, vol. 9, no. 7, pp. 1514–1519, 2022, doi: 10.1039/D2QI00140C.
- [119] H. He *et al.*, ‘Metal–organic framework supported Au nanoparticles with organosilicone coating for high-efficiency electrocatalytic N₂ reduction to NH₃’, *Appl Catal B*, vol. 302, p. 120840, Mar. 2022, doi: 10.1016/j.apcatb.2021.120840.
- [120] L. Wen *et al.*, ‘Oxygen Vacancy Engineering of MOF-Derived Zn-Doped Co₃O₄ Nanopolyhedrons for Enhanced Electrochemical Nitrogen Fixation’, *ACS Appl Mater Interfaces*, vol. 13, no. 12, pp. 14181–14188, Mar. 2021, doi: 10.1021/acsami.0c22767.
- [121] M. Cong *et al.*, ‘Selective nitrogen reduction to ammonia on iron porphyrin-based single-site metal–organic frameworks’, *J Mater Chem A Mater*, vol. 9, no. 8, pp. 4673–4678, 2021, doi: 10.1039/D0TA08741F.
- [122] Y. Sun *et al.*, ‘Asymmetric acidic/alkaline N₂ electrofixation accelerated by high-entropy metal–organic framework derivatives’, *Carbon Energy*, vol. 5, no. 3, Mar. 2023, doi: 10.1002/cey2.263.

- [123] H. He, H.-M. Wen, H.-K. Li, and H.-W. Zhang, 'Recent advances in metal–organic frameworks and their derivatives for electrocatalytic nitrogen reduction to ammonia', *Coord Chem Rev*, vol. 471, p. 214761, Nov. 2022, doi: 10.1016/j.ccr.2022.214761.
- [124] M. Yoshida, T. Ogawa, Y. Imamura, and K. N. Ishihara, 'Economies of scale in ammonia synthesis loops embedded with iron- and ruthenium-based catalysts', *Int J Hydrogen Energy*, vol. 46, no. 57, pp. 28840–28854, Aug. 2021, doi: 10.1016/j.ijhydene.2020.12.081.
- [125] M. Yoshida, T. Ogawa, and K. N. Ishihara, 'Economic limitation of recent heterogeneous catalysts for ammonia synthesis', *Cleaner Chemical Engineering*, vol. 10, p. 100119, Dec. 2024, doi: 10.1016/j.clce.2024.100119.
- [126] H. Ishaq and I. Dincer, 'Investigation and optimization of a new hybrid natural gas reforming system for cascaded hydrogen, ammonia and methanol synthesis', *Comput Chem Eng*, vol. 148, May 2021, doi: 10.1016/j.compchemeng.2021.107234.
- [127] O. Siddiqui and I. Dincer, 'Optimization of a new renewable energy system for producing electricity, hydrogen and ammonia', *Sustainable Energy Technologies and Assessments*, vol. 44, p. 101023, Apr. 2021, doi: 10.1016/j.seta.2021.101023.
- [128] Y. E. Yuksel, M. Ozturk, and I. Dincer, 'Development of a novel combined energy plant for multigeneration with hydrogen and ammonia production', *Int J Hydrogen Energy*, vol. 46, no. 57, pp. 28980–28994, Aug. 2021, doi: 10.1016/j.ijhydene.2020.12.113.
