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Presented by:

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Thesis Title:

Process Simulation of Ammonia as a Hydrogen Carrier for Storage and Transportation

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Abstract

This thesis presents a simulation study of ammonia synthesis and decomposition using Aspen Plus. The work evaluates process conditions, energy requirements, and yields to provide insights into the feasibility and efficiency of ammonia as a hydrogen carrier. The results highlight ammonia's dual role as both an industrial product and an enabler for hydrogen storage and transport, emphasizing its importance in future sustainable energy systems.

By integrating process modeling with energy transition needs, the study demonstrates the potential of ammonia to support the development of a reliable hydrogen economy.

Keywords: Hydrogen economy; Ammonia synthesis; Ammonia decomposition; Hydrogen storage; Aspen Plus simulation; Sustainable energy.

الملخص

تعرض هذه الأطروحة دراسة محاكاة لعمليتي إنتاج الأمونيا وتفكيكها باستخدام برنامج Aspen Plus ، حيث تم تقييم ظروف التشغيل، المتطلبات الطاقوية، ونسب المردود بهدف توضيح الجدوى والكفاءة لاستخدام الأمونيا كناقل للهيدروجين. وقد أبرزت النتائج الدور المزدوج للأمونيا، سواءً كمنتج صناعي مهم أو كوسيط فعّال لتخزين ونقل الهيدروجين، مؤكدةً أهميتها في أنظمة الطاقة المستدامة المستقبلية.

ومن خلال دمج نماذج العمليات مع متطلبات الانتقال الطاقوي، تبيّن هذه الدراسة الإمكانات الكبيرة للأمونيا في دعم تطوير اقتصاد هيدروجيني موثوق ومستدام.

الكلمات المفتاحية : اقتصاد الهيدروجين؛ إنتاج الأمونيا؛ تفكيك الأمونيا؛ تخزين الهيدروجين؛ محاكاةAspen Plus ؛ الطاقة المستدامة.

Contents

List of Figures

List of Tables

General Introduction

In recent years, the global demand for alternative and sustainable energy sources has been steadily increasing, driven by concerns over climate change, environmental degradation, and the depletion of fossil fuel reserves. Among the various candidates, hydrogen has emerged as a highly promising energy carrier due to its exceptional energy content and the fact that its utilization results in zero greenhouse gas emissions at the point of use. This unique combination makes hydrogen a central element in the ongoing transition towards a low-carbon energy system.

Nevertheless, the practical deployment of hydrogen faces significant challenges, particularly with respect to its storage and transportation. Conventional methods often require either very high pressures or extremely low temperatures, both of which are technically demanding and costly. To overcome these limitations, ammonia (NH_3) has been identified as one of the most efficient hydrogen carriers. Ammonia can be liquefied under moderate conditions, enabling safe and economical storage and long-distance transportation. Moreover, it can be decomposed to release high-purity hydrogen when needed, while also benefiting from an already well-established global infrastructure for its production, handling, and distribution.

This thesis consists of the following sections:

- **Chapter 1 – General Overview of Hydrogen**

This chapter introduces hydrogen as a clean energy carrier, highlighting its properties, production methods, and storage challenges. It emphasizes hydrogen's strategic role in decarbonization and the transition to sustainable energy systems.

- **Chapter2 – Ammonia Properties**

The second chapter explores ammonia's physical, chemical, and historical aspects, stressing its importance in fertilizers and industrial uses. It also presents ammonia's potential as a hydrogen carrier due to its favorable storage and transport characteristics.

- **Chapter 3 – Thermodynamic Analysis of Ammonia**

This chapter provides a thermodynamic evaluation of ammonia synthesis and decomposition, analyzing equilibrium, enthalpy, entropy, and Gibbs free energy. It explains the effect of temperature and pressure on reaction feasibility and efficiency.

- **Chapter 4 – Ammonia Synthesis and Decomposition Simulation**

Chapter four focuses on process modeling using Aspen Plus, simulating both ammonia synthesis and decomposition. It details flowsheets, operating conditions, and methodological steps to replicate industrial processes.

- **Chapter 5 – Results and Discussion**

The final chapter presents simulation outcomes for ammonia synthesis and decomposition, analyzing conversion rates, yield, and the influence of operating parameters. It demonstrates ammonia's dual role as a vital industrial product and a hydrogen energy vector .

- **Conclusion**:

A summary of the main findings and implications of the study, as well as recommendations for future research or applications.

