

FMH606 Master's Thesis 2024

Process Technology

Simulation of ammonia cracker process with Aspen HYSYS



Vahid Farokhi

Faculty of Technology, Natural sciences and Maritime Sciences
Campus Porsgrunn

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Student: Vahid Farokhi

Supervisor: Per Morten Hansen

Co-Supervisor: Lars Erik Øi

External partner: Wärtsilä, Grønn Plattform Project

Summary:

Ammonia is recognized as a promising marine fuel due to its potential to reduce emissions especially CO₂, serving both as an energy carrier and a clean fuel. In 2018, the International Maritime Organization (IMO) set targets to reduce greenhouse gas emissions from international shipping by at least 50% by 2050, aiming for complete elimination by 2100.

This MSc thesis is a continuation of the work done in the MSc group project (at USN, autumn 2023). New contributions include addressing the weaknesses identified in that project by reducing some of the proposal simplifying assumptions.

In this study, a centralized ammonia cracking process is simulated using Aspen HYSYS V12 with available data from the literature. In the simulation phase, a base case was established, then four other cases were simulated with the aim to maximize energy recovery from the waste heat of the cracker product. The improvement evolved through different versions of the improved case, culminating in the final version. For the base case with no heat recovery, the produced H₂/NH₃ total feed on a kg/kg basis was evaluated as 0.1282 while for the final version of the improved case it was calculated to 0.1404.

To determine the most efficient case, the Levelized Cost of Hydrogen (LCOH) was evaluated and compared. The final version of the improved case, with the highest hydrogen production rate (585.8 kgmoles/h hydrogen from 500 kgmoles/h total ammonia feed) and the lowest LCOH (less than 6 USD/kg H₂), was deemed the most efficient.

Recommendations for further work include tackling inherent uncertainties in the simulation like inclusion of catalyst data, defining furnace instead of Gibbs reactor and using data from the adsorption module of Aspen to precisely model the adsorption phenomena and conducting uncertainty analysis on the LCOH evaluations to obtain more reliable techno-economic analysis.

Preface

This document is prepared as part of the FMH606 master's thesis course, under the supervision of Associate Professor Per Morten Hansen and Professor Lars Erik Øi at the University of South-Eastern Norway, Campus Porsgrunn. This thesis pursue the primary objective of the Wärtsilä green platform project which is to promote the use of ammonia as a hydrogen carrier in the energy market. This strategy involves transporting hydrogen in the form of ammonia with one ship and then transferring it to another vessel equipped with an onboard cracker unit.

In autumn 2023, four USN students and I collaborated to establish our MSc group project based on the goals defined in the Wärtsilä green platform project. However, for simplicity, we made some simplifying assumptions. In this MSc thesis, as a continuation of the group project, I have worked on refining the simulations presented in that project to address the assumptions and make the results more reliable with respect to experimental data from the literature. Additionally, a techno-economic analysis has been conducted to identify the most efficient case among those presented.

The MSc project report is available upon request. Please note that understanding the report may require some software skills, specifically in the use of Aspen HYSYS (version 12).

I would like to express my heartfelt gratitude to my supervisors, whose support, knowledge, and motivation have played a crucial role in shaping the direction and substantial content of this thesis.

Porsgrunn, 25th of May 2024

Vahid Farokhi

Contents

| | | |
|----------|---|-----------|
| 1 | Introduction | 7 |
| 1.1 | Background | 7 |
| 1.2 | Objectives and perspectives | 8 |
| 1.3 | Methodology | 8 |
| 2 | Literature review | 10 |
| 2.1 | General overview | 10 |
| 2.2 | Ammonia cracking simulation..... | 12 |
| 3 | Ammonia cracking simulation | 16 |
| 3.1 | Methodology and software | 16 |
| 3.2 | Base case | 18 |
| 3.2.1 | <i>Description.....</i> | <i>19</i> |
| 3.2.2 | <i>Results</i> | <i>21</i> |
| 3.3 | Energy consumption improved case..... | 22 |
| 3.3.1 | <i>Model description, improved cases</i> | <i>22</i> |
| 3.3.2 | <i>Simulation results comparison, MSc thesis cases.....</i> | <i>26</i> |
| 3.4 | Cost estimation | 27 |
| 3.4.1 | <i>Methodology.....</i> | <i>27</i> |
| 3.4.2 | <i>Base model</i> | <i>30</i> |
| 3.4.3 | <i>Improved model (1st version)</i> | <i>32</i> |
| 3.4.4 | <i>Improved model (2nd version)</i> | <i>33</i> |
| 3.4.5 | <i>Improved model (3rd version).....</i> | <i>34</i> |
| 3.4.6 | <i>Improved model (Final version).....</i> | <i>34</i> |
| 3.4.7 | <i>Comparison of the models.....</i> | <i>35</i> |
| 4 | Discussion..... | 37 |
| 4.1 | Results comparison..... | 37 |
| 4.2 | Uncertainty of the results | 38 |
| 4.3 | Recommendation for future studies | 38 |
| 5 | Conclusion | 40 |
| 6 | References..... | 42 |
| 7 | Appendices..... | 44 |

Nomenclature

Units

| | |
|--------------------|--------------------------------|
| kgmoles/h | Molar flow, moles per hour |
| kg/h | Mass flow, kilograms per hour |
| kJ/h | Heat flow, kilojoules per hour |
| Nm ³ /h | Normal cubic meter per hour |

Symbols

| | |
|------------|--|
| ΔG | The Gibbs free energy change, kJ/mol |
| ΔH | The enthalpy change, kJ/mol |
| T | Temperature, Celsius (°C) and Kelvin (°K) |
| P | Pressure, Pascal (Pa), Kilopascal (kPa), Megapascal (MPa), Bar (bar) |

Chemical Formulas

| | |
|------------------|-----------------|
| CH ₄ | Methane |
| CO | Carbon monoxide |
| CO ₂ | Carbon dioxide |
| H ₂ | Hydrogen |
| MeOH | Methanol |
| N ₂ | Nitrogen |
| N ₂ O | Nitrous oxide |
| NH ₃ | Ammonia |
| NO _x | Nitrogen oxides |
| SO _x | Sulphur oxides |

Acronyms

| | |
|-----------------------------------|---|
| Ru/Al ₂ O ₃ | Catalyst composed of ruthenium (Ru) supported on aluminum oxide (Al ₂ O ₃) |
| CCS | Carbon capture and storage |
| CRF | Cost Recovery Factor |
| C _{RM} | Raw Material Cost |
| C _L | Labor Cost |
| C _U | Utility Cost |
| EEDI | Energy Efficiency Design Index |
| EEXI | Efficiency Existing Ship Index |
| FCI | Fixed Capital Investment |
| GHG | Greenhouse gas |
| HE | Heat Exchanger |
| HRS | Hydrogen Refueling Stations |
| HYSYS | Hyprotech Systems |
| IMO | International Maritime Organization |
| LCOH | Levelized Cost of Hydrogen |
| LNG | liquefied natural gas |
| PFD | Process Flow Diagram |
| PM | particulate matter |
| PR | Peng-Robinson |
| PSA | Pressure Swing Adsorber |
| TCI | Total Capital Investment |
| TSA | Temperature Swing Adsorber |
| UHC | Unburned hydrocarbons |
| WCI | Working Capital Investment |

1 Introduction

This thesis explores the potential of ammonia as a hydrogen carrier and clean fuel, particularly in the maritime industry. The introduction will provide an in-depth background on the environmental impact of traditional marine fuels and the industry's shift towards sustainable alternatives. Then, the objectives and perspectives of the research will be outlined, focusing on simulating the ammonia cracking process and optimizing it for better energy efficiency and cost-effectiveness. Finally, the methodology employed in this study will be briefly introduced.

1.1 Background

Ships play a significant role in global warming by releasing various greenhouse gases (GHGs) such as carbon dioxide (CO_2), nitrous oxide (N_2O), and methane (CH_4). This occurs as they consume more than 300 million tons of fossil fuels annually. Considering increasing awareness regarding the environmental impact of conventional marine fuels and stricter emissions standards, the maritime industry is actively pursuing sustainable alternatives. The Paris Agreement has spurred the industry to commit to reducing greenhouse gas (GHG) emissions. In 2018, the International Maritime Organization (IMO) initiated a strategy aiming to cut GHG emissions by at least 50% by 2050 compared to 2008 levels. While specific tactics to achieve this target are still in development, the IMO has implemented interim measures like the Energy Efficiency Design Index (EEDI) for new vessels and the Energy Efficiency Existing Ship Index (EEXI) for existing ships, started in 2023. These measures are part of a broader initiative to align with the industry's long-term emission reduction goals and promote sustainability. The adoption of alternative, low-carbon marine fuels, notably ammonia (NH_3), is a crucial strategy, with liquefied natural gas (LNG) and methanol (MeOH) also emerging as cleaner fuel options, albeit not entirely carbon-free, while still being compatible with existing infrastructure.[1]

Ammonia plays a dual role, serving as both an efficient energy carrier and a clean fuel. Its effectiveness as an energy carrier stems from its capacity to store and transport hydrogen efficiently, eliminating the need for energy-intensive cryogenic storage. Additionally, ammonia can directly function as a low-emission fuel, particularly in internal combustion engines, where it has the potential to significantly decrease emissions of CO_2 , CO, unburned hydrocarbons (UHC), particulate matter (PM), and sulfur oxides (SO_x). As a result, ammonia presents itself as a versatile solution for hydrogen transport and environmentally friendly combustion, offering significant potential for reducing carbon emissions within the shipping industry[2].

This MSc thesis is a continuation of a group project carried out at USN in autumn 2023. The initial project included a brief literature review on ammonia as a hydrogen carrier and focused on thermal ammonia cracking using Aspen HYSYS V12 software. However, the group made several simplifying assumptions in their simulations and did not assess or optimize process costs. Addressing these issues is the main objective of this MSc thesis.

1.2 Objectives and perspectives

In this section, the study outlines the primary objectives and perspectives guiding the research on simulating ammonia cracking. The study aims to achieve several key objectives. First, it seeks to simulate the ammonia cracking process within Aspen HYSYS V12 which is known to be an improvement of the simulation performed in the group project in autumn 2023. This phase involves modeling the ammonia cracking through Gibbs free energy minimization by the aid of Gibbs reactors. Second, the research explores approaches to improve the process of cracking from an energy-consumption point of view. Finally, the study shows a rough cost estimation and optimization based on available data in the literature.

The study is based on the idea that ammonia is more convenient to transport than liquid hydrogen and shows potential as a substitute for hydrogen, which is crucial for clean energy purposes and cutting down greenhouse gas emissions. It acknowledges the importance of simulation tools like Aspen HYSYS V12 for understanding and refining intricate chemical processes. Additionally, it recognizes the significance of energy and cost optimization in improving the efficiency and sustainability of ammonia cracking for hydrogen production.

Note that the complete problem description of the MSc thesis can be found in Appendix A.

1.3 Methodology

In this section, the methodology of the simulation is briefly introduced. A more detailed explanation will be provided in the “Ammonia Cracking Simulation” section.

The core focus of this study is on simulating the ammonia cracking process, utilizing Aspen HYSYS V12 alongside the Peng-Robinson fluid package. The ammonia combustion reaction is modeled as an equilibrium reaction, with kinetic parameters determined by minimizing Gibbs free energy. The simulation is founded on several pivotal assumptions, outlined as follows:

- To enable the combustion of ammonia, a Gibbs reactor was specified instead of a furnace. This step was essential because ammonia could not be defined as fuel within a furnace in Aspen HYSYS V12.
- Defining catalyst kinetics is out of scope of this thesis, hence, the process utilizes Gibbs energy minimization for ammonia cracking. This method presumes thermal cracking, depending on heat to decompose ammonia into hydrogen.
- Instead of utilizing a Temperature Swing Adsorber (TSA) and Pressure Swing Adsorber (PSA), combination of cooler/heat exchanger(s) and component splitters were employed. Compared to the group project (autumn 2023), energy and pressure losses will be considered across the furnace and some other equipment.

Regarding the above-mentioned methodology, a base model will be defined. Next step, the waste heat from the cracker outlet stream (mixture of hydrogen, nitrogen, and unreacted ammonia) will be utilized to preheat the ammonia stream entering the cracker and other streams (air, nitrogen, and the ammonia as fuel to the furnace). For this purpose, a new improved model will be simulated.

Then, to examine the potential of the waste heat of the Gibbs reactor product, the ratio of the ammonia as fuel to the total ammonia feed will be adjusted. To achieve this goal, a second version of the improved case will be generated.

Next by defining the third version of the improved case, an investigation will be performed into the area and numbers of heat exchangers to find out the most efficient configuration.

Finally, the final version of the improved case with a configuration of reasonable cost and energy consumption will be proposed according to a basis of calculated Levelized cost of hydrogen (LCOH).

2 Literature review

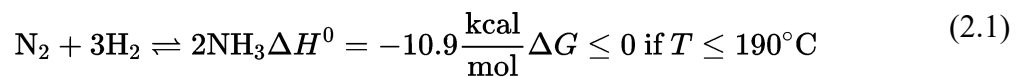
In this chapter, a review of the previous works done in the simulation of ammonia is presented.