- [129] Y. E. Yuksel, M. Ozturk, and I. Dincer, 'Design and analysis of a new solar hydrogen plant for power, methane, ammonia and urea generation', *Int J Hydrogen Energy*, vol. 47, no. 45, pp. 19422–19445, May 2022, doi: 10.1016/j.ijhydene.2021.12.162.
- [130] M. E. Demir and I. Dincer, 'Development and assessment of a solar driven trigeneration system with storage for electricity, ammonia and fresh water production', *Energy Convers Manag*, vol. 245, p. 114585, Oct. 2021, doi: 10.1016/j.enconman.2021.114585.
- [131] F. B. Juangsa and M. Aziz, 'Integrated system of thermochemical cycle of ammonia, nitrogen production, and power generation', *Int J Hydrogen Energy*, vol. 44, no. 33, pp. 17525–17534, Jul. 2019, doi: 10.1016/j.ijhydene.2019.05.110.
- [132] D. Wen and M. Aziz, 'Flexible operation strategy of an integrated renewable multi-generation system for electricity, hydrogen, ammonia, and heating', *Energy Convers Manag*, vol. 253, p. 115166, Feb. 2022, doi: 10.1016/j.enconman.2021.115166.
- [133] Z. Su *et al.*, 'Multi-objective optimization and techno-economic evaluation of a capture/separation/liquefaction scheme in a zero emission power/liquid N₂/liquid CO₂ production system based on biomass gasification and supercritical CO₂ oxy-combustion cycle and ion transport membrane and Claude cycle', *Sep Purif Technol*, vol. 314, p. 123566, Jun. 2023, doi: 10.1016/j.seppur.2023.123566.
- [134] O. Palone, G. G. Gagliardi, M. Mechelli, L. Cedola, and D. Borello, 'Techno-economic analysis of sustainable methanol and ammonia production by chemical looping hydrogen generation from waste plastic', *Energy Convers Manag*, vol. 292, Sep. 2023, doi: 10.1016/j.enconman.2023.117389.
- [135] Khasani, W. Prasadha, A. Widyatama, and M. Aziz, 'Energy-saving and environmentally-benign integrated ammonia production system', *Energy*, vol. 235, p. 121400, Nov. 2021, doi: 10.1016/j.energy.2021.121400.
- [136] R. Privat *et al.*, 'Teaching the Concept of Gibbs Energy Minimization through Its Application to Phase-Equilibrium Calculation', *J Chem Educ*, vol. 93, no. 9, pp. 1569–1577, Sep. 2016, doi: 10.1021/acs.jchemed.6b00205.
- [137] A. Shamiri and N. Aliabadi, 'Modeling and performance improvement of an industrial ammonia synthesis reactor', *Chemical Engineering Journal Advances*, vol. 8, Nov. 2021, doi: 10.1016/j.cej.2021.100177.
- [138] R. F. Baddour, P. L. T. Brian, B. A. Logeais, and J. P. Eymery, 'Steady-state simulation of an ammonia synthesis converter', *Chem Eng Sci*, vol. 20, no. 4, pp. 281–292, Apr. 1965, doi: 10.1016/0009-2509(65)85017-5.