Chapter 1

General Overview of Hydrogen

Introduction

The challenge of climate change is promoting energy systems towards transition technologies that allow for decreasing greenhouse gas emissions. Hydrogen is being considered a potential player in national and international strategies and increasingly being applied to different sectors from industry to transport, but overall, environmental sustainability remains a question to be answered. Hydrogen is a carbon-free molecule with the highest energy content per mass unit and is seen as a key energy carrier in future low-carbon scenarios, thus promoting the development of a hydrogen economy. Hydrogen is a colorless, odorless, non-toxic gas that is ignited easily and burns with a pale blue, almost invisible flame, making it lighter than air vapors. It is a high-risk gas because of its wide flammable and explosive range (4–74% in air), and only a small amount of energy is required for its ignition. This, together with very low temperatures, represents a challenge for the safe handling of hydrogen. Hydrogen gives up both electrons upon oxidation to form only water. Despite its high gravimetric energy density, hydrogen has a low volumetric energy density, even in liquid form, compared to other transportation fuels.

Hydrogen could potentially play a significant role in the provision of electricity, heat, industry, and transport and energy storage in a low-carbon emissions energy system if produced from renewable and waste material energy sources.

1. Hydrogen Overview

Hydrogen, composed of a nucleus housing a proton and an orbiting electron, represents the most basic and lightweight atom. Its significance lies in being the most prevalent element on our planet. Typically found in a demineralized state, hydrogen occurs naturally only as part of a molecule, primarily in hydrocarbons and water. It manifests as a gas at standard temperature and pressure (293.15 K and 1 atm), having an extraordinarily low boiling point of -252.76 °C (20.3 K) under ambient pressure. Additionally, hydrogen, is also, under normal conditions, colorless, odorless, and non-toxic, making it environmentally neutral.

Changes in the state of hydrogen occur within a narrow range of temperature and pressure. The process of liquefaction relies primarily on cooling rather than compression. This liquefaction process significantly increases the density of hydrogen, by a factor of 800. To put it in perspective, LPG has a factor of 250 and natural gas has a factor of 600. This makes hydrogen liquefaction an interesting transportation method for long distances. The transportation temperature is extremely low (-253°C), necessitating a highly efficient insulation system to prevent hydrogen from evaporating. Alternatively, hydrogen can be transported in its gaseous form under moderate or high pressures.

Property	**Hydrogen**
Density (gaseous)	0.089 kg/m3 (0°C, 1 bar)
Density (liquid)	70.79 kg/m3 (-253°C, 1 bar)
Lower heating value (LHV)	120.1 MJ/kg
Higher heating value (HHV)	141.88 MJ/kg
Specific volume	12.1 m3/kg
Specific heat Cp	14.310 kJ/kgK
Gas constant R	4.126 kJ/kg°C
Thermal conductivity	0.182 W/m °C
Heat of combustion	144000 kJ/kg

Table 1.1: Thermodynamic properties of hydrogen (at 25°C and 1 atm)

1.2 Hydrogen Environmental Impacts

Hydrogen is not exactly an energy source, but rather what is called an energy carrier or energy vector, meaning a medium that allows the storage of energy that can be converted in a second time into other forms, such as electricity or combustion. However, molecular hydrogen (H2) is quite rare on our planet (present in the atmosphere only in extremely small quantities being 14.4 times lighter than air, it is not retained by it, but disperses into space) and therefore must be produced, either from water using electrolysers (which split the water molecule H2O through electrolysis) or from gas or even oil. Under certain conditions that depend on how it is produced,

hydrogen can represent a sustainable energy solution and can complement or replace energy sources with a greater environmental impact [1].

The main advantages of hydrogen listed below:

- Abundance: The most abundant source of hydrogen on Earth is water. Through processes like electrolysis and electrochemical conversion with a fuel cell, the only by-products produced are oxygen and water. Its availability is therefore limitless.

- High Energy Density: Although its low density, hydrogen has exceptional energy density. One kg of hydrogen releases 4.1 times more energy than 1 kg of coal, 2.8 times more than 1 kg of petrol and 2.4 times more than 1 kg of natural gas.

- Renewable Energy Storage: Hydrogen enables the long-term storage of excess renewable energy for future use.

- Lightweight: While hydrogen storage has a lower theoretical efficiency compared to battery storage, it can be up to 10 times lighter. This reduces both volume and mass requirements for energy storage, even taking into account the weight of the tanks used for storage.

- Environmental Cleanliness: When produced from renewable sources, hydrogen production is carbon neutral. Its use in a fuel cell doesn't emit CO2, NOx, or fine particles. It only releases pure water and heat, devoid of any minerals. In fact, the ambient air that enters the cell for the chemical reaction exits much purer after being filtered upstream of the process.

- Quick Recharge: In the realm of mobility, hydrogen refueling can be done in a matter of minutes, in contrast to several hours for its battery equivalent. This is a major advantage for the future of electric mobility.

Despite these favorable attributes and the significant contributions hydrogen offers in terms of climate protection, it is essential to conduct a more comprehensive assessment of hydrogen production in relation to climate protection. The categorization of hydrogen into various "colors" aims to offer insights into its production methods, the energy sources employed, and the extent of its climate-friendliness.