2.1 General overview

The maritime sector plays a crucial role in the world economy, handling 80% of global cargo transportation. However, its heavy reliance on fossil fuels makes it a significant contributor to climate change, as a result of considerable greenhouse gas emissions. Ships alone account for nearly 3% of the world's CO₂ equivalent emissions. In response, the International Maritime Organization (IMO) launched a strategy in 2018 aiming to cut greenhouse gas emissions by at least 50% by 2050 compared to 2008 levels. Researchers are exploring various approaches to achieve these reductions, such as integrating technologies like wind and solar power, implementing slow-steaming practices, recovering waste, and applying hull coatings to enhance vessel efficiency. [1]. Furthermore, the embrace of alternative fuels could result in a global reduction in CO₂ emissions. Among these fuels under investigation is pure hydrogen. Yet, its high expenses, storage complexities, and the energy required for compression and liquefaction raise doubts about whether hydrogen will emerge as the dominant energy source for transportation. Another promising alternative is ammonia, regarded as an effective carrier for hydrogen, especially favored by the maritime sector. [2].

Currently, ammonia holds significant promise in driving the transition towards a low-carbon future. Despite its lower heating value of 18.6 MJ/kg (40% of gasoline's energy density), it offers combustion without carbon emissions and boasts a high gravimetric hydrogen content of 17.8%, placing it among the leading energy carriers. With a volumetric energy density of 12.7 MJ/L, it surpasses compressed hydrogen at 69 MPa and 25 °C threefold and lithium-based batteries nearly tenfold. Ammonia presents a compelling solution for the global transportation, storage, and shipping of renewable energy. Moreover, an established liquid ammonia transport network within the fertilizer industry can be repurposed to ensure a dependable, readily accessible, and safe distribution of ammonia as a low-carbon energy carrier. It can also be converted back into hydrogen or utilized directly as fuel, further enhancing its versatility [3].

In 1914, Haber and Bosch developed an industrial method that utilized an iron-based catalyst to create ammonia from mixtures of nitrogen and hydrogen [3].



Presently, ammonia production predominantly depends on fossil fuels, employing the energy-intensive Haber-Bosch process to combine hydrogen and nitrogen, resulting in significant energy consumption and CO₂ emissions. Although ammonia is increasingly being considered as a marine fuel, its production using renewable energy, known as "green" ammonia, is essential for emission reduction. However, the cost-effectiveness of green ammonia is currently lower, and most ammonia production still relies on fossil fuels. An alternative approach, termed "blue ammonia," incorporates carbon capture and storage (CCS) but encounters challenges related to early-stage development and cost-effectiveness [4]. Nonetheless, although ammonia holds promise, it's crucial to investigate inventive approaches, such as ammonia cracking, to

fully realize its potential for hydrogen production and pave the way for a sustainable era of energy utilization.

As the use of ammonia as a hydrogen carrier gains traction, two distinct approaches to its cracking emerge, centralized and decentralized ammonia cracking which is demonstrated in Figure 2.1.

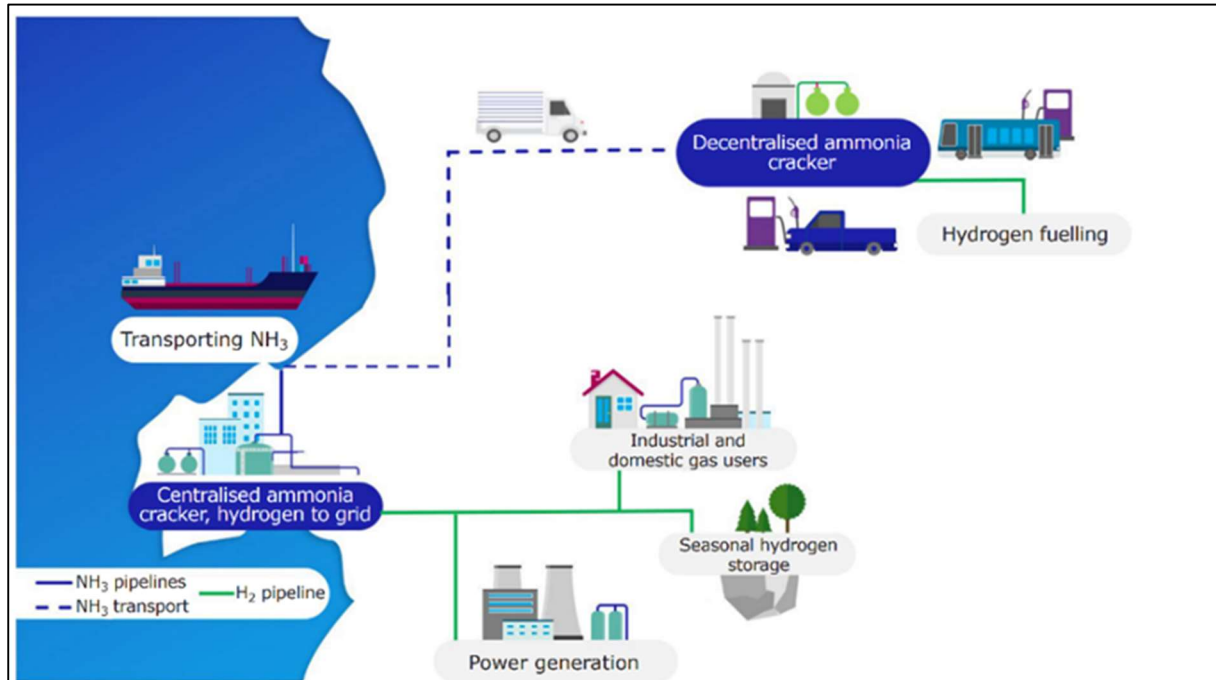


Figure 2.1: The production of hydrogen from ammonia through both centralized and decentralized processing schemes, along with the potential applications of hydrogen [5].

In the centralized scenario, ammonia is transported to a large processing plant where it undergoes cracking to produce hydrogen, which is then distributed to different usage points. Conversely, in the decentralized scenario, ammonia is transported to the site of use, where it is processed onsite to generate hydrogen. The decision between these approaches is influenced by various factors. Centralized systems offer economies of scale and operational efficiency, while decentralized systems entail lower initial costs and operate independently of hydrogen networks. The chosen approach may evolve over time as hydrogen technology advances. The economic viability of these methods is influenced by technology selections and external factors such as hydrogen and ammonia prices [5].

The primary goals of this literature review are centered on utilizing Aspen HYSYS V12 for simulating ammonia cracking. Specific aspects covered in the review include establishing heat recovery and recycle streams within the process, simulating the ammonia cracking process using Aspen HYSYS V12, optimizing the energy consumption and cost of ammonia cracking process, and evaluating the uncertainties and limitations associated with the simulation and calculations. These collective efforts aim to contribute to a deeper understanding of ammonia cracking processes, with a particular focus on their modeling and optimization.

2.2 Ammonia cracking simulation

In 2021, Cha et al. [6] developed an efficient process for sustainable green hydrogen production through ammonia decomposition. Their study employed Aspen Plus for process simulation, utilizing the Peng Robinson thermodynamic model. The process flow diagram is depicted in the Appendix B, Figure 7.1. Pure NH_3 from liquid storage is initially released through a feed valve (10–2.5 bar) at the process outset. The system considers two primary energy sources: isobutane and hydrogen-containing PSA off-gas. Isobutane serves as the start-up heat source to achieve steady-state conditions before transitioning to H_2 in the PSA off-gas, mirroring experimental conditions. For simplicity, it was assumed that 25% of the annual operational time (or 8000 h) would utilize isobutane as fuel. The main heat sinks in the process include ammonia heating, recycled ammonia desorption from the adsorbent material (with a temperature increase from 31 to 310 °C), and endothermic reaction heat from ammonia decomposition. It was assumed that all systems would achieve an ammonia conversion rate of 99%. The flue gas heat released the adsorbed NH_3 , recycling it back into the system. A significant portion of the hydrogen was separated using a PSA section, as the remaining products primarily consisted of a 3:1 mixture of H_2/N_2 . Due to its cost-effectiveness, activated carbon was selected as the adsorbent material, and the PSA section was modeled using Park et al.'s [7] experimentally determined adsorption isotherms of N_2 and H_2 on activated carbon. Under fixed conditions of 2.5 bar and 20 °C, it was determined that approximately 71% of the hydrogen could be recovered (with a purity of 99 mol%), utilizing approximately 200 kg of activated carbon per kilo mole of the PSA inlet gas. The simulation results exhibited a high level of accuracy when compared to experimental results [6].

Another study conducted last year was carried out by Lee et al. [8], focusing on carbon-free hydrogen production using an induction heating-based reactor for ammonia decomposition to achieve a hydrogen production rate of 150 Nm_3/h . This study was conducted both experimentally and through simulation. The process design consists of a reactor for ammonia decomposition, a pre-heater for warming, an adsorption column, and a pressure swing adsorption unit (PSA). Additionally, other equipment such as a tank for storing liquefied ammonia, a pump, heat exchange devices, and another pre-heater for the liquefied ammonia are included (Figure 7.2). As external heat is required for ammonia breakdown, electricity from clean sources like renewables is utilized to ensure the process remains carbon-free and produces green hydrogen. Activated carbon columns are employed to prevent any residual ammonia from entering the PSA columns, which are specifically designed for on-site hydrogen production. For the simulation, liquefied ammonia is supplied from the storage tank, the pressure is increased via a pump, and the ammonia flows into a pre-heater to be heated using residual heat generated from the ammonia decomposition reaction. Notably, some experimental data is utilized in the simulation, including a fixed hydrogen recovery rate of 79% for the PSA, and an assumed ammonia conversion rate of over 90.0% based on experiment results obtained using the induction heating reactor at 600 °C and pressure 7 barg. The data for each stream in the process simulation is provided in their paper [8].

Restelli et al. [9] conducted an exhaustive techno-economic analysis of green hydrogen production using ammonia in 2023. This study encompasses various hydrogen production processes, including the centralized ammonia cracking process, wherein all stored ammonia in the inlet is converted to hydrogen and simulated using Aspen Plus. The process flow diagram for this simulation is depicted in Figure 2.2. [9]

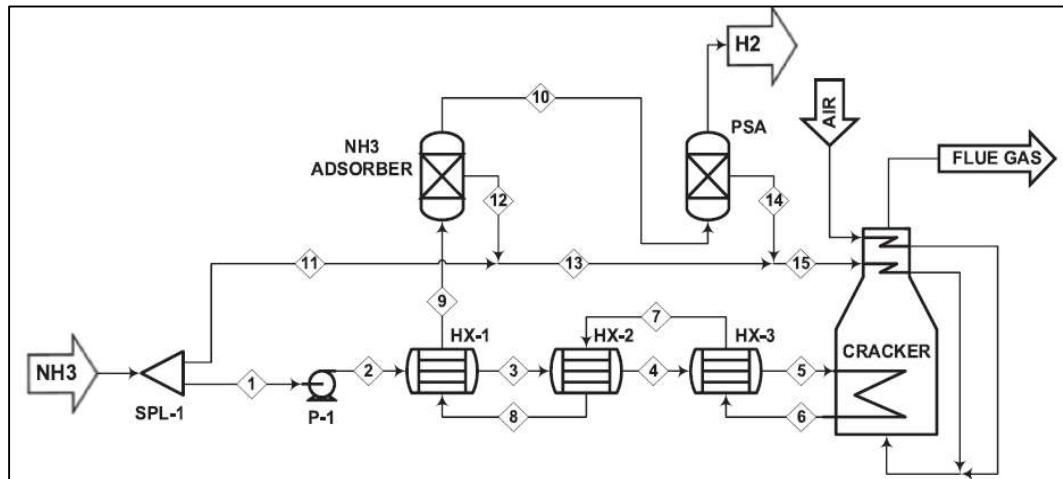


Figure 2.2: Process flow diagram of centralized ammonia cracking [9].

The ammonia stream is pressurized to 30 bars and undergoes preheating in a series of heat exchangers before entering the cracking reactor, leveraging the high enthalpic content of the reaction products. The simulation of this reactor utilizes the Gibbs module within Aspen Plus. Consequently, the conversion of ammonia aligns with thermodynamic equilibrium at the reactor's operating conditions, set at 30 bars and 900 °C. These conditions are in line with those commonly utilized for commercially available nickel-based catalysts. To facilitate the cracking reaction, the required heat is generated by combusting a portion of the supplied ammonia, combined with waste streams containing a high H₂ content originating from the purification section. Air is utilized as an oxidizer in slightly excess quantities to ensure complete combustion. Following the reaction stage, the separation of the hydrogen product from any unreacted ammonia and nitrogen is achieved through PSA. Subsequently, the resulting hydrogen can be distributed based on the requirements of the end user. The specifications of the inlet and outlet streams, including temperature, pressure, and molar composition of each stream in this process, are outlined in Table 2.1 [9].

Table 2.1: Inlet and outlet stream specifications [9].

| Stream Name | NH ₃ | H ₂ | AIR | FLUE GAS |
|------------------|-----------------|----------------|--------|----------|
| T [°C] | -27.6 | 25.47 | 25 | 139 |
| P [bara] | 1.3 | 30 | 1.01 | 1.01 |
| H ₂ | 0 | 0.999 | 0 | 0.0003 |
| N ₂ | 0 | 0.001 | 0.79 | 0.775 |
| H ₂ O | 0 | 0 | 0 | 0.191 |
| NO | 0 | 0 | 0 | 0.0029 |
| NH ₃ | 1 | 0 | 0 | 0 |
| O ₂ | 0 | 0 | 0.21 | 0.0309 |
| FTOT [kgmoles/h] | 592.33 | 698.07 | 608.13 | 999.28 |

Regarding the simplicity of the work done by Restelli et al. [9], it was decided to use their simulation as the basis for the group project in autumn 2023. However, for a more elaborate

ammonia cracking simulation, one needs to have reliable data such as the pressure, temperature, and composition of the inlet/outlet streams to/from the NH_3 adsorber and PSA. In the paper of Restelli et al. [9] no such data is available.