- [139] D. Annable, 'Application of the Temkin kinetic equation to ammonia synthesis in large-scale reactors', *Chem Eng Sci*, vol. 1, no. 4, pp. 145–154, 1952, doi: 10.1016/0009-2509(52)87011-3.
- [140] D. C. Dyson and J. M. Simon, 'Kinetic Expression with Diffusion Correction for Ammonia Synthesis on Industrial Catalyst', *Industrial & Engineering Chemistry Fundamentals*, vol. 7, no. 4, pp. 605–610, Nov. 1968, doi: 10.1021/i160028a013.
- [141] C. P. P Singh and D. N. Saraf, 'Simulation of Ammonia Synthesis Reactors', 1979. [Online]. Available: <https://pubs.acs.org/sharingguidelines>
- [142] S. R. Upreti and K. Deb, 'OPTIMAL DESIGN OF AN AMMONIA SYNTHESIS REACTOR USING GENETIC ALGORITHMS', 1997.
- [143] B. V. Babu and R. Angira, 'Optimal design of an auto-thermal ammonia synthesis reactor', *Comput Chem Eng*, vol. 29, no. 5, pp. 1041–1045, Apr. 2005, doi: 10.1016/j.compchemeng.2004.11.010.
- [144] E. P. Carvalho, C. Borges, D. Andrade, J. Y. Yuan, and M. A. S. S. Ravagnani, 'Modeling and optimization of an ammonia reactor using a penalty-like method', *Appl Math Comput*, vol. 237, pp. 330–339, Jun. 2014, doi: 10.1016/j.amc.2014.03.099.
- [145] J. Fuller, Q. An, A. Fortunelli, and W. A. Goddard, 'Reaction Mechanisms, Kinetics, and Improved Catalysts for Ammonia Synthesis from Hierarchical High Throughput Catalyst Design', *Acc Chem Res*, vol. 55, no. 8, pp. 1124–1134, Apr. 2022, doi: 10.1021/acs.accounts.1c00789.
- [146] J. M. Méndez González and M. Díaz de León Cabrero, 'Absence of evidence is not evidence of absence: Multiple steady states in ammonia synthesis', *Chemical Engineering Research and Design*, vol. 113, pp. 256–263, Sep. 2016, doi: 10.1016/j.cherd.2016.08.006.
- [147] D. Wen and M. Aziz, 'Flexible operation strategy of an integrated renewable multi-generation system for electricity, hydrogen, ammonia, and heating', *Energy Convers Manag*, vol. 253, Feb. 2022, doi: 10.1016/j.enconman.2021.115166.
- [148] M. E. Demir and I. Dincer, 'Development and assessment of a solar driven trigeneration system with storage for electricity, ammonia and fresh water production', *Energy Convers Manag*, vol. 245, Oct. 2021, doi: 10.1016/j.enconman.2021.114585.
- [149] F. B. Juangsa and M. Aziz, 'Integrated system of thermochemical cycle of ammonia, nitrogen production, and power generation', *Int J Hydrogen Energy*, vol. 44, no. 33, pp. 17525–17534, Jul. 2019, doi: 10.1016/j.ijhydene.2019.05.110.
- [150] P. Dange *et al.*, 'Recent Developments in Microbial Electrolysis Cell-Based Biohydrogen Production Utilizing Wastewater as a Feedstock', *Sustainability*, vol. 13, no. 16, p. 8796, Aug. 2021, doi: 10.3390/su13168796.
- [151] S. Dahiya, S. Chatterjee, O. Sarkar, and S. V. Mohan, 'Renewable hydrogen production by dark-fermentation: Current status, challenges and perspectives', *Bioresour Technol*, vol. 321, p. 124354, Feb. 2021, doi: 10.1016/j.biortech.2020.124354.
- [152] M. Aziz, 'Integrated hydrogen production and power generation from microalgae', *Int J Hydrogen Energy*, vol. 41, no. 1, pp. 104–112, Jan. 2016, doi: 10.1016/j.ijhydene.2015.10.115.
- [153] A. T. Wijayanta and M. Aziz, 'Ammonia production from algae via integrated hydrothermal gasification, chemical looping, N₂ production, and NH₃ synthesis', *Energy*, vol. 174, pp. 331–338, May 2019, doi: 10.1016/j.energy.2019.02.190.
- [154] S. Liu, Y. Yang, L. Yu, and X. Li, 'Thermodynamic and environmental analysis of solar-driven supercritical water gasification of algae for ammonia synthesis and power production', *Energy Convers Manag*, vol. 243, p. 114409, Sep. 2021, doi: 10.1016/j.enconman.2021.114409.
- [155] P. Arora, I. Sharma, A. Hoadley, S. Mahajani, and A. Ganesh, 'Remote, small-scale, "greener" routes of ammonia production', *J Clean Prod*, vol. 199, pp. 177–192, Oct. 2018, doi: 10.1016/j.jclepro.2018.06.130.

