Simulation of Ammonia Cracker Process with Aspen HYSYS

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Abstract: This paper presents simulations of an ammonia cracker process using Aspen HYSYS. Ammonia is identified as both a promising low-emission maritime fuel and an energy carrier. This study focuses on converting ammonia to hydrogen through an ammonia cracker process. In the literature, there are found simulations of similar processes, but not much about optimization of the ammonia cracker process. A centralized ammonia cracking process was designed using the Peng-Robinson fluid package and Gibbs reactor in Aspen HYSYS. Gibbs reactors were employed to simulate both the cracker and the furnace (ammonia combustion reaction). Simplified assumptions included using a 100 % efficient splitter instead of a pressure swing adsorber. The ammonia feed had a molar flow rate of 500 kmole/h. The simulations included a base case scenario and an improved case for energy optimization. The base case scenario resulted in a total production of 0.13 kg of hydrogen per kg of ammonia feed. The improved case resulted in a production of 0.14 kg hydrogen. This was due to using the energy content present in the hydrogen and nitrogen product streams for warming up the ammonia before entering the cracker. This work demonstrates that Aspen HYSYS is a useful tool for optimizing the energy efficiency of an ammonia cracker process.

Keywords: Ammonia cracking, hydrogen, Aspen HYSYS, Aspen Plus, simulation, energy optimization

1. INTRODUCTION

Ammonia is a zero-emission energy carrier that could play a vital role in the shift towards more sustainable energy systems. A promising option is to transport the energy carrier as ammonia by ship and then transfer it to another ship equipped with an onboard cracker unit. The ammonia could then be converted into hydrogen in the cracker process before it is transported to the onshore (and offshore) end-users. Plans are known for building a maritime pilot/demonstration facility for ammonia cracking within the next couple of years (Wärtsilä, 2023). However, there is a need for additional research and development to obtain the level of knowledge needed to materialize the idea and build a large-scale facility. Simulation of the ammonia cracker process is a key step in the development to establish the mass and energy balance of the system and improve the process parameters with respect to energy usage and cost. This paper presents results from ammonia cracking simulations using Aspen HYSYS V12.

2. LITERATURE

Thermal and catalytic cracking of ammonia are mature technologies that involve the controlled decomposition of ammonia into nitrogen and hydrogen, by applying heat and/or suitable catalysts. The interest in the use of ammonia as an energy carrier has increased in recent years which is reflected in an increasing number of scientific publications. Machaj et al. (2022) published a review paper on the use of ammonia in the maritime sector highlighting that the price of green ammonia is expected to drop significantly by 2050. Mallouppas, Ioannou and Yfantis (2023) examined key barriers to the use of green ammonia as an alternative fuel in the maritime industry. The barriers included high production costs, availability, the challenge of ramping up current ammonia production and the development of ammonia-specific regulations (Mallouppas et al., 2023). Ashcroft and Goddin (2023) published a technical review of the ammonia cracking process, comparing centralized and localized hydrogen production by ammonia decomposition. Minimizing capital and operations costs are important aspects to consider in designing industrial solutions for ammonia cracking. Optimizing the recovery of waste streams containing ammonia and hydrogen could contribute to higher energy efficiency (Ashcroft and Goddin, 2023). Hansson et al. (2023) published an article on energy systems modeling and multi-criteria decision analysis to examine the potential role of ammonia as a marine fuel. They concluded that while the use of ammonia is promising, there are still unresolved issues that need to be addressed before it can be introduced on a large scale as a maritime fuel.

Ammonia cracking has been given increasing interest in clean energy production and industrial chemistry. It offers a sustainable path to produce high-purity hydrogen, a crucial resource for fuel cells, and as a heat source (Speight, 2023).

Regardless of the scale of hydrogen production, ammonia is cracked by applying heat, typically through the combustion of a fuel or an energy source such as electricity. When ammonia is thermally decomposed, it produces a 1:3 molar ratio of nitrogen and hydrogen. See Equation 1.