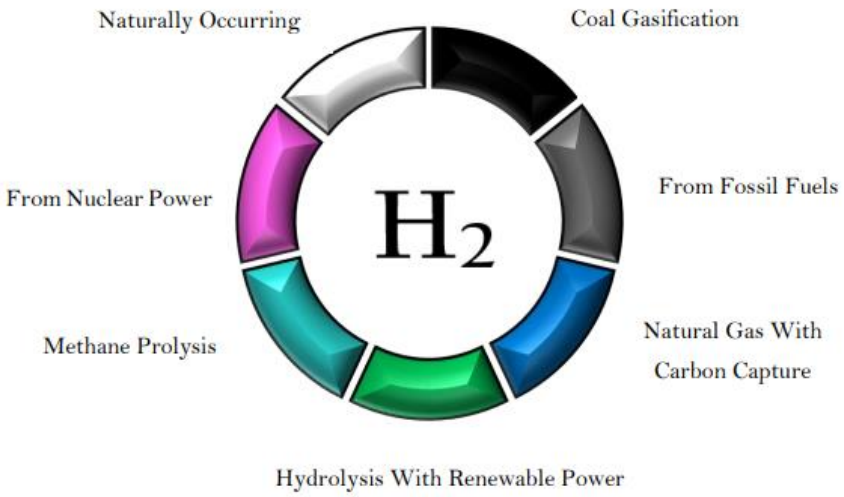


Figure 1.1: Hydrogen coloring codes

- **Black/Brown:** Black or brown hydrogen is produced from coal. The black and brown colors refer to the type bituminous (black) and lignite (brown) coal. The gasification of coal involves conversion of coal from its solid state into gaseous form. It is a method used to produce hydrogen. However, it is a very polluting process, and CO2 and carbon monoxide are produced as by-products and released to the atmosphere [2].

- **Grey:** Currently, this is the most common form of hydrogen production. Grey hydrogen is derived through the steam reforming of fossil fuels like natural gas or coal. This process results in the direct release of CO2 into the atmosphere. For every tonne of hydrogen produced, ten tonnes of carbon dioxide are emitted, making grey hydrogen harmful to the climate.

- **Blue:** Similar to grey hydrogen, blue hydrogen is produced mainly from natural Gas using a process called “steam reforming “, in which both natural gas and heated water are

carried in the form of steam, but the CO2 emissions are captured and stored (CCS) underground or utilized (CCU) rather than being released into the atmosphere.

- **Turquoise:** This represents a new entry in the spectrum of hydrogen colors and its large-scale production has not yet been proven [3]. This kind of hydrogen is generated through a thermal process in which natural gas undergoes methane pyrolysis, resulting in the production of hydrogen and solid carbon. Consequently, turquoise hydrogen is generally not entirely climate-neutral when considering the entire production process and the subsequent treatment of carbon as a byproduct [3].

- **Pink/Purple:** Like green hydrogen is generated through electrolysis but in this process, the electricity is generated by nuclear power that is after used to split water into hydrogen and oxygen. The term "pink" is used to represent the combination of the red colour associated with nuclear energy and the blue color commonly associated with hydrogen (this is why it is also referred to purple).

- **Green:** is generated without emitting greenhouse gases. It is produced by the electrochemical process of electrolysis, in which water (H2O) is split into its 2 elemental components, hydrogen (H2) and Oxygen (O2), using electricity produced by renewable energy sources like solar or wind power or also hydroelectric power. This means that the entire process is carried out without emitting greenhouse gases. As a result, green hydrogen is considered a clean and sustainable energy carrier with the potential to play a significant role in reducing carbon emissions in various industries, including transportation, energy storage, and industrial processes.

Table 2 reports a summary of the main hydrogen categories with a focus on the processes and products:

Color		Fuel	Process	Products
	Black/Brown	*Coal*	*Steam reforming or gasification*	H_2+$CO_{2(released)}$
	White	*N/A*	*Naturally Occurring*	H_2
	Grey	*Natural Gas*	*Steam Reforming*	H_2+$CO_{2(released)}$
	Blue	*Natural Gas*	*Steam Reforming*	H_2+$CO_{2(\%captured\ and\ stored)}$
	Turquoise	*Natural Gas*	*Pyrolysis*	H_2+$C_{(solid)}$
	Pink/Purple	*Nuclear Power*	*Catalytic Splitting*	H_2+O_2
	Green	*Renewable Electricity*	*Electrolysis*	H_2+O_2

Table 1.2: Hydrogen Type Summary

1.3 Hydrogen Production Methods

Hydrogen in molecular form can be produced from many different sources, and in many different ways. In the context of energy systems, hydrogen is best thought of as an energy carrier, more akin to electricity than the fossil fuels that we extract from the earth's crust. Hydrogen can be produced from any hydrocarbon fuel because by definition these fuels contain hydrogen. Hydrogen can also be produced from various biological materials and from water. The "water-splitting" process is called electrolysis, and it is the oldest known electrochemical process. [4].