In 2023, Devkota et al.[10] undertook the process design and simulation of onsite hydrogen production from ammonia decomposition. The designed process, illustrated in Figure 2.3, was modelled using Aspen Plus, with the Peng-Robinson model employed to estimate its thermodynamic properties. The study utilized a feed of 4000 kg/h of pure ammonia at 298 K and 10 bar pressure as the basis for calculations. They considered approximately 9% of the ammonia total feed as fuel to the furnace to generate the necessary thermal energy. The reactor product contains a small fraction of uncracked ammonia, which was separated from the forming gas (a mixture of hydrogen and nitrogen) using a two-bed temperature swing adsorption unit (TSA). They claimed that the recovered heat from the flue gas and product gas streams is sufficient to meet the thermal energy requirements for the TSA operation. The uncracked ammonia was then mixed with fresh fuel ammonia and air before being returned to the fired furnace via a preheater [10].

Then, the hydrogen and nitrogen-containing stream was directed to a four-bed pressure swing adsorption unit for hydrogen purification. They considered a significant fraction of hydrogen gas along with nitrogen in the waste stream from the pressure swing adsorption, which was sent to the ammonia-fired furnace to generate thermal energy. They believe that this recycled stream contributes to fuel savings in NH_3 , enhances the adiabatic flame temperature, and increases laminar flame velocity when blended [10].

The study employed a steady-state model of a multi-catalytic packed bed reactor for ammonia decomposition, with an intermediate heating system incorporated to improve the reaction rate. Ammonia could undergo decomposition at either atmospheric pressure or higher. Decomposition at elevated pressure could potentially reduce costs but might marginally decrease conversion rates. Additionally, it is worth noting that in their study, ammonia gas was heated in a fired furnace to achieve a decomposition temperature of 773 K before entering the reactor, and a catalyst consisting of $\text{Ru}/\text{Al}_2\text{O}_3$ was utilized for the decomposition [10].

Devkota et al. also optimized ammonia decomposition, combustion, and NO_x reduction by dividing the catalytic bed, increasing ammonia decomposition efficiency from 34.6% to 97.21%. The process produces 514 kg/h of 99.99% pure hydrogen from 4000 kg/h of ammonia, saving 22% of fuel through techniques such as waste heat preheating and combustion. Hydrogen introduction raises adiabatic flame temperature and NO_x emissions, reduced by 30% through flue gas recirculation for sustained efficiency. This aligns with broader energy optimization goals, emphasizing process integration, waste heat recovery, and combustion efficiency, addressing environmental impact through NO_x reduction [10].

Devkota et al. assessed the techno-economic and environmental aspects of hydrogen production from ammonia decomposition. Their economic analysis encompasses detailed cost estimation, sensitivity analysis of process and economic parameters, uncertainty analysis, and profitability assessment based on their simulation results. They investigated the impact of different process parameters and evaluated economic parameters (CAPEX and OPEX) for the assessment of LCOH [10].

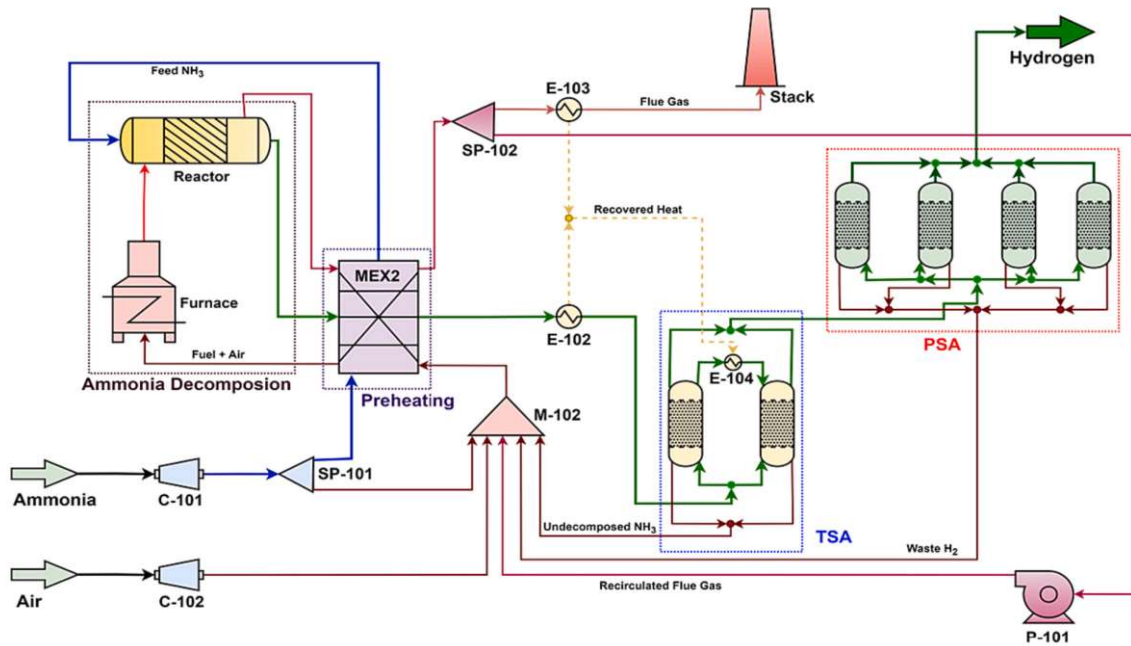


Figure 2.3: Process flow diagram of ammonia cracking, simulated by Devkota et al. [10].

They have provided more details on the process development of ammonia decomposition, combustion, NO_x analysis, and NO_x controls, in their previously published study [11].

Due to the novelty of their work and the availability of data simulation data and cost estimation parameters, their study([10] & [11]) was chosen as the basis for simulation in this thesis.

3 Ammonia cracking simulation

The primary goal of the Wärtsilä Green Platform project [12] is to promote the utilization of ammonia as a hydrogen carrier in the energy sector. The strategy entails transporting hydrogen in the form of ammonia via one vessel and then transferring it to another vessel equipped with an onboard cracker unit. This unit will operate by converting the ammonia into hydrogen through a cracking process. Simulation of the ammonia cracking process is a pivotal phase in the project's advancement. The primary objective of this thesis is to enhance the reliability of the simulation model presented in the group project (autumn 2023) using Aspen HYSYSV12. The main additional objectives include improving the model's energy efficiency and conducting a techno-economic evaluation to justify the selection of the most efficient model among all the cases presented in this thesis.

3.1 Methodology and software

According to the literature review, two methods for converting ammonia into hydrogen have been considered. The first method involves a centralized approach, wherein ammonia is transported and then cracked into hydrogen at the destination port. The second method entails transporting ammonia to Hydrogen Refueling Stations (HRS), where it is converted into hydrogen [9].

In the group project conducted in autumn 2023, the ammonia cracking unit was considered as an onboard centralized station. Therefore, as this thesis builds upon the group project, the simulation processes are conducted using available open data from the literature to model this approach accordingly.

To model the ammonia cracking process, Aspen HYSYS V12 was chosen primarily for its simplicity and accepted reliability. Considering the pressure, temperature, and composition of the streams in this process, the Peng-Robinson fluid package was deemed most suitable. For the reactions, specifically for burning ammonia as fuel, equation (3.1), the "Gibbs reaction only" type was selected.



In this study, the ammonia cracking model presented by Devkota et al. [10] depicted in Figure 2.3 is simulated regarding the data availability. In this process design, liquid ammonia with an initial condition of 25 °C, 1 MPa, and a molar flow rate of 500 kgmoles/h, is divided into two separate flows, one designated for use as cracker feedstock, and the other part is utilized as fuel to the furnace. The product stream from the decomposition unit contained a small amount of unreacted ammonia. Table 3.1 shows the specification of the inlet/outlet streams to/from the decomposition reactor for the simulation model of Devkota et al. [10]

Table 3.1: specifications of the ammonia cracking reactor, [10]

| | Inlet | Outlet |
|-----------------|---------------------------|--------|
| Temperature, K | 773 | 702 |
| Pressure, bar | 10 | 9.995 |
| Flowrate, kg/h | 3640 | 3640 |
| | Composition, mole percent | |
| NH ₃ | 100 | 2.80 |
| H ₂ | 0 | 24.30 |
| N ₂ | 0 | 72.90 |

The unreacted ammonia was separated from the decomposed hydrogen and nitrogen gas mixture using a two-bed TSA unit. It was then sent to the furnace along with the fresh fuel, air, and nitrogen stream from a PSA. [11]

The waste heat from the product is a noticeable source of energy since it has a high temperature of around 450 °C that can be utilized in energy optimization. In a study performed by Devkota et al., it is noted that more than 99.99% pure hydrogen was produced using a four-bed PSA unit. In the waste stream from the PSA, they considered a significant amount of hydrogen along with nitrogen gas, hence it was routed to the furnace to produce thermal energy. These recycled streams contributed to ammonia saving, as well as increased adiabatic flame temperature and laminar flame velocity [11].

Theoretical combustion studies of ammonia with air were conducted using the Gibbs reactor model in Aspen Plus V.12. The Gibbs reactor model is suitable for combustion processes due to its ability to predict maximum forward and backward reaction progress based on Gibbs free energy. Various separation technologies, such as cryogenic, absorption, membrane, and adsorption, can be employed to recover unreacted ammonia. For large-scale ammonia decomposition, the absorption/desorption process is typically more economical [13]. However, for small-scale onsite hydrogen production, the adsorption/desorption process is more cost-effective compared to absorption/desorption [14], [15]. Among these, adsorption stands out as an effective option with lower energy and operating costs for gas separation [11].

In this MSc thesis, a double bed Temperature Swing Adsorption (TSA) system was chosen for ammonia separation from the forming gas. The required energy for the TSA was two orders of magnitude lower than the waste energy of the reactor product.

In this thesis, the TSA was modeled by a component splitter and the heat and pressure drop calculation was performed according to the pressure, temperature, and composition of the inlet/outlet streams to/from the TSA. All these data are taken from the paper of Devkota et al. [11], where they have incorporated purity and recovery data from open-source literature. The operating conditions of the ammonia removal unit are outlined in Table 3.2. [11]

Table 3.2: specifications of the TSA in study by Devkota et al., [11]

| | Adsorption bed | | Desorption bed |
|-----------------|----------------|--------|--------------------------|
| | Input | Output | NH ₃ recovery |
| Temperature, K | 300 | 300 | 693 |
| Pressure, bar | 9.995 | 9.808 | 9.505 |
| Flowrate, kg/h | 3640 | 3442 | 198 |
| | Composition, % | | |
| NH ₃ | 2.80 | 0.00 | 100 |
| H ₂ | 24.30 | 75.00 | Trace |
| N ₂ | 72.90 | 25.00 | Trace |

In the study performed by Devkota et al. [11], a PSA process consisting of four beds and eight steps, with two pressure equalizations, was implemented for hydrogen separation from nitrogen. The forming gas stream from the TSA unit was directed to the PSA unit. For this analysis, hydrogen purity and recovery were set at 99.99% and 80%, respectively. [11]

In this study, the PSA was modeled by a component splitter and the heat and pressure drop calculation was performed according to the pressure, temperature, and composition of the inlet/outlet streams to/from the PSA. The relevant process parameters of the nitrogen removal unit are detailed in Table 3.3.

Table 3.3: specifications of the PSA in study by Devkota et al., [11]

| | Adsorption bed | | Desorption bed |
|-----------------|-------------------------------------|-------------------------|--------------------------------------|
| | Feed N ₂ /H ₂ | Product: H ₂ | Waste N ₂ /H ₂ |
| Temperature, K | 300 | 300 | 300 |
| Pressure, bar | 9.808 | 9.31 | 1.5 |
| Flowrate, kg/h | 3442 | 514 | 2928 |
| | Composition, % | | |
| NH ₃ | 0 | 0.00 | 0.00 |
| H ₂ | 75 | 99.99 | 0.3444 |
| N ₂ | 25 | 0.01 | 65.56 |

3.2 Base case

This section presents and examines the results obtained from the base case model simulated in this study. This base model is constructed according to literature studies, especially the work performed by Devkota et al. and it is essential to emphasize that no heat recovery or energy optimization measures were incorporated in this model.

3.2.1 Description

Figure 3.1 illustrates the Process Flow Diagram (PFD) of the base model as presented in the group project (autumn 2023) for simulating ammonia cracking.