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The first time ammonia was cracked thermally was by Bruke in 1933. This process was conducted at temperatures between 550 - 600 °C and achieved a 90% conversion rate (Yousefi Rizi and Shin, 2022). Different reactor types for NH_3 cracking are discussed by Mukherjee et al. (2018).

$$2NH_{3\,(g)} \xrightarrow{Heat} N_{2(g)} + 3H_{2(g)} \tag{1}$$

Table 1. Ammonia conversion at different temperatures in an ideal Gibbs reactor simulation (Chiuta et al., 2013).

Temperature (°C)	Ammonia conversion (%)
250	89.2
300	95.7
350	98.1
400	99.1
450	99.5
500	99.7
600	99.9
700	99.95

This section presents a brief review of the simulation studies of hydrogen production using the ammonia cracking process. A literature search showed that a majority of the process simulations were done in Aspen Plus. This preference is likely due to Aspen Plus being more flexible and therefore more suitable for these simulation tasks compared to the Aspen HYSYS software.

Chiuta et al. (2013) simulated the ammonia cracking reaction in HSC Chemistry 7 software through Gibbs free energy minimization. The results, presented in Table 1, demonstrate an increase in equilibrium conversion with rising temperature.

Cha et al. (2021) conducted a study on an efficient process for sustainable green hydrogen production from ammonia decomposition, using Aspen Plus for simulation. The Peng Robinson thermodynamic model was applied in this simulation. Pure NH_3 from liquid storage was released through a feed valve (10–2.5 bar) at the start of the process. The main heat sinks in the process included Ammonia heating, recycled ammonia desorption from the adsorbent material (by raising the temperature from 31 to 310 °C), and endothermic reaction heat from ammonia decomposition. The majority of the hydrogen was separated using a pressure swing adsorption (PSA) section, as the remaining products were primarily a 3:1 mixture of H_2/N_2. At fixed conditions with a pressure of 2.5 bar and a temperature of 20 °C, the results showed that 71 % of the hydrogen could be recovered (with a purity of 99 mol%). The process used approximately 200 kg of activated carbon per kmole of the PSA inlet gas. The simulation results showed good agreement with the experimental results. (Cha et al., 2021).

Devkota et al. (2023) published a study on the process design and simulation of onsite hydrogen production from ammonia decomposition. The designed process was modeled using Aspen Plus, with Peng-Robinson equation of state employed to estimate the thermodynamic properties. The study utilized a feed rate of 4000 kg/h of pure ammonia, maintained at a temperature of 298 K and a pressure of 10 bar, as the input parameters for the calculations. Given the endothermic nature of the decomposition reaction, the necessary heat energy was generated by burning carbon-free ammonia, requiring about 9% of fresh feed. The resulting product stream contained a small amount of unreacted ammonia, which was subsequently separated and sent to the furnace after being mixed with fresh fuel and air.

The waste stream from this process, containing a large amount of hydrogen and nitrogen gas, was recycled to the furnace for thermal energy production. The study employed a steady-state model of a multi-catalytic packed bed reactor for ammonia decomposition, incorporating an intermediate heating system to enhance the reaction rate. Additionally, the ammonia gas was preheated in a fired furnace to achieve a decomposition temperature of 773 K before entering the reactor, utilizing the catalyst Ru/Al_2O_3 for the decomposition process (Devkota et al., 2023).

Another study was published by Lee et al. (2023) on carbon-free hydrogen production using an induction heating-based reactor for ammonia decomposition, achieving a hydrogen production rate of 150 Nm^3/h. This study was conducted both experimentally and through simulation. The process design included a reactor for ammonia decomposition, a pre-heater, an adsorption column, and a pressure swing adsorption (PSA) unit. To maintain a carbon-free process and produce green hydrogen, the external heat for ammonia decomposition was supplied using electricity from renewable energy sources. The hydrogen recovery rate of the PSA was fixed at 79 % and incorporated into the process simulation. Experimental results demonstrated that the induction heating reactor achieved an ammonia conversion exceeding 90 % at a temperature of 600 °C and a pressure of 7 barg. This conversion rate was subsequently used as an assumption for the conversion reactor model in the process simulation.