- [156] Y. Tatemichi, K. Kuroda, T. Nakahara, and M. Ueda, 'Efficient ammonia production from food by-products by engineered *Escherichia coli*', *AMB Express*, vol. 10, no. 1, p. 150, Dec. 2020, doi: 10.1186/s13568-020-01083-7.
- [157] H. Edwardes-Evans, M. Perez, and J. Burgess, 'Interactive: Platts Ammonia price chart', S&P Global Commodity Insights.
- [158] M. Aziz, A. TriWijayanta, and A. B. D. Nandiyanto, 'Ammonia as effective hydrogen storage: A review on production, storage and utilization', *Energies (Basel)*, vol. 13, no. 12, Jun. 2020, doi: 10.3390/en13123062.
- [159] N. Salmon and R. Bañares-Alcántara, 'Impact of grid connectivity on cost and location of green ammonia production: Australia as a case study', *Energy Environ Sci*, vol. 14, no. 12, pp. 6655–6671, Dec. 2021, doi: 10.1039/d1ee02582a.
- [160] S. R. Upreti and K. Deb, 'OPTIMAL DESIGN OF AN AMMONIA SYNTHESIS REACTOR USING GENETIC ALGORITHMS', 1997.
- [161] M. H. Khademi and R. S. Sabbaghi, 'Comparison between three types of ammonia synthesis reactor configurations in terms of cooling methods', *Chemical Engineering Research and Design*, vol. 128, pp. 306–317, Dec. 2017, doi: 10.1016/j.cherd.2017.10.021.
- [162] M. I. Temkin, 'Kinetics of heterogeneous catalysis', *J. Phys. Chem*, vol. 14, pp. 1153–1158, 1940.
- [163] M. Peris, 'Understanding Le Châtelier's principle fundamentals: five key questions', *Chemistry Teacher International*, vol. 4, no. 3, pp. 203–205, Oct. 2022, doi: 10.1515/cti-2020-0030.
- [164] C. A. Vancini and D. J. Borgars, *Synthesis of ammonia*. Macmillan, 1971. Accessed: Nov. 11, 2023. [Online]. Available: <https://cir.nii.ac.jp/crid/1130000795353148928.bib?lang=en>
- [165] M. Shah, 'CONTROL SIMULATION IN AMMONIA PRODUCTION', *Ind Eng Chem*, vol. 59, no. 1, pp. 72–83, Jan. 1967, doi: 10.1021/ie50685a010.
- [166] S. S. Elnashaie, M. E. Abashar, and A. S. Al-Ubaid, 'Simulation and optimization of an industrial ammonia reactor', *Ind Eng Chem Res*, vol. 27, no. 11, pp. 2015–2022, Nov. 1988, doi: 10.1021/ie00083a010.
- [167] K. V. Reddy and A. Husain, 'Modeling and simulation of an ammonia synthesis loop', *Industrial & Engineering Chemistry Process Design and Development*, vol. 21, no. 3, pp. 359–367, Jul. 1982, doi: 10.1021/i200018a001.
- [168] L. J. Gillespie and J. A. Beattie, 'The Thermodynamic Treatment of Chemical Equilibria in Systems Composed of Real Gases. II. A Relation for the Heat of Reaction Applied to the Ammonia Synthesis Reaction. The Energy and Entropy Constants of Ammonia. A Correction.', *Physical Review*, vol. 37, no. 5, pp. 655–655, Mar. 1931, doi: 10.1103/PhysRev.37.655.
- [169] A. T. Mahfouz, S. S. Elshishini, and S. S. E. H. Elnashaie, 'STEADY-STATE MODELLING AND SIMULATION OF AN INDUSTRIAL AMMONIA SYNTHESIS REACTOR - I. REACTOR MODELLING.', *Modelling, simulation & control. B*, vol. 10, no. 3, 1987.
- [170] C. R. Harris *et al.*, 'Array programming with NumPy', *Nature*, vol. 585, no. 7825, pp. 357–362, Sep. 2020, doi: 10.1038/s41586-020-2649-2.
- [171] P. Virtanen *et al.*, 'SciPy 1.0: fundamental algorithms for scientific computing in Python', *Nat Methods*, vol. 17, no. 3, pp. 261–272, Mar. 2020, doi: 10.1038/s41592-019-0686-2.
- [172] R. C. Dunbar, 'Deriving the Maxwell distribution', *J Chem Educ*, vol. 59, no. 1, p. 22, Jan. 1982, doi: 10.1021/ed059p22.
- [173] M. J. Azarhoosh, F. Farivar, and H. Ale Ebrahim, 'Simulation and optimization of a horizontal ammonia synthesis reactor using genetic algorithm', *RSC Adv.*, vol. 4, no. 26, pp. 13419–13429, 2014, doi: 10.1039/C3RA45410J.
- [174] R. Storn and K. Price, 'Differential Evolution - A Simple and Efficient Heuristic for Global Optimization over Continuous Spaces', *Journal of Global Optimization*, vol. 11, no. 4, 1997, doi: 10.1023/A:1008202821328.