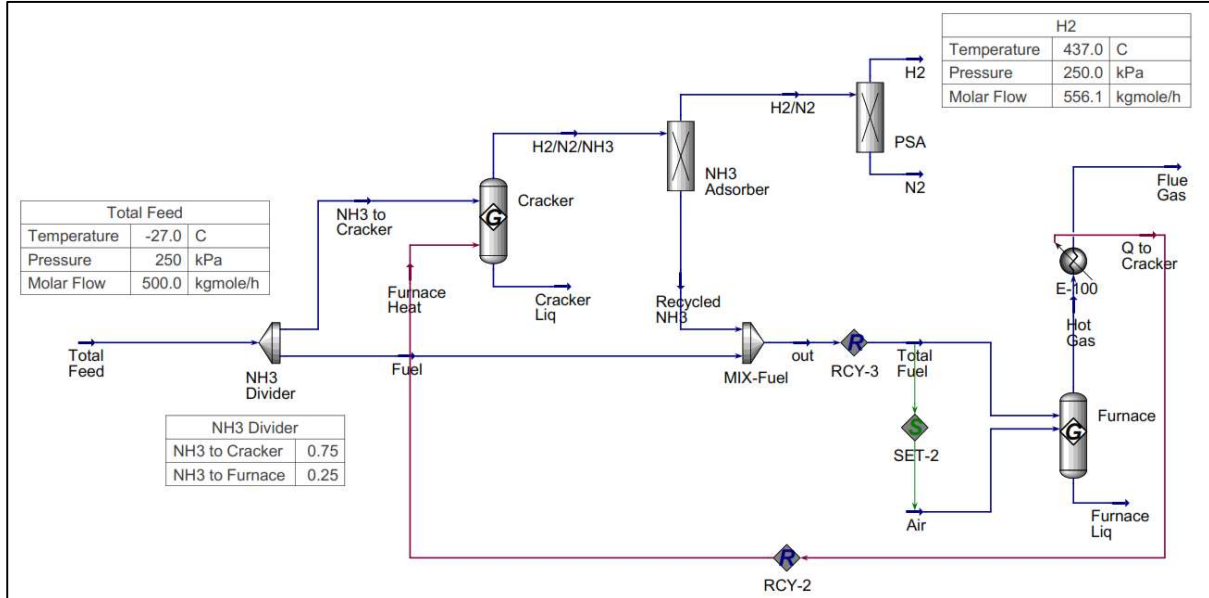


Figure 3.1: PFD of ammonia cracking (Base model), group project (autumn 2023)

It is important to mention that certain challenges were encountered, leading to the introduction of simplifying assumptions, which were addressed in detail in the group project report. Here, the encountered issues are briefly summarized as follows:

- Defining a furnace in Aspen HYSYS V12 that could utilize ammonia as a fuel. To address this problem, a Gibbs reactor was introduced instead of the furnace, and then supplied heat for the cracker reactor.
- In the cracker reactor, minimization of Gibbs energy was opted. In the group project, this choice was made due to lack of catalyst data and kinetic reactions. Some catalyst data are available in Devkota et al. paper, however, it is not part of the scope in this thesis and hence will be discarded.
- Defining an adsorber to separate the unreacted ammonia and a Pressure Swing Adsorber for separation of nitrogen from hydrogen. In the group project, for this purpose, two component splitters were considered. In this thesis, the problem was tackled similarly but in a more realistic way which will be discussed in the following.

Figure 3.2 presents the Process Flow Diagram (PFD) of the base model simulated in this thesis, considering the above-mentioned notes for simulating ammonia cracking.

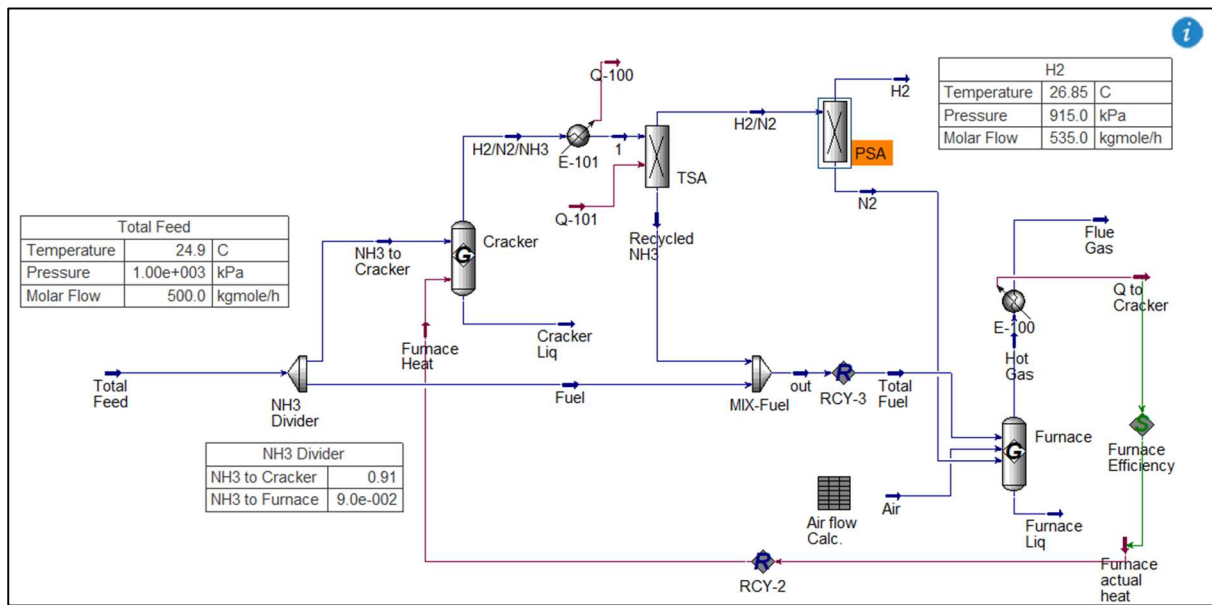


Figure 3.2: PFD of ammonia cracking (Base model), present study.

Comparing the base case in this study to the base case in the group project (autumn 2023), these points are worth mentioning:

- As mentioned earlier, this study uses the paper of Devkota et al. as the basis for simulation hence some certain data such as the pressure and temperature of the feed and the proportion of the ammonia as fuel is different from the group project. In this study for the base case only 9% of the fresh feed ammonia was considered to generate heat energy required for ammonia cracking while for the base case in the group project it was 25%.
- Note that in the group project the component splitters were introduced under the assumption of no heat and pressure losses, with 100% efficiency which seems unrealistic. In this thesis, a Temperature Swing Adsorber and a Pressure Swing Adsorber were simulated for separation of unreacted ammonia and hydrogen purification respectively. The pressure loss and energy consumed were calculated according to available data in Table 3.2 and Table 3.3 [11].
- In the group project, the reactor product was sent to the ammonia adsorber (a simple component splitter), at very high temperature, which is not applicable, since the ammonia will be adsorbed to the surface of the bed at a relatively low temperature, whereas in this study, the product is cooled down to 25 °C before entering the adsorption column of the TSA.
- Pressure and heat loss have been allocated for Gibbs reactors and splitters while in the group project no pressure and heat loss were considered. the pressure losses are based on the pressure streams in the Devkota et al. paper [11]. An efficiency of 90% was assigned to the furnace as a rule of thumb.
- Unlike the group project, since the PSA is not ideal (with an efficiency of 80%), the nitrogen stream out of the PSA contains 35% hydrogen on molar basis which is sent to the furnace to be burnt along with the ammonia as fuel, unreacted ammonia, and air.

- The unreacted ammonia in the group project was considered to be pure ammonia due to 100% efficiency of the ammonia adsorber while in this study the TSA is not ideal and regarding the adopted experimental data of the inlet/outlet streams in Devkota et al. paper [11], the unreacted ammonia stream out of the nonideal TSA contains 26% hydrogen and 9% nitrogen on molar basis which is sent to the furnace to be burnt along with the ammonia as fuel, air and nitrogen streams.
- According to introduction of a new stream to the furnace, a stoichiometric calculation was performed to completely burn the hydrogen contained in the nitrogen and unreacted ammonia streams.

3.2.2 Results

As previously indicated, a centralized ammonia cracking system was considered in this thesis, with an ammonia feed rate of 500 kgmoles/h at an inlet pressure of 1 MPa and temperature of 25 °C. For the base scenario, 455 kgmoles/h of ammonia was introduced as the feedstock stream (NH₃ to the Cracker), constituting 91% of the total feed. This feed enters the Gibbs reactor proposed as the cracker unit. Considering all above-mentioned assumptions, the resulting product is a mixture of hydrogen, nitrogen, and unreacted ammonia, with a total molar flow rate of 893.4 kgmoles/h. The ammonia conversion rate achieved for the base case in the cracker is 98.15%.

It is important to note that the heat required for the Gibbs reactor to achieve this conversion rate is generated by burning 9% of the total feed as fuel (65 kgmoles/h), in addition to the unreacted ammonia (25.4 kgmoles/h) separated by the TSA. The separated H₂/N₂ stream is then directed to another component splitter, which simulates the application of a PSA with proposed pressure and energy losses, resulting in a final production of 535 kgmoles/h hydrogen and 333 kgmoles/h of nitrogen. Note that 35% mole of the nitrogen stream is hydrogen that is sent to be burnt in the furnace.

Considering the total ammonia feed of 500 kgmoles/h and the final hydrogen production of 535 kgmoles/h, the overall yield of ammonia to hydrogen for the entire process is 71.33%. The simulation results of the base case are presented in Table 3.4.

Table 3.4: Results of the process simulation, the base case

| | | | | |
|----------|------------------------------|-------|--|--|
| Ammonia | Total Feed (kgmoles/h) | 500 | Cracker feed (kgmoles/h) | 455 |
| | Ammonia as fuel (kgmoles/h) | 45 | Burned in Furnace (kgmoles/h) | NH ₃ (16.6) H ₂ (6.6) |
| | Cracker conversion (%) | 98.15 | Total Conversion (%) | 71.33 |
| Hydrogen | Total Production (kgmoles/h) | 535 | Total hydrogen to ammonia (kgmoles/kgmoles)/ (kg/kg) | 1.07/ 0.1282 |

By review of the simulation results for the base case, some points are worth discussing:

The high conversion of ammonia in the cracker, 98.15%, is due to the high amount of energy supplied by burning about 12.32% of the total ammonia in the furnace plus a small amount of hydrogen in the unreacted ammonia stream.

The amount of waste energy taken by the cooler located between the cracker and the TSA is considerable and equal to 11.3 GJ/h which could be considered as a potential source for optimization and improvement of the system.

Compared to the base case in the group project, the hydrogen production has decreased by 3.7% which is mainly attributed to the assigned efficiency of 90% to the furnace. The energy optimization will be performed and presented as the improved case in the following section.

3.3 Energy consumption improved case

In this section, efforts have been made to utilize the available waste heat within the process, which is the heat absorbed by a cooler (later replaced with a heat exchanger) located between the cracker and the TSA (Figure 3.2).

Note that in the group project (autumn 2023), the waste heat was taken as the heat of the hydrogen and nitrogen product streams since no heat loss was considered across the NH_3 adsorber that is unreasonable, because as mentioned earlier, the cracker product stream must be cooled down before entering the NH_3 adsorber hence the temperature of the ammonia contacting the adsorber bed will be low enough (around 25 °C), leaving not much heat to be used for optimization downstream the TSA.

To pursue improvement of the base model from the energy consumption point of view, a new case known as the "energy consumption improved case" was introduced. Henceforth, we will simply denote it as the "improved case" for simplicity.

3.3.1 Model description, improved cases

For the improved case, firstly, five shell and tube heat exchangers were employed to transfer heat between the cracker hot product and the following streams to cool down the product to an acceptable temperature of 25 °C before entering the TSA.

1. Ammonia stream to the cracker, HE#1
2. The air stream to the furnace, HE#2
3. The nitrogen stream from the PSA, HE#3
4. The ammonia as fuel, HE#4
5. The cold-water stream, adjusting the final product temperature to 25 °C. HE#5

The flowsheet of the first version of the improved case is shown in Figure 3.3.

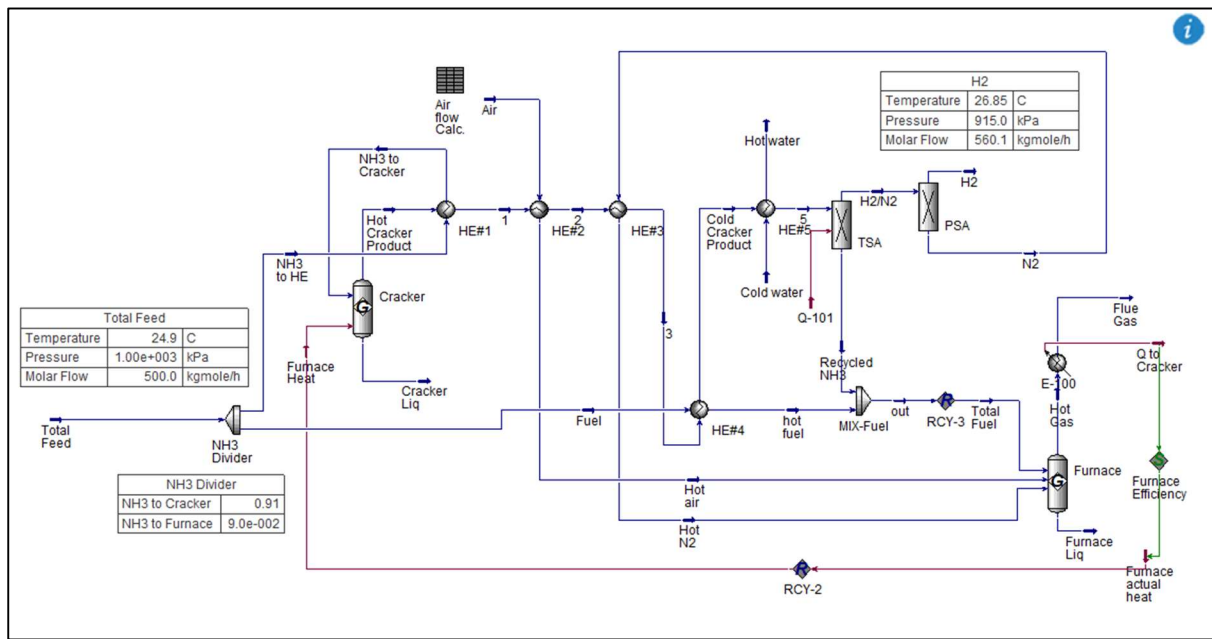


Figure 3.3: PFD of ammonia cracking (improved model), 1st version.

At this stage, the minimum approach temperatures proposed for the heat exchangers are 30 °C for HE#2 to HE#4 and 20 °C for HE#5, except for HE#1. This choice is made because assuming a similar minimum approach temperature for HE#1 would result in most of the heat being transferred by this heat exchanger, leaving only a small amount of energy for the rest of the heat exchangers. Further discussion on this matter will be presented later in this thesis.