Restelli et al. (2023) conducted a comprehensive techno-economic analysis of green hydrogen production via ammonia decomposition. This research includes various hydrogen production processes, including a centralized ammonia cracking process where all the stored ammonia in the inlet is converted to hydrogen. The process was simulated using Aspen Plus (Restelli et al., 2023). The process flow diagram of this simulation is shown in Fig. 1. In this process, the Ammonia stream is pressurized to 30 bar and preheated through in a series of heat exchangers, before being directed to the cracking reactor, taking advantage of the high enthalpic content of the reaction products. The reactor simulation was conducted using the Gibbs module within Aspen Plus. Consequently, the conversion of ammonia aligns with thermodynamic equilibrium at the reactor's operating conditions of 30 bar and 900 °C. These conditions are consistent with those typically used for commercially available nickel-based catalysts. To facilitate the cracking reaction, the necessary heat is generated by combusting a portion of the supplied ammonia, combined with waste streams possessing a high H_2 content that originate from the purification section. Air is employed 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 pressure swing adsorption (PSA).

3. METHODS

The central focus of this study is the simulation of the ammonia cracking process, employing Aspen HYSYS V12 with the Peng-Robinson fluid package. The ammonia combustion reaction is modelled as an equilibrium reaction, with equilibrium parameters determined through the minimization of Gibbs free energy. The simulation is based on the following key assumptions:

Assumption 1. To facilitate the combustion of ammonia, a Gibbs reactor (furnace) was defined. This was necessary since ammonia alone did not exhibit combustion reactions in the furnace.

Assumption 2. In the absence of catalyst data, the process employs the minimization of Gibbs energy for ammonia cracking. This approach assumes thermal cracking, relying on heat to break down ammonia into hydrogen.

Assumption 3. Instead of using adsorber and Pressure Swing Adsorber (PSA) units, a component splitter was employed. This approach assumes no temperature or pressure losses and assumes 100% efficiency in separating unreacted ammonia, hydrogen, and nitrogen in both separation units.

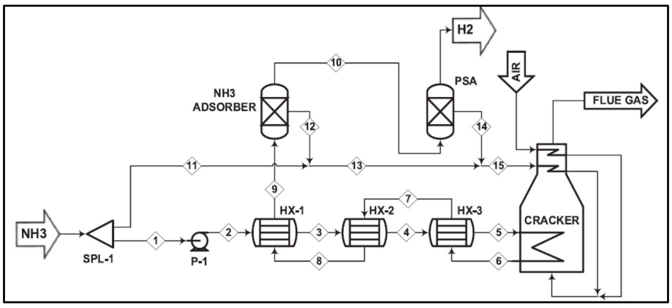


Fig. 1. Process flow diagram of centralized ammonia cracking (Restelli et al., 2023).

Finally, the study optimizes energy within the process by using waste heat from outlet streams (hydrogen and nitrogen) to preheat the ammonia stream heading to the cracker. To achieve this, two coolers are introduced to lower the temperatures of the hydrogen and nitrogen streams to ambient levels. The combined heat from these streams is then employed to preheat the ammonia using a heater, facilitated by a recycling manipulator. This optimization not only improves ammonia pre-heating but also reduces ammonia consumption as fuel, thereby increasing the efficiency of the ammonia-cracking process.

Based on the literature review, the process design proposed by Restelli et al. (2023) was selected as the basis for the Aspen HYSYS simulation work presented in this article. Specifications for the streams are given in Table 2. The chemical reaction used in the main combustion reaction in this study is specified in (2).

Table 2. Inlet and outlet stream specifications.

Stream name / Parameter	**NH_3**	**H_2**	**AIR**	**FLUE GAS**
Temperature (°C)	-27.6	25.5	25.0	139
Pressure (bar)	1.3	30	1.01	1.01
Feed TOTAL (kmoles/h)	592.33	698.07	608.13	999.28
Mole Fractions				
H_2	0	0.999	0	0.0003
N_2	0	0.001	0.79	0.775
H_2O	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

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O + Heat \qquad (2)$$

4. RESULTS AND DISCUSSION

4.1 Base case

Figure 2 depicts the Process Flow Diagram (PFD) of the base model for simulation of ammonia cracking. Simplifying assumptions were listed at the start of Section 3 (methods).