- [175] J. Qiang and C. Mitchell, 'A Unified Differential Evolution Algorithm for Global Optimization', *IEEE Transactions on Evolutionary Computation*, no. 7, 2014.
- [176] R. Turton, *Analysis, Synthesis, and Design of Chemical Processes Fourth Edition*, vol. 53, no. 9, 2013.
- [177] S. Jenkins, 'Chemical Engineering Plant Cost Index', *Chemical Engineering*.
- [178] C. Arnaiz del Pozo and S. Cloete, 'Techno-economic assessment of blue and green ammonia as energy carriers in a low-carbon future', *Energy Convers Manag*, vol. 255, p. 115312, Mar. 2022, doi: 10.1016/j.enconman.2022.115312.
- [179] K. Bastani, S. Heydar Rajaei Shooshtari, and D. Lotfi Moghaddam, 'Optimization of ammonia production unit using polymeric membrane: Re-design of ammonia synthesis reactor feeding strategy and methane removal', *Chem Eng Sci*, vol. 300, p. 120613, Dec. 2024, doi: 10.1016/j.ces.2024.120613.
- [180] J. C. Morud and S. Skogestad, 'Analysis of Instability in an Industrial Ammonia Reactor', *AIChE Journal*, vol. 44, no. 4, 1998, doi: 10.1002/aic.690440414.
- [181] D. Flórez-Orrego and S. de Oliveira Junior, 'Modeling and optimization of an industrial ammonia synthesis unit: An exergy approach', *Energy*, vol. 137, 2017, doi: 10.1016/j.energy.2017.06.157.
- [182] G. Soave, 'Equilibrium constants from a modified Redlich-Kwong equation of state', *Chem Eng Sci*, vol. 27, no. 6, 1972, doi: 10.1016/0009-2509(72)80096-4.
- [183] D. R. Woods, *Rules of Thumb in Engineering Practice*. 2007. doi: 10.1002/9783527611119.
- [184] M. Wang *et al.*, 'Can sustainable ammonia synthesis pathways compete with fossil-fuel based Haber–Bosch processes?', *Energy Environ Sci*, vol. 14, no. 5, pp. 2535–2548, 2021, doi: 10.1039/D0EE03808C.
- [185] International Energy Agency, 'Global average levelised cost of hydrogen production by energy source and technology, 2019 and 2050', <https://www.iea.org/reports/the-future-of-hydrogen>.
- [186] Intratec, 'Nitrogen Price | Industrial Utilities', <https://www.intratec.us/products/water-utility-costs/commodity/nitrogen-price>.
- [187] Thunder Said Energy, 'Cryogenic air separation: costs and energy economics?', thundersaidenergy.com.
- [188] C. Fúnez Guerra, L. Reyes-Bozo, E. Vyhmeister, M. Jaén Caparrós, J. L. Salazar, and C. Clemente-Jul, 'Technical-economic analysis for a green ammonia production plant in Chile and its subsequent transport to Japan', *Renew Energy*, vol. 157, pp. 404–414, Sep. 2020, doi: 10.1016/j.renene.2020.05.041.
- [189] Saudi Central Bank, 'Deposit Interest Rate in Saudi Arabia', www.sama.gov.sa.
- [190] ASHRAE, *2018 ASHRAE Handbook Refrigeration*. 2018.
- [191] Saudi Electric Company, 'Consumption Tariffs', <https://www.se.com.sa/en/OurServices/ColumnC/Bills-and-Consumption/ConsumptionTariffs>.
- [192] M. Shacham and N. Brauner, 'A hundred years of chemical equilibrium calculations - The case of ammonia synthesis', *Education for Chemical Engineers*, vol. 13, pp. 17–23, Oct. 2015, doi: 10.1016/j.ece.2015.09.001.
- [193] Y. Kojima and M. Yamaguchi, 'Ammonia as a hydrogen energy carrier', *Int J Hydrogen Energy*, vol. 47, no. 54, pp. 22832–22839, Jun. 2022, doi: 10.1016/j.ijhydene.2022.05.096.
- [194] M. Koike, H. Miyagawa, T. Suzuoki, and K. Ogasawara, 'Ammonia as a hydrogen energy carrier and its application to internal combustion engines', in *Sustainable Vehicle Technologies*, Elsevier, 2012, pp. 61–70. doi: 10.1533/9780857094575.2.61.
- [195] K. Machaj *et al.*, 'Ammonia as a potential marine fuel: A review', *Energy Strategy Reviews*, vol. 44, p. 100926, Nov. 2022, doi: 10.1016/j.esr.2022.100926.
- [196] A. Valera-Medina *et al.*, 'Ammonia combustion in furnaces: A review', *Int J Hydrogen Energy*, vol. 49, pp. 1597–1618, Jan. 2024, doi: 10.1016/j.ijhydene.2023.10.241.