1.3.1 Steam Methane Reforming

Methane reforming (SMR) is the process by which natural gas or other methane stream, such as biogas or landfill gas, is reacted with steam in the presence of a catalyst to produce hydrogen and carbon dioxide. When starting with natural gas, SMR is approximately 72% efficient in producing hydrogen on a lower heating value basis. The efficiency can be somewhat lower with sources of methane that include sulfur or other impurities that require a pre-treatment cleanup step to remove the impurities upstream of the SMR process [4].

1.3.2 Gasification of Coal and Other Hydrocarbons

In the partial oxidation (POX) process, also known more generally as "gasification," hydrogen can be produced from a range of hydrocarbon fuels, including coal, heavy residual oils, and other low-value refinery products. The hydrocarbon fuel is reacted with oxygen in a less than stoichiometric ratio, yielding a mixture of carbon monoxide and hydrogen at 1200° to 1350°C.

1.3.3 Electrolysis of Water

Electrolysis is the process by which water molecules are split directly into hydrogen and oxygen molecules using electricity and an electrolyzer device. The overall electrolysis reaction is:

e - + H2O -> ½ O2 + H2 the two most common types of electrolyzers are alkaline (use a potassium hydroxide electrolyte) and PEM (use a solid polymer membrane electrolyte). A schematic of an alkaline electrolysis system is provided in Figure 7. The electrolysis reaction produces pure oxygen as a by-product along with pure hydrogen. The oxygen can then be used for productive purposes such as enriching the oxygen content of greenhouses for food production Hydrogen can be produced via electrolysis of water from any electrical source, including utility grid power, solar photovoltaic (PV), wind power, hydropower, or nuclear power. Electrolysis is currently done at a wide range of scales, from a few kW to up to 2,000 kW per electrolyzer [4].

1.3.4 Hydrogen from Biomass

Biomass conversion technologies can be divided into thermo-chemical and biochemical processes. Thermo-chemical processes tend to be less expensive because they can be operated at higher temperatures and therefore obtain higher reaction rates. They involve either gasification or pyrolysis (heating biomass in the absence of oxygen) to produce a hydrogen-rich stream of gas known as "syngas" (a blend of hydrogen and carbon monoxide). They can utilize a broad range of biomass types [4].

1.4 Applications of Hydrogen

Hydrogen has a wide range of applications across various industries due to its versatility as an energy carrier and its ability to serve as a clean and efficient fuel. Here are some of the main applications of hydrogen in different industries [5]:

*** Transportation:**

- Fuel Cell Vehicles (FCVs): Hydrogen is used as a fuel in fuel cell vehicles, where hydrogen reacts with oxygen in a fuel cell to produce electricity, powering the vehicle's electric motor. FCVs emit only water vapor as a byproduct, making them a zero-emission transportation option.
- Hydrogen-powered Vehicles: Hydrogen can also be used directly in internal combustion engines or as a blend with traditional fuels in vehicles.

*** Energy Storage:**

- Grid Balancing: Hydrogen can be used as an energy storage medium to balance supply and demand on the electrical grid. Excess electricity, particularly from renewable sources like wind or solar, can be used to produce hydrogen through electrolysis. The hydrogen can then be stored and converted back to electricity when needed.

- Seasonal Energy Storage: Hydrogen has the potential for long-term and seasonal energy storage, providing a solution for storing excess energy generated during peak times for use during periods of high demand.

*** Industrial Processes:**

- Hydrogen as a Feedstock: Hydrogen is a crucial feedstock for various industrial processes, including the production of ammonia for fertilizers, petroleum refining, and the production of chemicals such as methanol.
- Metal Production: In industries like steel production, hydrogen can be used as a reducing agent to remove oxygen from iron ore, reducing carbon emissions.

*** Power Generation:**

- Combined Heat and Power (CHP) Systems: Hydrogen can be used in CHP systems to generate both electricity and heat for industrial and residential applications.

*** Space Exploration:**

- Rocket Propulsion: Hydrogen, often in combination with oxygen, is used as a propellant in rocket engines for space exploration.

*** Healthcare:**

- Industrial Applications: Hydrogen is used in various industrial applications, including the production of hydrogen peroxide and in the synthesis of certain chemicals used in pharmaceuticals.

***Welding and Metal Processing:**

- Metal Reduction: Hydrogen is used in metal reduction processes, such as the reduction of tungsten and titanium.

These applications demonstrate the versatility of hydrogen across multiple sectors, and ongoing developments in hydrogen technologies, infrastructure, and policies are expected to expand its role in addressing energy and environmental challenges globally.