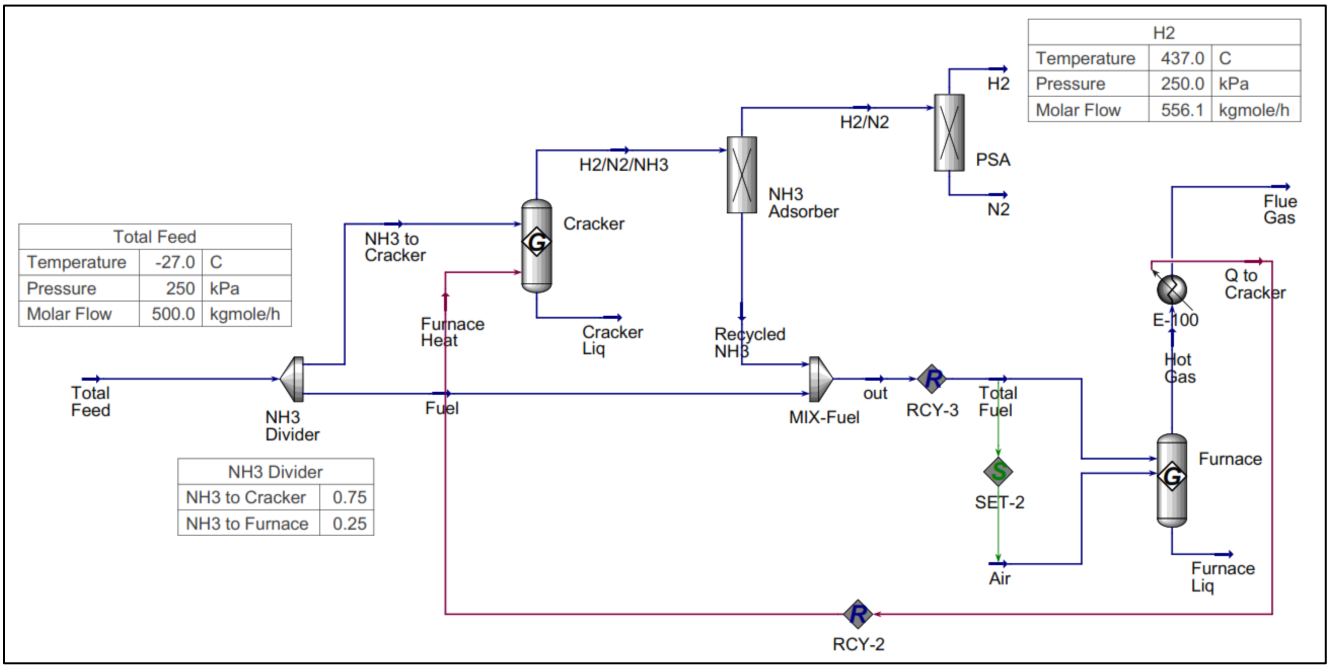


Fig. 2. Aspen HYSYS Process Flow Diagram (PFD) of ammonia cracking (Base case model).

Simulation results from the base case are presented in Table 3.