The addition of these heat exchangers is projected to increase the final hydrogen production by 4.8%, resulting in a value of 560.1 kgmoles/h compared to 535 kgmoles/h for the base model. While this demonstrates an improvement, it may not necessarily be deemed favorable as it's essential to consider the cost implications of installing new equipment to achieve this production increase. This aspect will be evaluated and discussed further in the cost estimation chapter.

Another important concern about optimization is the conversion rate of ammonia in the cracker reactor. For the first version of improved case, the Gibbs reactor conversion rate is 99.94% which implies that further optimization of energy for this simulation may be unnecessary, unless lowering the heat supplied to the Gibbs reactor by decreasing the amount of ammonia used as fuel in the furnace. The reason is that higher heat provision for a reactor with nearly complete conversion, would require additional ammonia for effective cracking.

To unlock optimization potential, the proportion of fuel to the total ammonia feed was reduced from 9% to 2%, while leaving the remaining parameters unchanged. This adjustment resulted in a hydrogen production of 582.2 kgmoles/h, representing an 8.8% increase compared to the base model. The second version of the improved case is illustrated in Figure 3.4.

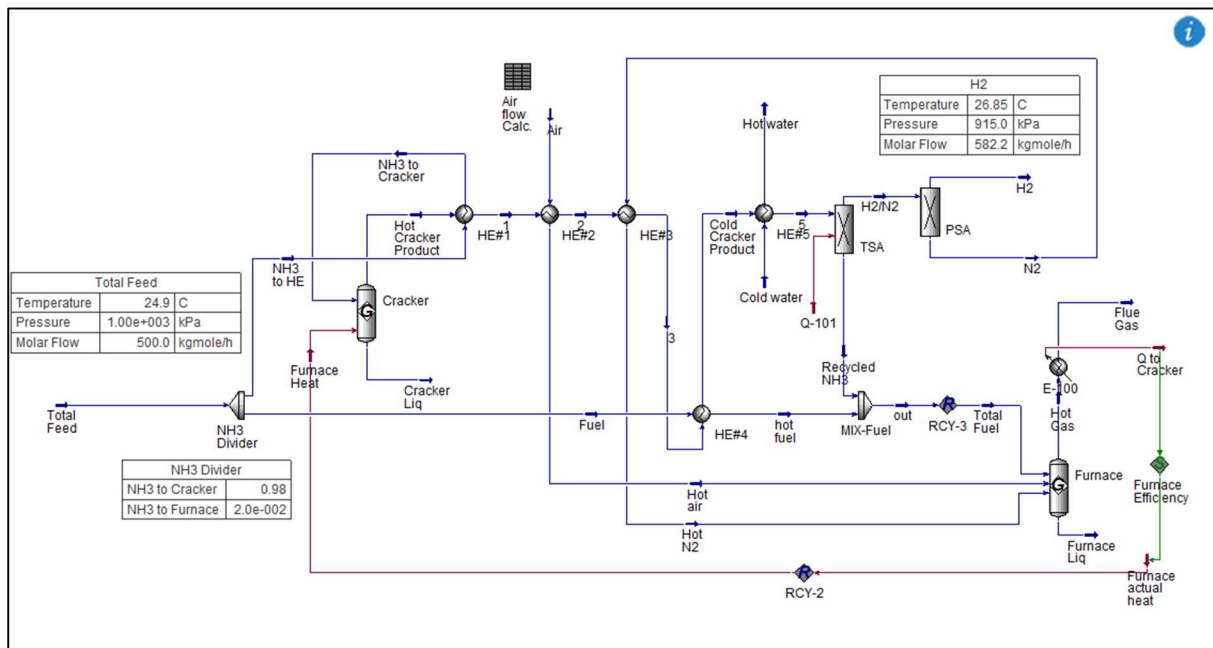


Figure 3.4: PFD of ammonia cracking (improved model), second version.

While the second version of the improved model demonstrates an 8.8% increase in hydrogen production compared to the base model, it is essential to assess the economic viability of installing the heat exchangers. This aspect will be explored in the cost estimation section. Additionally, the next step involves adjusting the minimum approach temperature of the heat exchangers to further optimize energy consumption and increase hydrogen production. The objective is to enhance heat transfer between the hot cracker product and the air, nitrogen, and fuel streams using HE#1 to HE#4, while minimizing heat transfer between the cracker product stream and cold water via HE#5. HE#1's proposed minimum approach temperature is set at 18 °C to maximize heat transfer and facilitate ammonia cracking by directly heating the ammonia stream. However, it's important to note that lowering the minimum approach temperature of HE#1 may lead to a decrease in the hot outlet stream temperature, potentially causing temperature cross errors in other heat exchangers.

For HE#2, HE#3, and HE#4, the minimum approach temperature is set at 15 °C. As for HE#5, the minimum approach temperature is set at 20 °C. This decision is based on ensuring that the final temperature of the cold cracker product remains at 25 °C (prior to entering the TSA), with the proposed inlet temperature of the cold-water being 5 °C. Figure 3.5 depicts the flowsheet for the third version of the improved case.

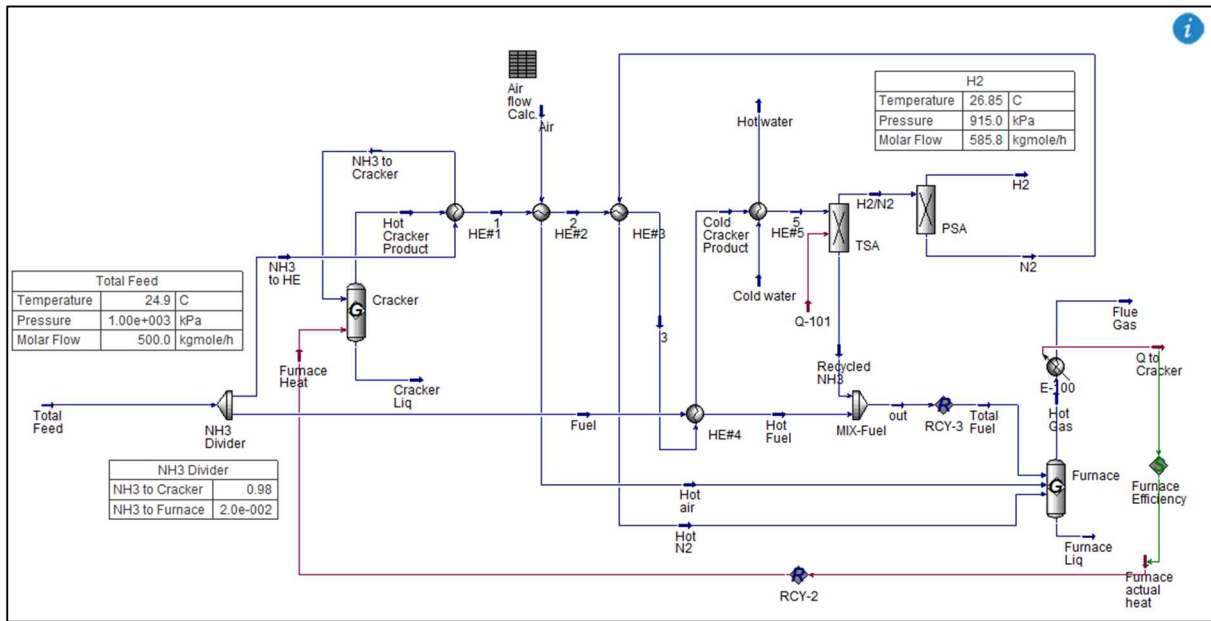


Figure 3.5: PFD of ammonia cracking (improved model), third version.

As depicted in the flowsheet for the third version, altering the minimum approach temperature for the heat exchangers has yielded a minor effect on hydrogen production, leading to increases of 9.4% and 0.6% compared to the base model and the second version of the improved case, respectively. Once again, it should be emphasized that the superiority of this model should be investigated considering the cost share of modified heat exchangers in terms of their area based on the updated minimum approach temperatures.

Considering the minimal duty of the heat exchangers, a final improved case will be outlined, wherein HE#2 and HE#3 have been excluded. While this could be a prudent suggestion given their minimal duty, further examination is warranted in the cost estimation section. This will involve defining a sensible parameter to account for hydrogen production costs, known as the levelized cost of hydrogen (LCOH). The process flowsheet for the final version of the improved case is illustrated in Figure 3.6.

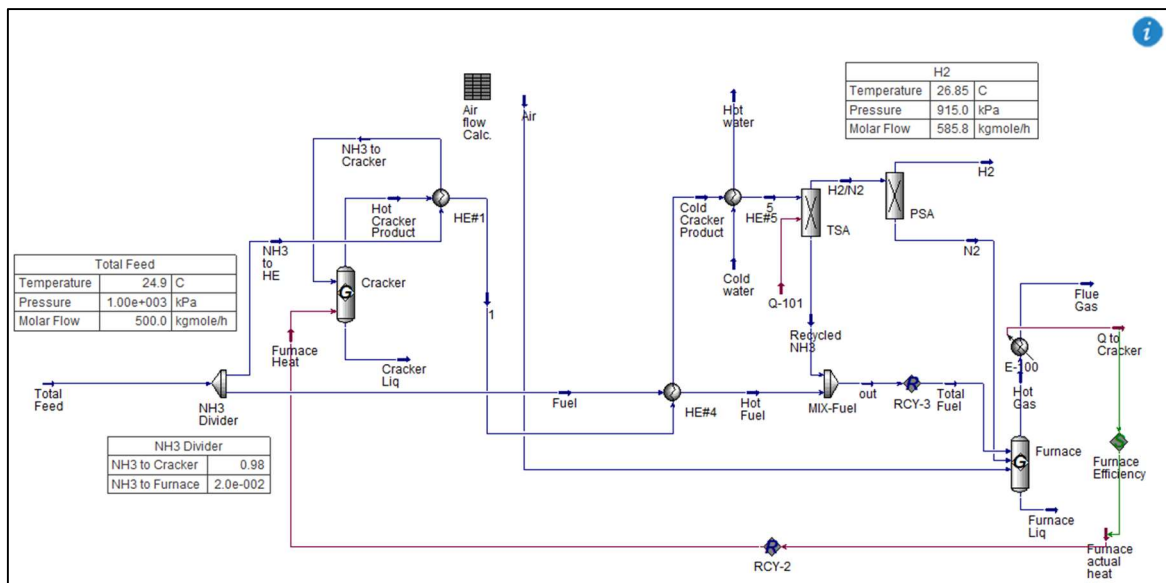


Figure 3.6: PFD of ammonia cracking (improved model), final version.

Following the description of the various versions of the improved case, the results will be presented in greater detail in the subsequent section for illustrative purposes.

3.3.2 Simulation results comparison, MSc thesis cases

In this part, the results of the improved case (1st, 2nd, 3rd, and final versions) will be presented and compared to the base model.

The total ammonia feed specification remains consistent for all models, with 500 kgmoles/h of ammonia at 25 °C and 1 MPa entering the process unit. Table 3.5 provides a comparison of the specifications and results across the models.

Table 3.5: Results comparison of the ammonia cracking simulation, the improved cases and the base model.

| Model name | Unit | Improved case | | | | |
|---|-----------------|---------------|-------------|-------------|-------------|---------------|
| | | Base case | 1st version | 2nd version | 3rd version | final version |
| Total feed | kmol/h | 500 | 500 | 500 | 500 | 500 |
| Ammonia to cracker | kmol/h | 455 | 455 | 490 | 490 | 490 |
| Ammonia to furnace | kmol/h | 45 | 45 | 10 | 10 | 10 |
| NH ₃ ratio as fuel | % | 9 | 9 | 2 | 2 | 2 |
| Cracker conversion rate | | 98.14% | 99.94% | 98.16% | 98.47% | 98.47% |
| Cracker product temperature | °C | 452 | 928 | 553 | 470 | 470 |
| Cracker heat | GJ/h | 40.95 | 55.17 | 44.14 | 44.8 | 44.8 |
| Furnace heat | GJ/h | 40.95 | 45.81 | 34.06 | 32.6 | 32.6 |
| Heat transferred to NH ₃ to cracker (HE#1) | GJ/h | - | 9.36 | 10.08 | 12.2 | 12.2 |
| Furnace share in cracking | % | 100 | 83.0 | 77.2 | 72.8 | 72.8 |
| HE#1 Share in cracking | % | - | 17.0 | 22.8 | 27.2 | 27.2 |
| No. of heat exchangers | - | 1 | 5 | 5 | 5 | 3 |
| Hydrogen production | kmol/h | 535 | 560.1 | 582.2 | 585.8 | 585.8 |
| Produced H ₂ /Total NH ₃ | Kgmoles/Kgmoles | 1.07 | 1.1202 | 1.1644 | 1.1716 | 1.1716 |
| | Kg/Kg | 0.1282 | 0.1343 | 0.1396 | 0.1404 | 0.1404 |

In comparison between the base case and the first version of the improved case, the addition of four new heat exchangers has augmented the heat provision for the cracker, leading to a higher conversion rate and an elevation in the cracker product temperature from 452 °C to 928 °C. This substantial increase in temperature has consequently facilitated a conversion rate of 99.94%.

For the first version of improved case, the share of cracking by means of HE#1 is about 17% (Table 3.5). As previously mentioned, for further improvement, it is required to change the share of heat generated by burning fuel to use the potential of energy optimization.