- [197] E. R. Morgan, ‘Techno-economic feasibility study of ammonia plants powered by offshore wind’, *University of Massachusetts - Amherst, PhD Dissertations*, 2013.
- [198] N. O. Lemcoff, ‘Nitrogen separation from air by pressure swing adsorption’, in *Surface Science and Catalysis*, vol. 120, 1999, pp. 347–370. doi: 10.1016/S0167-2991(99)80557-6.
- [199] M. Cheng, P. Verma, Z. Yang, and R. L. Axelbaum, ‘Flexible cryogenic air separation unit—An application for low-carbon fossil-fuel plants’, *Sep Purif Technol*, vol. 302, p. 122086, Dec. 2022, doi: 10.1016/j.seppur.2022.122086.
- [200] A. Ursua, L. M. Gandia, and P. Sanchis, ‘Hydrogen Production From Water Electrolysis: Current Status and Future Trends’, *Proceedings of the IEEE*, vol. 100, no. 2, pp. 410–426, Feb. 2012, doi: 10.1109/JPROC.2011.2156750.
- [201] B. Lee, D. Lim, H. Lee, and H. Lim, ‘Which water electrolysis technology is appropriate?: Critical insights of potential water electrolysis for green ammonia production’, *Renewable and Sustainable Energy Reviews*, vol. 143, p. 110963, Jun. 2021, doi: 10.1016/j.rser.2021.110963.
- [202] A. R. Smith and J. Klosek, ‘A review of air separation technologies and their integration with energy conversion processes’, *Fuel Processing Technology*, vol. 70, pp. 115–134, 2001, [Online]. Available: www.elsevier.com/locate/fuproc
- [203] C. Mao, L. Yu, J. Li, J. Zhao, and L. Zhang, ‘Energy-confined solar thermal ammonia synthesis with K/Ru/TiO₂-xHx’, *Appl Catal B*, vol. 224, pp. 612–620, May 2018, doi: 10.1016/j.apcatb.2017.11.010.
- [204] H. Nami, P. V. Hendriksen, and H. L. Frandsen, ‘Green ammonia production using current and emerging electrolysis technologies’, *Renewable and Sustainable Energy Reviews*, vol. 199, p. 114517, Jul. 2024, doi: 10.1016/j.rser.2024.114517.
- [205] Aspen Technology, ‘Aspen HYSYS V14 User Guide’, 2022, *Aspen Technology, Inc, Bedford, MA: V14*.
- [206] National Renewable Energy Laboratory, ‘System Advisor Model™’, Jun. 30, 2024, *Golden, CO: Version 2023.12.17 (SAM™ 2023.12.17)*. Accessed: Nov. 27, 2024. [Online]. Available: <https://sam.nrel.gov>
- [207] L. Niu, Y. Hou, W. Sun, and S. Chen, ‘The measurement of thermodynamic performance in cryogenic two-phase turbo-expander’, *Cryogenics (Guildf)*, vol. 70, pp. 76–84, Sep. 2015, doi: 10.1016/j.cryogenics.2015.06.002.
- [208] A. Zaccara *et al.*, ‘Renewable Hydrogen Production Processes for the Off-Gas Valorization in Integrated Steelworks through Hydrogen Intensified Methane and Methanol Syntheses’, *Metals (Basel)*, vol. 10, no. 11, p. 1535, Nov. 2020, doi: 10.3390/met10111535.
- [209] Y. Muazzam *et al.*, ‘Thermo-Economic Analysis of Integrated Hydrogen, Methanol and Dimethyl Ether Production Using Water Electrolyzed Hydrogen’, *Resources*, vol. 11, no. 10, p. 85, Sep. 2022, doi: 10.3390/resources11100085.
- [210] P. Millet and S. Grigoriev, ‘Water Electrolysis Technologies’, in *Renewable Hydrogen Technologies*, Elsevier, 2013, pp. 19–41. doi: 10.1016/B978-0-444-56352-1.00002-7.
- [211] M. F. A. Kamaroddin, N. Sabli, and T. A. T. Abdullah, ‘Hydrogen Production by Membrane Water Splitting Technologies’, in *Advances In Hydrogen Generation Technologies*, InTech, 2018. doi: 10.5772/intechopen.76727.
- [212] G. F. Froment, K. B. Bischoff, and J. De Wilde, *Chemical Reactor Analysis and Design*, 3rd ed. Wiley, 2011.
- [213] D. Flórez-Orrego and S. de Oliveira Junior, ‘Exergy assessment of single and dual pressure industrial ammonia synthesis units’, *Energy*, vol. 141, pp. 2540–2558, Dec. 2017, doi: 10.1016/j.energy.2017.06.139.
- [214] D. Flórez-Orrego and S. de Oliveira Junior, ‘On the efficiency, exergy costs and CO₂ emission cost allocation for an integrated syngas and ammonia production plant’, *Energy*, vol. 117, pp. 341–360, Dec. 2016, doi: 10.1016/j.energy.2016.05.096.