1.5 Hydrogen Storage

Hydrogen storage is a critical element for the development of a sustainable energy system. Due to its extremely low density (1kg of H_2 occupies about 12 m^3 at room temperature and atmospheric pressure), storing hydrogen in an effective, safe, and reliable manner is the most significant challenge. Currently, there are three different methods for hydrogen storage:

- Compressed gas storage.
- Cryogenic liquid storage.
- Material-based storage (also referred to as "solid-state").

Among these, the first two are by far the most common, while the last method is currently less mature.

Hydrogen has the highest energy content per unit mass, containing three times the energy of diesel with the same weight (~140 MJ/kg compared to ~45 MJ/kg). However, in terms of volume, hydrogen exhibits a low energy density (0.01 MJ/L), as indicated in the table 7. Compared to conventional hydrocarbons, storing hydrogen with equivalent energy content will require larger tanks or an increase in density. This highlights a crucial [6]

FUEL	*SPECIFIC ENERGY DENSITY (MJ/kg)*	*VOLUMETRIC ENERGY DENSITY (MJ/L)*
HYDROGEN	120-142	0,01
PETROL/GASOLINE	44-46	34,2
DIESEL	42-46	38,6
METHANOL	22,7	15,6
BIODIESEL	42	33
NATURAL GAS	50-55	0,03

Table 1.3: Energy Densities for Different Fuels

1.5.1 Hydrogen Storage Methods:

As mentioned earlier, hydrogen storage must take place in a way that significantly increases its energy density. It is known that to increase the density of a gas, either the pressure must be increased, or the temperature must be reduced.

1.5.2 Storage in gaseous form:

This is currently one of the simplest, most common and efficient storage technologies in use. High-pressure hydrogen is stored in thick-walled tanks (mainly of cylindrical or quasi-conformable shape) made of high strength materials to ensure durability. The storage tank design, which is based on classic deterministic engineering approaches, is not yet optimized. The tanks are actually over-sized; there is inefficient use of material and a rather poor assessment of the pressure vessel lifetime. Compressed gas hydrogen storage vessels can be classified in four types as: [07].

Type I: they are constructed from metal, are employed to store industrial gas at pressures ranging from 150 to 300 bars. While they are widely utilized and cost-effective, their weight makes them unsuitable for vehicle applications.

- Type II: they are equipped with a durable metal ring liner surrounded by carbon or glass fiber material. The operating pressure for this tank is typically 100 to 500 bars, and it is mainly used in industrial applications.

- Type III: they are equipped with an internal metal liner to prevent hydrogen leakage through diffusion. They are encased in composite materials to withstand mechanical stress. This design, involving thinner metal and increased use of composites, results in lighter tanks compared to Types I and II. It is often found in vehicles and can store hydrogen at pressures up to 350 bars,

- Type IV. They employ a high-density polymer liner for gas diffusion prevention, enclosed by a carbon fiber compound. They come with metal valves for hydrogen refueling and can handle pressures of up to 700 bars.

Figure 1.2: Hydrogen Cylinders and Tube Trailer

1.5.3 Liquid state storage:

In the liquid state, possible methods include:

- Liquid hydrogen.
- Ammonia: Ammonia stands out as a promising hydrogen carrier due to its high hydrogen content and ease of transport. It is generated by combining hydrogen and nitrogen, providing a means for subsequent hydrogen release through a process called "ammonia cracking." Continued research and development are crucial for widespread implementation.
- LOHCs: Liquid Organic Hydrogen Carrier Systems involves liquid organic compounds to store hydrogen. These compounds can absorb and release hydrogen, making them a potential solution for safe and efficient hydrogen storage.

Storing hydrogen in liquid form through liquefaction allows for high storage densities even at atmospheric pressure. However, it requires a significant amount of energy due to hydrogen's extremely low boiling point (-253°C at 1 bar).

Another factor to consider is the boil-off rate, which is the rate of evaporation of liquid hydrogen. Due to the extremely low boiling temperature, effectively insulating the tank and maintaining cryogenic temperatures for extended periods is challenging.

This results in notable losses, as the evaporation of liquid hydrogen increases pressure, leading to the release of gas through safety valves. The heat transference from the surroundings to the stored liquid hydrogen and thus the boil-off rate is reduced by minimizing the surface-to-volume ratio of the vessels by making them spherical [7].

Figure 1.3: Liquid Hydrogen Tanks

1.5.4 Storage using materials (or "solid-state")

The solid-state storage techniques have captured the attention of researchers worldwide and are being studied and developed as technology for the future energy system. They are in the testing phase.

Metal hydrides: exploit the crystalline chemical structures of metal hydrides, creating interstitial sites where dissociated hydrogen molecules can bind. This allows for a significant amount of hydrogen to be stored in compact volumes.