In the second version of the improved case, the percentage of ammonia used as fuel decreases from 9% in the first version to 2%, resulting in a lower cracker conversion rate of 98.16% and a cracker product temperature of 553 °C. Despite a 20% reduction in total heat provided to the cracker compared to the first version (55.17GJ/h in the 1st version versus 44.14GJ/h in the 2nd version, see Table 3.5), there is a 4% increase in hydrogen production. This increase is attributed to a rise in the proportion of heat provided by HE#1 for cracking, from 17% to 22.8%, achieved by reducing the ammonia fuel rate.

As mentioned earlier, from the second version to the third version of the improved case, all parameters remain unchanged except for the minimum approach temperature of the heat exchangers. By lowering this parameter, especially for HE#1, the area and thus the heat transfer via this heat exchanger noticeably increase. Comparing the results for these two versions in Table 3.5, the proportion of heat provided by HE#1 for ammonia cracking has increased from 22.8% to 27.2%, resulting in a slight 0.6% increase in hydrogen production. The adjustment of the minimum approach temperature will directly impact the cost of the heat exchangers, which will be examined in the cost estimation section.

The final version of the improved case, as indicated in the Table 3.5, mirrors the results of the third version. The only difference is the exclusion of HE#2 and HE#3 due to their negligible heat transfer and area, which will marginally reduce costs. However, their installation serves no practical purpose.

While comparing the results for all models reveals an increase in the index of produced hydrogen to total feed ammonia, ranging from 0.1282 to 0.1404 kg/kg, a detailed cost estimation is required to determine the optimal model among them. This will be discussed extensively in the following section.

3.4 Cost estimation

In this section, an itemized cost estimation will be conducted based on the study by Devkota et al. First, a summary of their methodology will be provided, followed by an explanation of the cost estimation performed in this study.

3.4.1 Methodology

Devkota et al. utilized the outcomes of their process simulation to carry out an economic assessment of hydrogen production through ammonia decomposition. They applied the 'Rules of Thumb in Engineering Practice' to compute the base costs of the principal equipment. The base costs of TSA and PSA in their study were obtained from publicly available literature [16].

Estimating the Levelized Cost of Hydrogen (LCOH) necessitates the determination of both Capital Expenditures (CAPEX) and Operating Expenditures (OPEX). CAPEX is computed from the cost recovery factor (CRF) and total capital investment (TCI). CRF and CAPEX can be calculated using the discount rate, i , and the plant's lifespan, n , as outlined in equations (3.2) and (3.3) [17], [18].

$$CRF = \frac{i(1+i)^n}{(1+i)^n - 1} \quad (3.2)$$

$$CAPEX = CRF \times TCI \quad (3.3)$$

OPEX for the process can be computed by factoring in various economic considerations, such as the costs of consumable materials, utilities, labor (including operating labor and supervisor costs), maintenance, operating supplies, laboratory charges, local taxes, insurance, financing, and general expenses. They determined the consumption rates of raw materials and utilities using simulation results, while the number of laborers and their corresponding salaries were estimated from publicly available literature and a book [19].

Once the costs of consumable materials, utilities, and labor have been determined, other economic parameters can be estimated. Subsequently, the Levelized Cost of Hydrogen (LCOH) was calculated according to equation (3.4) [13].

$$LCOH = \frac{(CRF \times TCI) + OPEX}{Annual\ Production\ Capacity} \quad (3.4)$$

Table 3.6 summarizes the primary assumptions utilized in their work for estimating the levelized cost of hydrogen which is also partly used in this study.

Table 3.6: List of assumption applied for LCOH estimation in study by Devkota et al.

| Parameter | Value |
|--|-----------|
| Ammonia cost, USD/kg | 0.52 |
| Cooling water at 298 K, USD/m ³ | 0.051* |
| Water cost, USD/m ³ | 1.5 |
| Discount rate, % | 10 |
| Plant working days, days/year | 330** |
| Plant life, Years | 25 |
| Adsorbent, USD/kg | 3.41 |
| Number of labors | 15 |
| Labor salary, USD/person-Year | 34.167 |
| C _U , USD/year | 1,871,300 |
| Hydrogen selling price, USD/kg of H ₂ | 9.06 |

*Note that the cooling water in this study is at 5C hence it has a different cost compared to this value.

**The annual working days in the proposed plant in this study is 167 days or 4000 hours.

Further calculations for production cost were conducted after determining the FCI, WCI, and TCI of the plant. To estimate the OPEX, economic parameters such as FCI, TCI, consumable material costs (C_{RM}), operating labor cost (C_L), and utilities (C_U) were computed, as outlined in Table 7.1.

The rates of consumption for raw material (ammonia), consumable materials (catalyst and adsorbents), and utilities were determined using simulation results, while their associated prices were estimated using unit costs outlined in Table 3.6.

Fixed capital investment (FCI), working capital investment (WCI), and total capital investment (TCI) for the ammonia cracking process plant were calculated using established economic parameters for chemical process plants, as detailed in Table 3.7.

Table 3.7: established economic factors for chemical process plants, Devkota et al., [10]

| Components | Factor, % |
|---|------------------|
| Fixed capital investment (FCI) | 504 |
| Direct costs | |
| -Purchased equipment cost | 100 |
| -Installation cost, including insulation and painting | 47 |
| -Instrumentation and controls (installed) | 36 |
| -Piping cost (installed) | 68 |
| -Electrical systems (installed) | 11 |
| -Buildings including all the facilities | 18 |
| -Yard improvements | 10 |
| -Service facilities (installed) | 70 |
| Total direct plant cost | 360 |
| Indirect costs | |
| -Engineering and supervision | 33 |
| -Construction expenses | 41 |
| -Legal expenses | 4 |
| -Contractor's fee | 22 |
| -Contingency | 44 |
| Total indirect plant cost | 144 |
| Working capital investment (WCI) | 89 |
| Total capital investment (TCI) | 593 |

After establishing the FCI, WCI, and TCI of the plant, additional computations will be undertaken to assess production costs. Estimating the OPEX involved calculating economic factors such as FCI, TCI, raw material costs (C_{RM}), operating labor cost (C_L), and utilities (C_U), as outlined in Table 7.1 in Appendix A.

The CAPEX can then be calculated based on the formula in Table 7.1, equation (3.5):

$$OPEX = C_{RM} + 2.3125C_L + C_U + 0.137FCI + 0.1TCI \quad (3.5)$$

The consumption of raw material (ammonia), consumable materials (catalyst and adsorbents), and utilities were determined based on their simulation results, with corresponding prices estimated using unit costs previously listed in Table 3.6.

In this study, the purchased equipment cost will be calculated using Aspen In-Plant Cost Estimator V12. To achieve this, all relevant data, including the equipment type (all) and duty (Furnace), as well as acceptable dimensions of the equipment, were imported. For heat exchangers, the required areas were calculated based on the simulation results obtained from Aspen HYSYS V12. Assuming a U value of 50 kW/m²*°C for all heat exchangers, the calculated UA was imported into the software.

After calculation of total purchased equipment for each model, regarding the itemized costs in Table 3.7, all the items will be evaluated including the direct costs, indirect costs, FCI, TCI and WCI. Then using equation (3.5) and Table 7.1, the CAPEX for all models can be evaluated.

Using equation (3.5), the OPEX will be calculated and afterwards by using equation (3.4), the LCOH could be calculated for all models.

The steps for calculating the LCOH for the models in this study are presented as follows:

3.4.2 Base model

According to steps explained above, the first stage is to import all equipment relevant data into the Aspen In-Plant Cost estimator. For this purpose, it is required to calculate the area of the heat exchanger. Table 3.8 presents the calculated area of the heat exchanger in base model.

Table 3.8: calculation of the area for heat exchanger(s) in base model

| Heat Exchanger | Duty GJ/h | Min. Approach Temp., °C | UA MJ/h-°C | U kw/m2-°C | A m ² |
|----------------|-----------|-------------------------|------------|------------|------------------|
| HE#5 | 11.1 | 20 | 99.1 | 50 | 551 |

Next step, all required data will be imported to Aspen In-Plant Cost Estimator V12. Figure 3.7 shows the imported data for the base model as an example in Aspen In-Plant Cost Estimator V12.

| Item | User Tag Number | Item Description | Model | No. Items | Equipment Cost (...) | Direct C |
|------|-----------------|------------------|--------------|-----------|----------------------|----------|
| 11 | 01 | Ammonia Cracker | AT REACTOR | | 168300 | |
| 1 | 02 | Furnace | FU REFORMER | | 1077800 | |
| 10 | HE#05 | HE-cold water | HE TEMA EXCH | | 147600 | |
| 3 | 04 | PSA adsorption | TW PACKED | | 54900 | |
| 4 | 05 | PSA desorption | TW PACKED | | 52500 | |
| 14 | 03 | TSA | TW TS ADSORB | | 201500 | |

Figure 3.7: Imported data in Aspen In-Plant Cost Estimator V12 for the base model.

Taking the itemized cost percentages presented in Table 3.7, by Devkota et al., TCI, WCI and FCI were calculated as illustrated in Table 3.9.

Table 3.9: Estimation of items involved in CAPEX calculation, base model.

| Cost item | Percentage share, % | Cost, USD |
|----------------------------------|---------------------|------------|
| Purchased Equipment | 100 | 1,702,600 |
| Total direct plant costs | 360 | 6,129,360 |
| Total indirect plant costs | 144 | 2,451,744 |
| Working capital investment (WCI) | 89 | 1,515,314 |
| Fixed capital investment (FCI) | 504 | 8,581,104 |
| Total capital investment (TCI) | 593 | 10,096,418 |

Next, to calculate the Cost Recovery Factor (CRF), we employed equation (3.2), selecting values for i (discount rate, %) and n (plant life in years) from Table 3.6. The calculated CRF was then used to evaluate the Capital Expenditure (CAPEX) according to equation (3.3), with the Total Capital Investment (TCI) obtained from the Table 3.9.

Regarding the formula for CAPEX presented by Devkota et al. in Table 7.1, it is required to calculate C_{RM} , C_L and C_U . For calculation of C_{RM} , in this study, ammonia and cold water were considered as required raw materials. Note that no catalyst was proposed in this study. The simulation provided data on the consumption rates of ammonia and cold water, as well as the flow rates of hydrogen production, with the ammonia price obtained from Table 3.6. For cold water of 5 °C, 0.5 USD/m³ was considered. C_L and C_U values in their paper were used in the OPEX calculations (Table 3.6). A working time of 4000 hours per year was considered for the ammonia cracking unit in this study.

To calculate the OPEX, one needs to evaluate C_L , C_U , C_{RM} , FCI and TCI. As mentioned earlier, C_L and C_U are taken from Table 3.6. The C_L is the product of number of labors and the salary while the C_{RM} is calculated by multiplying the working days by the consuming flow rate by the cost for raw materials, namely cold water and ammonia. Note that the adsorber consumption was disregarded from calculation of C_{RM} due to lack of data for rate of adsorber bed consumption. For water and ammonia, the calculations are as follows:

$$C_{RM} \text{ for water : } 4.15 \text{ m}^3/\text{h} * 4000 \text{ h} * 0.5 \text{ USD/m}^3 = 8,300 \text{ USD}$$

$$C_{RM} \text{ for ammonia : } 8515 \text{ kg/h} * 4000 \text{ h} * 0.52 \text{ USD/kg} = 17,711,200 \text{ USD}$$

$$\text{Total } C_{RM} = 8,300 \text{ USD} + 17,711,200 \text{ USD} = 17,719,500 \text{ USD}$$

The FCI and TCI values for the base case were evaluated as presented in Table 3.9.

After evaluation of all these parameters, the OPEX for the base model can be simply evaluated using equation (3.5):

$$\begin{aligned} OPEX(\text{base model}) &= 17,719,500 + 2.3125(512,505) + 1,871,300 \\ &+ 0.137(8,581,104) + 0.1(10,096,418) = 22,961 \text{ MUSD} \end{aligned}$$

The CAPEX of the plant is then simply determined by equations (3.3) as 1.112 MUSD,. Note that this OPEX represents one year of operation. Subsequently, the Levelized Cost of Hydrogen (LCOH) was evaluated according to equation (3.4). For the base case, the LCOH is estimated to be 5.5 USD/kg of H₂.

3.4.3 Improved model (1st version)

The procedure to calculate the LCOH is the same as that for the base model, hence, to avoid repetition, the steps are summarized as below:

Required area of the heat exchangers for the improved model (1st version) is presented in Table 3.10.

Table 3.10: calculation of the area for heat exchanger(s), 1st version of the improved model

| Heat Exchanger | Duty GJ/h | Min. Approach Temp., °C | UA MJ/h-°C | U kw/m2-°C | A m ² |
|----------------|-----------|-------------------------|------------|------------|------------------|
| HE#1 | 9.36 | 573 | 12.9 | 50 | 72 |
| HE#2 | 7.57 | 30 | 65.1 | 50 | 362 |
| HE#3 | 2.71 | 30 | 31 | 50 | 172 |
| HE#4 | 1.18 | 30 | 13 | 50 | 72 |
| HE#5 | 3.94 | 20 | 105 | 50 | 582 |

Next, all required data will be imported to Aspen In-Plant Cost Estimator V12 to calculate total purchased equipment. Then, using the itemized cost list presented in Table 3.7, TCI, WCI and FCI were calculated as shown in Table 3.11.

Table 3.11: Estimation of items involved in CAPEX calculation, improved model (1st version)

| Cost item | Percentage share, % | Cost, USD |
|----------------------------------|---------------------|------------|
| Purchased Equipment | 100 | 2,001,300 |
| Total direct plant costs | 360 | 7,204,680 |
| Total indirect plant costs | 144 | 2,881,872 |
| Working capital investment (WCI) | 89 | 1,781,157 |
| Fixed capital investment (FCI) | 504 | 10,086,552 |
| Total capital investment (TCI) | 593 | 11,867,709 |

Similarly, calculating the CRF, the CAPEX is then evaluated. Regarding the CAPEX formula in Table 7.1, C_{RM} , C_L and C_U need to be calculated. For C_{RM} , like base model, certain prices were considered for ammonia and cold water. Working hours were again considered as 4000 hours per year for the unit in this study.