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Publications from Thesis Work

CONFERENCE PRESENTATIONS

1. **Adnan, A. (presenter)**, Al Mukahhil, A., Imteyaz, B., Mokheimer, E.M.A., Parametric Analysis of Non-Adiabatic Internal Direct Cooling Ammonia Synthesis Reactor [Technical Paper Presentation], CSME/CFD2024, Canadian Society for Mechanical Engineering (CSME) and the CFD Society of Canada (CFDSC), Toronto, Canada

Other Publications

JOURNAL PAPERS

1. **Adnan, A.**, Mahmud, S., Uddin, M.R., Modi, A., Ehsan, M.M., Salehin, S., Energy, Exergy, Exergoeconomic, and Environmental (4E) analyses of thermal power plants for municipal solid waste to energy application in Bangladesh, Elsevier, *doi.org/10.1016/j.wasman.2021.08.006*
2. Mahmud, S., **Adnan, A.**, Khan, S.S., Rahman, M.H., Study of Incident Drag Response of Hyperloop Pod Based on Change in Aerodynamic Brake Plate Orientation, Transactions of the Canadian Society for Mechanical Engineering, Canadian Science Publishing, *doi.org/10.1139/tcsme-2020-0038*

CONFERENCE PRESENTATIONS

1. **Adnan, A.**, Hasan, A., Shakeel, M.R., Mokheimer, E.M.A., Application of Machine Learning Classification Models in the Prediction of Lean Flame Blowout for Premixed Methane Combustion [Paper Presentation], 12th European Combustion Meeting, The British Section of the Combustion Institute (BCI), Edinburgh, UK
2. Mahmud, S., Khan, S.S., **Adnan, A.**, Rahman, M.H. (presenter), Effect of Variation of Aerodynamic Brake Plate Orientation on Incident Drag of Hyperloop Pod [Paper Presentation], 10th TSME International Conference on Mechanical Engineering, Thai Society of Mechanical Engineers, Pattaya, Thailand

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