Additionally, due to the relatively weak bonds, the process of creating and breaking them requires less energy [7]. In metal hydride tanks, hydrogen is stored through reversible chemical reactions that occur between a metal alloy and gaseous hydrogen. The solid metal hydride acts like a sponge capable of absorbing and releasing hydrogen.

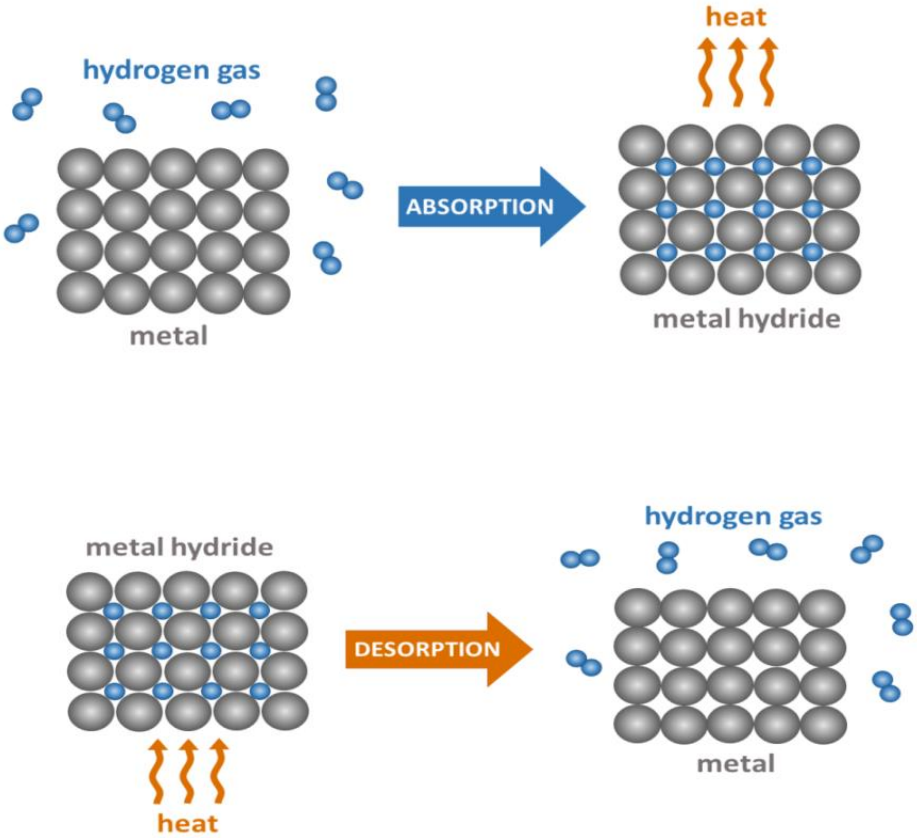


Figure 1.4: Metal Hydride Storage Processes

Hydrogen storage technology	Benefits	Barriers
Compressed gas cylinders	Well-understood up to pressures of 200 bar; generally available, can be low cost	Only relatively small amounts of H_2 are stored at 200 bar, fuel and storage energy densities at high pressure (700 bar) are comparable to liquid hydrogen, but still lower than gasoline and diesel, high pressure storage still under development
Liquid tanks	Well-understood technology, good storage density possible	Very low temperatures require super insulation, cost can be high, some hydrogen is lost through evaporation, energy intensity of liquid hydrogen production, energy stored still not comparable to liquid fossil fuels
Metal hydrides	Some technology available, solid-state storage, can be made into different shapes, thermal effects can be used in subsystems; very safe	Heavy, can degrade with time, currently expensive, filling requires cooling circuit
Carbon structures	May allow high storage density, light, may be cheap	Not fully understood or developed ,early promise remains unfulfilled

Table 1.4: Benefits and barriers of hydrogen storage solutions

1.6 Transportation of hydrogen

Hydrogen technology for transportation is progressing, but there are several challenges to consider. These include technical challenges related to infrastructure, such as compressor reliability and the construction of hydrogen fueling stations. The cost of resources and materials is another significant challenge along with the total carbon footprint of producing hydrogen components compared to batteries. Additionally, there are concerns about the ethics of the supply chain and sourcing of materials. Other challenges include the need for standardization and market readiness of materials, connectors, and compressors. Safety considerations, such as fire risk, pressurized vessel safety, and workforces training are also important. Finally, transportation

and distribution issues, such as pipeline leaks and cracking, need to be addressed before hydrogen can scale in the transportation industry [8].