For the first version of the improved model, the OPEX and CAPEX of the plant were determined as 23.344 MUSD and 1.307 MUSD, respectively. Note that this OPEX is for one year of operation.

In the first version of the improved model, the LCOH is estimated to be 5.4 USD/kg of H₂ which is slightly lower than the base model.

3.4.4 Improved model (2nd version)

Required area of the heat exchangers for the improved model (2nd version) is presented in Table 3.12.

Table 3.12: calculation of the area for heat exchanger(s), 2nd version of the improved model

| Heat Exchanger | Duty GJ/h | Min. Approach Temp., °C | UA MJ/h-°C | U kw/m ² -°C | A m ² |
|----------------|-----------|-------------------------|------------|-------------------------|------------------|
| HE#1 | 10.1 | 75 | 49.6 | 50 | 276 |
| HE#2 | 0.53 | 30 | 12.8 | 50 | 71 |
| HE#3 | 0.26 | 30 | 6.93 | 50 | 38 |
| HE#4 | 0.21 | 30 | 6.14 | 50 | 34 |
| HE#5 | 1.10 | 20 | 54.8 | 50 | 304 |

Next, all required data will be imported to Aspen In-Plant Cost Estimator V12 to calculate total purchased equipment. TCI, WCI and FCI were calculated as shown in Table 3.13.

Table 3.13: Estimation of items involved in CAPEX calculation, improved model (2nd version)

| Cost item | Percentage share, % | Cost, USD |
|----------------------------------|---------------------|------------|
| Purchased Equipment | 100 | 1,940,400 |
| Total direct plant costs | 360 | 6,985,440 |
| Total indirect plant costs | 144 | 2,794,176 |
| Working capital investment (WCI) | 89 | 1,726,956 |
| Fixed capital investment (FCI) | 504 | 9,779,616 |
| Total capital investment (TCI) | 593 | 11,506,572 |

For the second version of the improved model, the OPEX and CAPEX of the plant were calculated as 23.271 MUSD and 1.267 MUSD, respectively.

For the second version of the improved model, the LCOH is estimated to be 5.2 USD/kg of H₂ which is lower than the base model.

3.4.5 Improved model (3rd version)

Required area of the heat exchangers for the improved model (3rd version) is presented in Table 3.14.

Table 3.14: calculation of the area for heat exchanger(s), 3rd version of the improved model

| Heat Exchanger | Duty GJ/h | Min. Approach Temp., °C | UA MJ/h-°C | U kw/m2-°C | A m ² |
|----------------|-----------|-------------------------|------------|------------|------------------|
| HE#1 | 12.2 | 18 | 111 | 50 | 619 |
| HE#2 | 0.0367 | 15 | 2.31 | 50 | 13 |
| HE#3 | 0.0004 | 15 | 0.026 | 50 | 0 |
| HE#4 | 0.0565 | 15 | 3.57 | 50 | 20 |
| HE#5 | 0.414 | 15 | 23.8 | 50 | 132 |

Next, all required data will be imported to Aspen In-Plant Cost Estimator V12 to calculate total purchased equipment. The TCI, WCI and FCI were calculated as shown in Table 3.15.

Table 3.15: Estimation of items involved in CAPEX calculation, improved model (3rd version)

| Cost item | Percentage share, % | Cost, USD |
|----------------------------------|---------------------|------------|
| Purchased Equipment | 100 | 1,866,900 |
| Total direct plant costs | 360 | 6,720,840 |
| Total indirect plant costs | 144 | 2,688,336 |
| Working capital investment (WCI) | 89 | 1,661,541 |
| Fixed capital investment (FCI) | 504 | 9,409,176 |
| Total capital investment (TCI) | 593 | 11,070,717 |

For the third version of the improved model, the OPEX and CAPEX of the plant were evaluated as 23.173 MUSD and 1.219 MUSD, respectively.

For the third version of the improved model, the LCOH is estimated to be 5.1 USD/kg of H₂ which is noticeably lower than the base model.

3.4.6 Improved model (Final version)

Required area of the heat exchangers for the improved model (Final version) is presented in Table 3.16.

Table 3.16: calculation of the area for heat exchanger(s), Final version of the improved model

| Heat Exchanger | Duty GJ/h | Min. Approach Temp., °C | UA MJ/h-°C | U kw/m2-°C | A m ² |
|----------------|-----------|-------------------------|------------|------------|------------------|
| HE#1 | 12.2 | 18 | 111 | 50 | 619 |
| HE#4 | 0.094 | 15 | 5.69 | 50 | 32 |
| HE#5 | 0.414 | 15 | 23.8 | 50 | 132 |

Next, all required data will be imported to Aspen In-Plant Cost Estimator V12 to calculate total purchased equipment. The TCI, WCI and FCI were calculated as shown in Table 3.17.

Table 3.17: Estimation of items involved in CAPEX calculation, improved model (Final version)

| Cost item | Percentage share, % | Cost, USD |
|----------------------------------|---------------------|------------|
| Purchased Equipment | 100 | 1,850,000 |
| Total direct plant costs | 360 | 6,660,000 |
| Total indirect plant costs | 144 | 2,664,000 |
| Working capital investment (WCI) | 89 | 1,646,500 |
| Fixed capital investment (FCI) | 504 | 9,324,000 |
| Total capital investment (TCI) | 593 | 10,970,500 |

For the final version of the improved model, the OPEX and CAPEX of the plant were determined as 23.151 MUSD and 1.208 MUSD, respectively. Note that this OPEX is for one year of operation.

For the final version of the improved model, the LCOH is estimated to be 5.09 USD/kg of H₂ which is noticeably lower than the base model.

3.4.7 Comparison of the models

In this section, the models are compared from the cost estimation point of view. Table 3.18, compares the LCOH values of the models presented in this thesis for 1, 5, and 10 years of operation.

Table 3.18: comparison of the LCOH calculated for different models for 1, 5 and 10 years of operation.

| | | LCOH (USD/kg H ₂) | | | |
|--------------------|------------|-------------------------------|-------------------------|-------------------------|---------------|
| Years on operation | Base model | Improved model | | | |
| | | 1 st version | 2 nd version | 3 rd version | Final version |
| 1 | 5.51 | 5.39 | 5.16 | 5.10 | 5.09 |
| 5 | 5.31 | 5.16 | 4.95 | 4.89 | 4.89 |
| 10 | 5.28 | 5.13 | 4.92 | 4.87 | 4.86 |

As seen in Table 3.18, the LCOH of the improved model (across all versions) is lower than that of the base model, indicating the feasibility of energy optimization. Furthermore, there is a decreasing trend in the evaluated LCOH from the first version to the final version of the improved models, demonstrating the effectiveness of optimization from both energy and cost estimation perspectives.

4 Discussion

In this chapter first, a comparison of the simulation results with the previous works in the literature is discussed. Next, the uncertainty of the results of the thesis is presented. At the end of this chapter some recommendations are proposed for future studies.

4.1 Results comparison

In this thesis, insights from the work of Devkota et al. were utilized to investigate efficient green hydrogen production through ammonia decomposition.

In the study performed by Devkota et al. [10], a feed consisting of 4000 kg/h of pure ammonia, maintained at a temperature of 25 °C and a pressure of 1 Mpa, served as the foundation for their computations. They implemented thermo-catalytic cracking in a multi-catalytic packed bed reactor with intermediate heating system (Figure 7.3). Heat for the cracking reaction was generated by combusting a portion of supplied ammonia mixed with H₂-enriched waste streams, resulting in a significant H₂ yield of 0.999 [10].

In this study, thermal cracking without a catalyst is adopted, relying solely on heat to break down ammonia into hydrogen. Introducing two Gibbs reactors, 9% of the total feed ammonia was directed to furnace as fuel in the base model and lowered to 2% in the improved cases. This methodology is in line with contemporary standards observed in both academic research and industrial applications within the realm of ammonia decomposition for green hydrogen production.

Table 4.1 presents the calculated ratio of produced hydrogen to the total ammonia feed on a kg/kg basis for different studies in the literature, the group project, and this study.

Table 4.1 : Results comparison of the ammonia cracking for different studies

| Study | Produced H ₂ /NH ₃ feed (kg/kg) | LCOH (USD/kg H ₂) |
|----------------------------------|--|----------------------------------|
| This study - base case | 0.128 | 5.51 |
| This study – final improved case | 0.140 | 5.09 |
| Group project – base case | 0.131 | - |
| Group project – improved case | 0.140 | - |
| Restelli et al. [9] | 0.140 | 6.79 |
| Lee et al. [8] | 0.127 | 6.98 |
| Devkota et al.[10] | 0.129 | 6.05 |

Upon reviewing the data presented in Table 4.1, the findings of this study indicate a similar hydrogen production to total ammonia feed ratio compared to other studies. However, when comparing the Levelized Cost of Hydrogen (LCOH) from this study with those of other

investigations, it is notably lower, even below 6 USD/kg H₂. This closely aligns with the results reported by Devkota et al., suggesting that their study served as a foundational basis for the LCOH calculation in this thesis, considering all parameters included in the Operating Expenditures (OPEX) and Capital Expenditures (CAPEX) calculations.

4.2 Uncertainty of the results

In this section, uncertainties regarding the results will be addressed. While this thesis aimed to enhance the models initially presented in the group project (autumn 2023) by incorporating energy and pressure losses across the equipment, as well as improving the model from energy consumption and economic perspectives, several uncertainties persist within the model and its simulation outcomes.

In this thesis, the work conducted by Devkota et al. served as the foundation for the simulation, wherein a multi-catalytic packed bed reactor was employed. In contrast, this study did not define any catalyst. While this difference may not significantly impact the amount of hydrogen production, it could influence the kinetics of ammonia cracking, thereby affecting the capacity of the process unit. Additionally, it could impact the consumable material costs (C_{RM}), the operating expenditure (OPEX), and consequently, the evaluated LCOH.

To mitigate uncertainty surrounding the definition of the TSA and PSA for separating unreacted ammonia and nitrogen from hydrogen, it is imperative to utilize experimental data encompassing pressure, temperature, and composition of the inlet and outlet streams to/from actual equipment. In this regard, available data from Devkota et al.'s paper was employed.

There remains a degree of uncertainty regarding the calculated LCOH due to the inherent uncertainty associated with each parameter involved in the formula. The estimated cost for each equipment in the process unit is not exact, as Aspen In-Plant Cost Estimator V.12 necessitates numerous parameters to precisely calculate the purchased cost. However, detailed information on these parameters is often lacking, necessitating certain assumptions to be made. These parameters include dimensions, material selection, and other related options for each equipment.

Additional uncertain parameters include the proportions of Fixed Capital Investment (FCI), Total Capital Investment (TCI), and Working Capital Investment (WCI) relative to the purchased equipment cost, which directly impact CAPEX calculation. Moreover, in OPEX evaluation, the calculated values of C_{RM} , C_L , and C_U , along with the CAPEX, introduce a certain degree of uncertainty.

The uncertainty in OPEX and CAPEX will impact LCOH evaluations. Although the evaluated value falls within the range of values obtained by other methods, it is prudent to interpret this value cautiously.

4.3 Recommendation for future studies

In this section, potential areas for future study will be outlined to address current research limitations.

In this project, the process design, informed by existing literature, allocated a portion of ammonia as fuel to power the cracking reactor, employing a Gibbs reactor instead of a furnace.

A potential avenue for future exploration could involve utilizing a furnace rather than an ideal Gibbs reactor for ammonia combustion. It is worth noting that Aspen HYSYS V12 presented limitations in utilizing ammonia as a fuel in the furnace.

Furthermore, the simulation in this project simplified the cracker to a Gibbs reactor. Future studies could enhance accuracy by incorporating reaction kinetics and considering the mass of catalyst within the cracking reactor.

Given that the adsorption/desorption process is cyclic and dynamic, Aspen Adsorption V.12 may offer a more appropriate choice for a comprehensive and precise representation compared to Aspen HYSYS V12.

A techno-economic analysis of hydrogen production from the ammonia cracking process was conducted, drawing partially from the methodology and available data presented by Devkota et al. However, due to the inherent uncertainty in techno-economic calculations, it is highly recommended to perform an uncertainty analysis, such as the Monte Carlo method, to yield more reliable results.

Investigating the environmental impact of burning ammonia in the furnace, which serves as an energy resource for the cracker, is essential due to the potential production of byproducts such as N_2O and NO_x , which have high global warming potential. Therefore, future projects could focus on assessing the environmental implications of different energy resources for the cracker to determine the most suitable option.

Also, a project can be done specifically in the purification of the produced hydrogen in the process of cracking ammonia, as this process do not have a 100% efficiency and the produced hydrogen needs to be purified in some cases (for example if the end user needs hydrogen to be used in a fuel cell).

5 Conclusion

This project aims to simulate ammonia cracking using Aspen HYSYS V12, with several key objectives. Firstly, it seeks to accurately model the ammonia cracking process, improving upon the simulation conducted during the autumn 2023 group project. Secondly, the research explores techniques to enhance the cracking process, specifically focusing on reducing energy consumption. Next, the study provides preliminary cost estimation and optimization using existing literature data to identify the most efficient case among defined scenarios. Finally, the simulation results are compared with available literature data. Additionally, recommendations are provided to address potential uncertainties and enhance result quality.