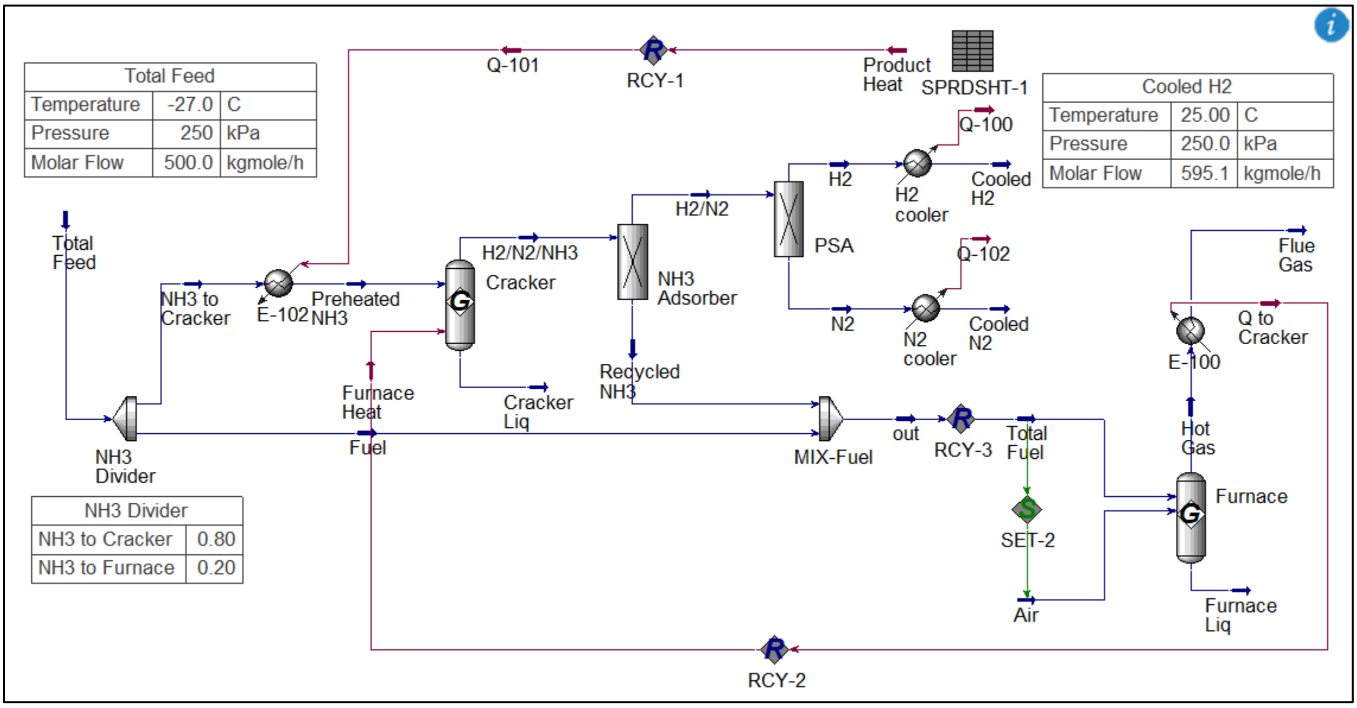
Table 3: Results from the process simulation - base case.

Species	Parameter	Unit	Value
NH_3	Total Feed	(kmoles/h)	500
	Cracker Feed	(kmoles/h)	375
	Unreacted	(kmoles/h)	4.3
	Burned in Furnace	(kmoles/h)	129.3
	Cracker conversion	(%)	99.42
	Total conversion	(%)	74.14
	Cracker yield on H_2	(%)	98.88
	Total yield on H_2	(%)	74.14
H_2	Total Production	(kmoles/h)	556.1
	Total H_2 to NH_3	(kmoles / kmoles)	1.11
	Total H_2 to NH_3	(kg/kg)	0.1316

4.2 Improved case

In this section, the available heat streams within the process, specifically the heat from the hydrogen and nitrogen product streams, were utilized to increase the hydrogen production, the desired final product. To achieve this objective, a new case was introduced, referred to as the "energy consumption improved case" or simply the "improved case".

To optimize the energy of the process, the energy flow from the outlet streams, namely the produced hydrogen and nitrogen, was used to preheat the ammonia stream fed to the cracker. For this purpose, and simulation simplicity, instead of defining heat exchangers, two coolers were introduced to cool down the hydrogen and nitrogen streams to ambient temperature. These two heat flows were then combined and used to preheat the ammonia stream to the cracker using a heater. Furthermore, optimizing the energy in this manner aids the ammonia cracking process by heating the ammonia stream to the cracker, allowing for an increased fraction of ammonia to be directed to the cracker. Consequently, this reduces the ammonia flow used in the furnace. As a result, the optimization not only involves utilizing waste heat to preheat the ammonia to the cracker but also results in burning less ammonia to supply heat for cracking. The flowsheet of the improved case is illustrated in Fig. 3.