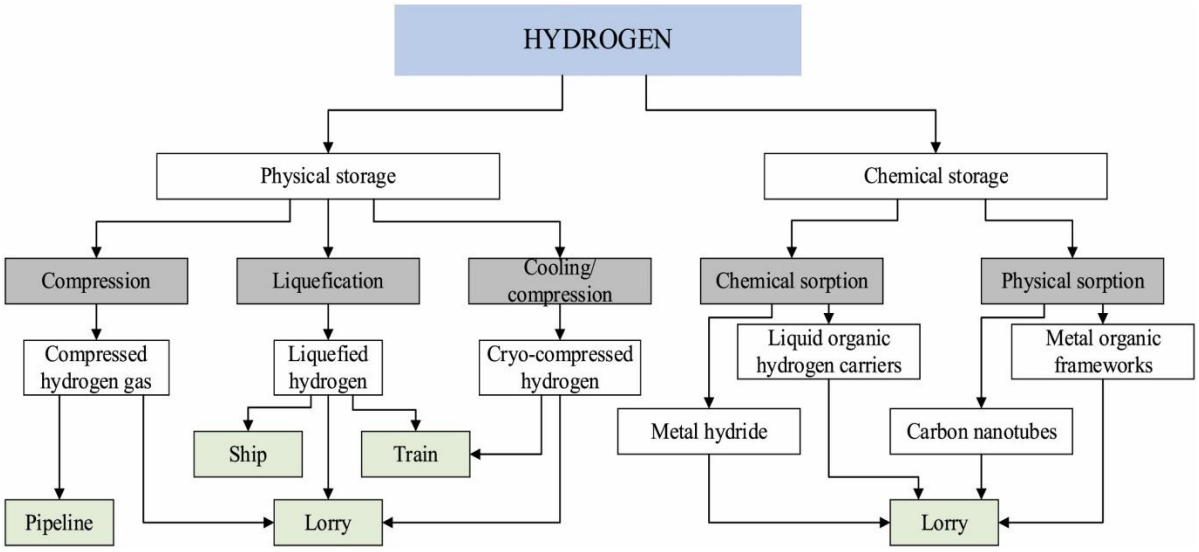


Figure 1.5: Hydrogen transportation methods [8].

1.6.1 PIPELINES (GASEOUS H_2)

Gaseous hydrogen can be transported in pipelines, like natural gas. Before injection, the hydrogen is mechanically compressed to the operating pressure of the pipeline. This is usually higher than the outlet pressure of electrolyzers. Depending on the pipeline's characteristics and local conditions, the hydrogen must be recompressed at certain distances along the pipeline before it reaches its destination. In addition, storage facilities (such as salt caverns or above-ground tanks) are required for buffering in case of volatile supply. As with natural gas pipelines, a mature hydrogen pipeline system with transmission and distribution grids also requires metering stations, control valves and gates to manage flows and ensure onward distribution to end users. Instead of building new pipelines, existing natural gas pipelines can be repurposed to transport hydrogen. The injection of hydrogen into existing gas grids is also under discussion, with blends of up to 20% hydrogen currently being tested in pilot projects.

1.6.2 AMMONIA

Ammonia (NH_3) is a bulk chemical that is normally synthesized from natural gas and mainly used as chemical feedstock, e.g. in fertilizer production. However, it can also serve as a clean hydrogen storage medium. The medium is produced by reacting hydrogen and nitrogen (derived from air via an air separation unit) to synthesize liquid ammonia, using a process that is very similar to the conventional production method (Haber-Bosch process). The liquid ammonia can then be transported in refrigerated tanks. Once it reaches its destination, the ammonia is broken down into its components, nitrogen and hydrogen, through an endothermic cracking process. The resulting gas mixture is then purified, and the nitrogen removed and released back into the atmosphere. Ammonia is already transported today, although most conventional ammonia is produced onsite at the place where it is further used [9].

1.6.3 LIQUEFIED HYDROGEN (LH_2)

The volumetric storage density of hydrogen can be significantly improved through liquefaction that is, cooling it below its boiling point of minus 253°C. After liquefaction, LH_2 is stored in specially insulated and double-hulled tanks. This limits heat transfer from the environment and subsequent losses due to evaporation, as built-up gas (boil-off) has to be vented. Under these conditions, LH_2 is already being transported via specially designed trailer trucks today. At the destination, LH_2 is usually vaporized into its gaseous form before use.

In production and offtake patterns. In addition, large-scale LH_2 transportation via vessels is still in the prototyping phase, leading to substantial investment costs. In general, the infrastructure required for liquefied hydrogen is more capital intensive along the value chain in comparison to competing carriers.

1.6.4 LIQUID ORGANIC HYDROGEN CARRIERS (LOHC)

Liquid organic hydrogen carriers are easily transported chemical compounds that can be reversibly hydrogenated and dehydrogenated. The hydrogenation process involves chemically binding hydrogen to the liquid compound so that it can be transported at atmospheric pressure like many other oil-like substances. At the destination, the hydrogen is released via an endothermic (heat-requiring) dehydrogenation process. The dehydrogenated LOHC can then be transported back to the hydrogen source for reuse. There are several organic carrier substances

available, among which toluene, dibenzyltoluene and benzyltoluene (so-called heat transfer fluids) are the most common. Here we focus on benzyltoluene.