In the initial phase of this project, a literature review was conducted covering general overview of ammonia as an energy carrier and then focusing on the simulation methodologies for ammonia cracking.

Subsequently, the methodology of the simulation in the thesis was explained. Aspen HYSYS version V12 was employed to simulate the ammonia cracking process. For this purpose, available articles were investigated for ammonia cracking simulation, and ultimately it was decided to use the work presented in reference [10] and [11] due to its reliability and especially availability of data.

In the simulation phase, initially a base case was established and then the cracking process was improved by harnessing the waste heat of the ammonia cracker products. For the first version of the improved case, four heat exchangers were added to the base model to capture the heat of the ammonia cracker product. In the second version of the improved case, the ratio of ammonia as fuel to the total ammonia feed was lowered from 9% to 2% to release the optimization potential since by burning high amount of fuel, the conversion rate of the reactor is very high resulting in low effectiveness of heat exchangers inclusion. For the third version of the base case, the minimum approach temperature of the heat exchangers was adjusted to produce more hydrogen and optimize heat exchangers. For the final version of the improved case, two heat exchangers with small areas were eliminated to make it more cost effective. Comparing the results for all models reveals an increase in the index of produced hydrogen to total feed ammonia, ranging from 0.1282 for the base case to 0.1404 kg/kg for the final version of the improved case.

Next, an itemized cost estimation was conducted for all above-mentioned simulation models based on the study of Devkota et al. First, a summary of their methodology was provided, followed by an explanation of the cost estimation performed in this thesis. The Levelized Cost of Hydrogen (LCOH) was calculated for each model and then compared to find out the most efficient case among defined models.

As shown in

Table 3.18, the LCOH values of all improved cases (5.39 down to 5.09 USD/ kg of H₂) are lower than that of the base model (with LCOH of 5.51 USD/kg of H₂ for one year of production), indicating the feasibility of energy optimization. Furthermore, there is a descending trend in the evaluated LCOH from the first version to the final version of the improved models, demonstrating the effectiveness of optimization from both energy and cost estimation perspectives.

In the discussion chapter, after comparing the simulation results with the previous works, the uncertainty of the results was discussed and accordingly, some recommendations were proposed for future studies.

Upon comparing the results of the thesis with the literature, presented in Table 4.1, the findings of this study indicate a similar hydrogen production to total ammonia feed ratio compared to studies of Restelli et al. [9] (0.14 kg/kg), Lee et al. [8] (0.129 kg/kg), Devkota et al.[10] (kg/kg) and the group project (USN, Fall 2023). The produced hydrogen to total feed ammonia for this MSc thesis was obtained 0.1404 kg/kg for the final version of the improved case.

However, when comparing the Levelized Cost of Hydrogen (LCOH) from this study with those of other investigations, it is notably lower, even below 6 USD/kg H₂. This closely aligns with the results reported by Devkota et al. [10], suggesting that their study served as a foundational basis for the LCOH calculation in this thesis.

While this thesis aimed to enhance the reliability of the models initially presented in the group project (autumn 2023), several uncertainties persist within the model and its simulation outcomes, that leaves potential areas for future study. Future research directions include but are not limited to:

- Exploring the use of a furnace instead of a Gibbs reactor for ammonia combustion, considering the limitations of Aspen HYSYS V12 in using ammonia as fuel.
- Improving simulation accuracy by incorporating reaction kinetics and catalyst mass within the cracking reactor could enhance the accuracy of cost estimation.
- Aspen Adsorption V12 may provide a more suitable option for accurately representing the cyclic and dynamic adsorption/desorption process compared to Aspen HYSYS V12.
- Conducting a techno-economic analysis based on Devkota et al.'s methodology, while advisable, requires an uncertainty analysis like the Monte Carlo method for more reliable results.
- Investigating the environmental impact of burning ammonia in the furnace, which can produce byproducts like N₂O and NO_x, is essential.
- Furthermore, future projects could focus on purifying the produced hydrogen, considering its incomplete efficiency in certain industries.

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7 Appendices

Appendix A: Signed project topic description



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Faculty of Technology, Natural Sciences and Maritime Sciences, Campus Porsgrunn

Project topic description FMH606-1 24V master's thesis

Title: Simulation of ammonia cracker process with Aspen HYSYS

USN supervisor: Per Morten Hansen, Lars Erik Øi

External partner: Wärtsilä, Green platform project

Task background:

Hydrogen, as a zero-emission energy carrier, holds substantial potential in transitioning towards more sustainable energy systems. However, it's important to highlight that hydrogen, given its low volumetric energy density compared to traditional fossil fuels, requires compression to high pressure, liquefaction, or conversion into a hydrogen carrier for practical transportation and storage. Among potential hydrogen carriers, ammonia emerges as a noteworthy option due to its carbon-free and dispatchable nature. Ammonia's remarkable advantage in carrying hydrogen per unit volume directly results in a lower cost per unit of stored energy compared to alternative solutions. In essence, ammonia exhibits the requisite characteristics to serve as an efficient and cost-effective CO₂-free energy storage vector.

Thus, to transport hydrogen to end users, whether onshore or offshore, one viable approach involves conveying the energy carrier as ammonia via ship and subsequently transferring it to another ship equipped with an onboard cracker unit. The ammonia can then undergo conversion into hydrogen through the cracker process before being transported to the end users. While there are ongoing plans to establish a maritime pilot or demonstration facility for ammonia cracking in the coming years, further research and development are imperative. The simulation of the ammonia cracker process is a pivotal step in advancing this development.

Project objectives:

- The general objective of the current project is to improve the model built by Aspen HYSYS in group project (Autumn 2023).
- The specific objective of the current project is to optimize the process from an energy standpoint and make a basis for cost optimization.

Task description:

- Literature review on simulation of ammonia cracking to find relevant works and data.
- Improvement of the simulation of the ammonia cracking by Aspen HYSYS v12, performed in the group project based on the available data and previous works in this field, including but not limited to:
 - Introduction of a base case on which these tasks will be performed:
 - ✓ Defining reasonable heat and pressure loss across different equipment
 - ✓ Employment of a pump in the downstream of the cracker
 - ✓ Definition of non-ideal adsorber and PSA and utilizing the unseparated ammonia and hydrogen as fuel in the furnace
 - ✓ Definition of catalyst kinetics (optional)

- After confirmation of the base case an energy-consumption improved case will be defined on which the following tasks will be implemented:
 - ✓ Energy optimization by employment of heat exchanger(s) and pinch method to reduce ammonia as fuel to the furnace.
 - ✓ Preliminary cost estimation to figure out approximations of CAPEX and OPEX
 - ✓ Cost optimization (optional)
 - ✓ Definition of multi-stage cracking (optional)
- Evaluation of the uncertainties and limitations in this project and recommendation for future studies

Student category:

Process Technology (PT)

Signatures:

Supervisor(s) (date and signature): Per Morten Hansen 26.01.2024



Student (date and signature): Vahid Farokhi 25.01.2024



Appendix B: Pictures and tables from process simulation literature review.

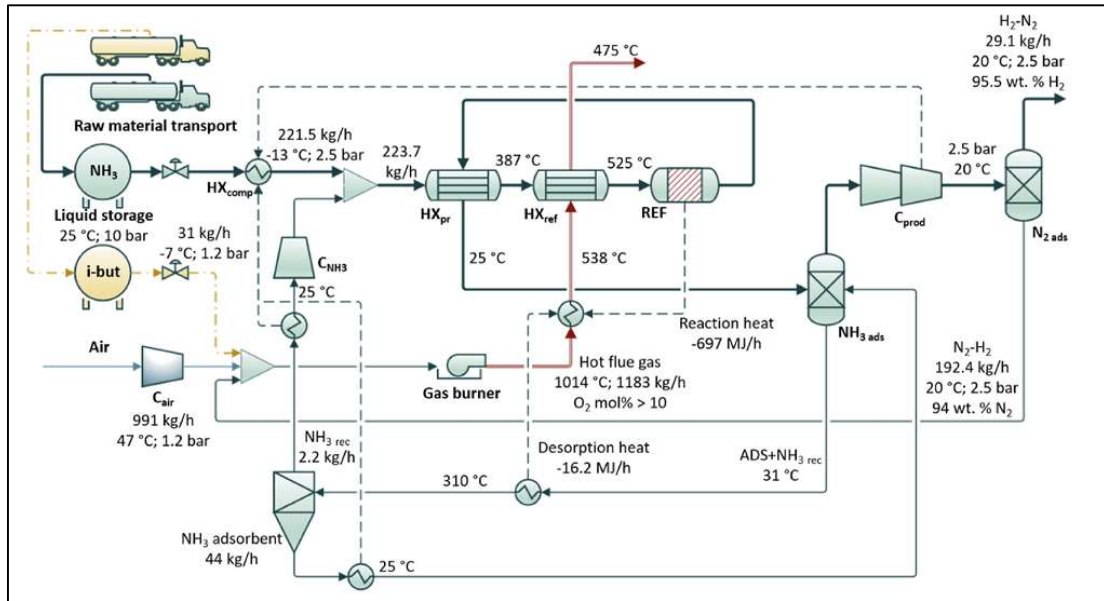


Figure 7.1: Process flow diagram of hydrogen production using green ammonia decomposition, [6]

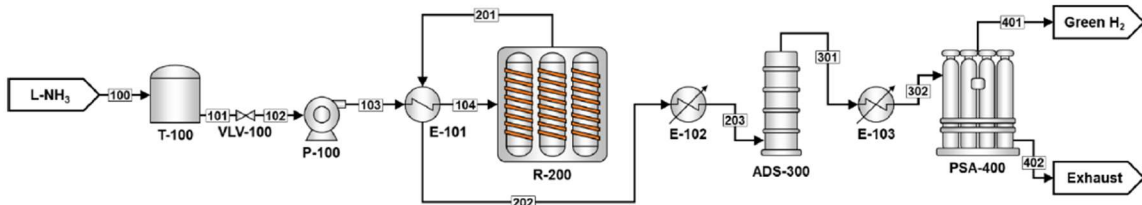


Figure 7.2: Green hydrogen production simulation [8]

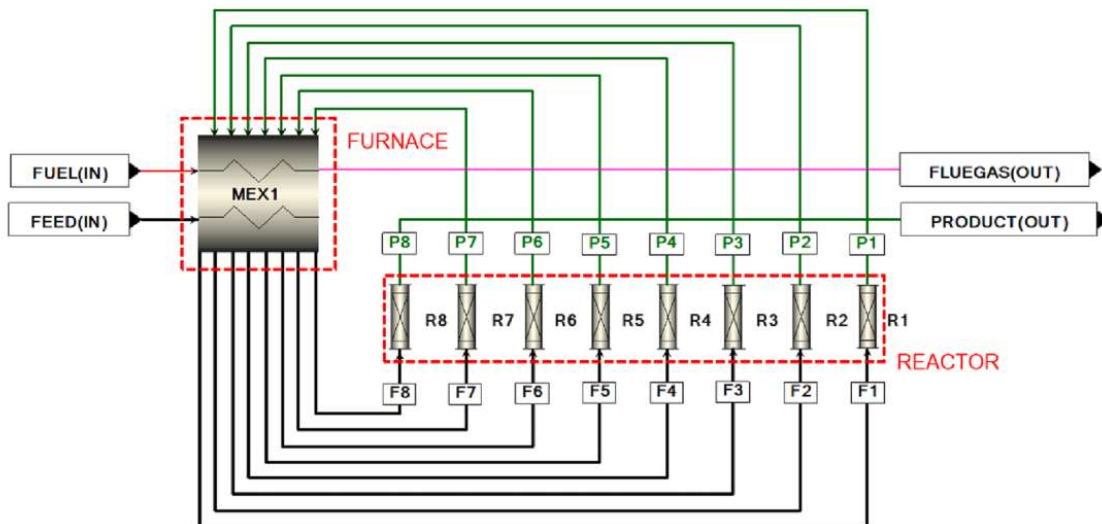


Figure 7.3: Multi-catalytic packed bed reactor with intermediate heating system. [11]

Table 7.1 : Estimation of total production cost (based on 4071 t/year of hydrogen production capacity), [10]

| Components | Factor |
|---|---|
| Manufacturing costs | |
| Direct production costs | |
| Consumable material costs (C_{RM}) | $1.00 \times C_{RM}$ |
| Operating labor cost (C_L) | $1.00 \times C_L$ |
| Direct supervision cost (C_S) | $0.15 \times C_L$ |
| Utilities (C_U) | $1.00 \times C_U$ |
| Maintenance (C_M) | $0.06 \times FCI$ |
| Operating supplies (C_{OS}) | $0.15 \times C_L$ |
| Laboratory charges (C_{LAB}) | $0.15 \times C_L$ |
| Total direct production costs | $C_{RM} + 1.45 C_L + C_U + 0.06 FCI$ |
| Fixed charges | |
| Local taxes (C_{LT}) | $0.025 \times FCI$ |
| Insurance (C_I) | $0.007 \times FCI$ |
| Financing (C_F) | $0.1 \times TCI$ |
| Total fixed charges | $0.032 FCI + 0.1 TCI$ |
| Plant overhead costs | $0.6325 C_L + 0.033 FCI$ |
| Total manufacturing costs | $C_{RM} + 2.0825 C_L + C_U + 0.125 FCI + 0.1 TCI$ |
| General Expenses | |
| Administrative costs (C_A) | $0.23 C_L + 0.012 FCI$ |
| Total operating expenditure (OPEX) | $C_{RM} + 2.3125 C_L + C_U + 0.137 FCI + 0.1 TCI$ |
| Total capital investment (TCI) | Table 1 |
| Capital expenditure (CAPEX) | Table 1 |
| LCOH / kg of H₂ | – |