Total Feed		
Temperature	-27.0	C
Pressure	250	kPa
Molar Flow	500.0	kgmole/h

Cooled H2		
Temperature	25.00	C
Pressure	250.0	kPa
Molar Flow	595.1	kgmole/h

NH3 Divider	
NH3 to Cracker	0.80
NH3 to Furnace	0.20

Fig. 3. Aspen HYSYS Flowsheet of the improved case.

The simulation results of the improved case are presented in Table 4.

Table 4. Results from the process simulation - improved case.

Species	Parameter	Unit	Value
NH_3	Total Feed	(kmoles/h)	500
	Cracker Feed	(kmoles/h)	400
	Unreacted	(kmoles/h)	3.26
	Burned in Furnace	(kmoles/h)	103.3
	Cracker conversion	(%)	99.6
	Total conversion	(%)	74.35
	Cracker yield on H_2	(%)	99.59
	Total yield on H_2	(%)	79.35
H_2	Total Production	(kmoles/h)	595.1
	Total H_2 to NH_3	(kmoles / kmoles)	1.19
	Total H_2 to NH_3	(kg/kg)	0.141

4.3 Discussions

The Gibbs reactor, which cracks the ammonia operates without any kinetic model and provides a similar conversion to the studies done by Chiuta et al. (2013) and Ojelade and Zaman (2021). This study has a 99.4% conversion at a cracker temperature of 437 °C in the base case and a 99.6% conversion at a cracker temperature of 466 °C in the energy-optimized case. This reflects on previous studies mentioned in the literature review. In Table 5, the obtained hydrogen production in the simulations is compared with literature values. It shows that the simulations in this work are in the same order of magnitude compared to earlier simulations. It also shows that 8 % increased hydrogen production from 0.131 to 0.141 is obtained by process improvements.

Simplifying assumptions have been made in the simulations in this work. Assumption 1 and 2 are that Gibbs equilibrium reactors are used to simulate the ammonia combustion and ammonia cracking reactions. This is also done in literature. These assumptions are optimistic, and more realistic simulations would result in lower cracker conversion and lower hydrogen production. Assumption 3 is that an ideal component splitter is used to simulate the PSA unit. This is also optimistic, and this tends to overestimate the hydrogen production.

Table 5. Results - comparison with previous studies.

Sources	hydrogen production (kg)/ ammonia feed (kg)
This study - base case	0.131
This study - improved case	0.141
Restelli et al. (2023)	0.140
Lee et al. (2023)	0.127
Devkota et al. (2023)	0.129

Heat exchange in the process is simulated with ideal heaters and cooling, and it is assumed no heat loss. These assumptions are assumed to be negligible because the heat loss is assumed to be much smaller than the heat of reactions. To make a comparison of these two fluid packages, the base case simulation was executed using both Peng Robinson and Soave-Redlich-Kwong (SRK). There was not a significant difference in the results of the two equation of state models.

In this work, a portion of ammonia was used as fuel to provide energy for the cracking reactor. This has been done in a Gibbs reactor instead of a furnace. Suggestions for further work include using a furnace, not an ideal Gibbs reactor for burning ammonia. Aspen HYSYS has a limitation of using ammonia as a fuel in the furnace. A potential for energy consumption is identified that can be investigated in future work. Also, energy optimization based on Pinch Technology can be conducted to improve the energy efficiency of the process.

Additionally, doing a techno-economic analysis of the hydrogen production from the ammonia cracking process can be valuable. As an example, this economic investigation can also consider the economic analysis of the energy resource for the cracker.

5. CONCLUSIONS

The paper showed results from simulations of an ammonia cracking process to produce hydrogen using Aspen HYSYS. Ammonia represents a promising way of transporting hydrogen over long distances. A base case that replicated previous work from literature was improved with respect to energy consumption. The improved case gave 0.141 kg hydrogen per 1 kg ammonia feed, marking an 8 % improvement. Recommendations for further work include using available experimental kinetic data and replacing the Gibbs reactor in Aspen HYSYS. Additionally, heat exchangers could be used instead of heaters and coolers to enable energy optimization analysis, perform equipment sizing, and conduct techno-economic evaluations.

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