Hydrogen transportation technology	Advantages	Disadvantages
Compressed hydrogen transportation in containers by road or rails	- No need to build special infrastructure (pipelines - Transport capacity can be scaled well to requirements on a small scale	- High weight and volume tanks - The pipeline also functions as an accumulator hydrogen storage tank - Small mass transport capacity
Liquefied hydrogen transportation in containers by road, rail or ship	- No need to build infrastructure (pipelines) - Possibility of transporting larger volumes	- Large liquefaction losses - Small mass transport capacity
Hydrogen transportation by pipeline with natural gas mixture	- Existing natural gas infrastructure (and biogas/biomethane) - Continuity of supply - Lower costs compared to transport by road/rail - Natural storage capacity	- A limited ratio of admixture to a certain percentage - The maximum hydrogen concentration is given by compatibility of the connected end devices (e.g. CNG, boilers, etc.)
Transportation Ammonia as hydrogen carrier	- transporting and handling the substance is already mature - Liquid ammonia also contains more hydrogen by volume than any of the other carriers	- Ammonia is a toxic fluid and precursor to air pollution - Toxicity may ultimately limit the application for end uses outside large-scale industry.
Liquid organic hydrogen carriers (LOHC)	- Transportation at normal temperature and pressure - Easy liquid handling - High hydrogen content both in terms of both by weight and volume - Great flexibility in terms of what is transported of quantity and distance transported	- Hydrogen storage and recovery is expensive - New technology

Table 1.5: Advantages and Disadvantages of hydrogen transportation technologies

1.7 Hydrogen production CO_2 emissions:

Currently, the most widely used method in the mass production of hydrogen is steam methane reforming (SMR), referred to as gray hydrogen. SMR is a mature production process whereby high-temperature steam (700°C–1,000°C) is used with a methane source (such as natural gas) to

produce hydrogen gas and carbon dioxide (CO_2). There is approximately 9 kg of CO_2 emitted per kg of hydrogen production. Gray hydrogen is used primarily for petroleum refining and ammonia production for agriculture fertilizer.

Industries are beginning to shift towards low emission or low carbon options for hydrogen production, often referred to as blue and green hydrogen, respectively. Steam methane reform combined with carbon capture and sequestration (CCS) technology is called blue hydrogen. Blue hydrogen in its current form captures anywhere from 50%-90% of the CO_2 produced by the reform process. Meanwhile, green hydrogen produced via renewable or nuclear power generation through electrolysis is a zero-carbon production method.

1.7.1 hydrogen production costs:

Gray and blue hydrogen are favorable near-term alternatives to green hydrogen as the SMR and CCS technologies are currently more established and less expensive compared to the electrolyzer technology used for green hydrogen production. As both the technologies and economies of scale behind green hydrogen improve in the coming years, its production cost will likely become more competitive with that of blue hydrogen [10].

	Natural gas SMR (Gray)	Natural gas SMR with CCS (Blue)	Renewable electricity with electrolyzer (Green)
Emissions (kg CO_2/kg H_2 produced)	~9	1-5	0
Cost ($/kg H_2)	$0.50-2.00	$1.00-4.00	$2.50-10.00

Table 1.6: Hydrogen production costs and CO_2 emissions (2021).

Chapter 2

Ammonia Properties

Introduction

Ammonia is the second-largest global chemical products, utilized as agricultural fertilizer, food production, industrial materials, refrigerants, and additives. Recently, the utilization of ammonia as the energy carrier (secondary energy source) has attracted many interests, due to its high volumetric hydrogen density, low storage pressure, high stability for long-term storage, high auto-ignition temperature, low condensation pressure, and lower gas density than air. in general, ammonia production includes the currently adopted thermochemical (Haber–Bosch), electrochemical, and photochemical cycle processes[11].

Currently, about 200 Mt/y of ammonia is manufactured globally , making it the world's second most commonly produced chemical after sulfuric acid (H_2SO_4). Similarly to hydrogen, ammonia can be produced from different primary energy sources, including biomass, coal, natural gas, solar, wind, geothermal, hydro and nuclear sources. Ammonia can be produced through different conversion technologies: thermochemical, electrochemical, photochemical and plasma. However, with the consideration of technological feasibility and total energy efficiency , in this work, three main conversion technologies (Haber–Bosch, electrochemical and thermochemical cycle processes) are described [11].

2. Ammonia

Ammonia is an intermediate product in the manufacture of nitrogenous fertilizers. It is also used for direct application to the soil and in aqua condition with solutions of other nitrogenous fertilizers like ammonium nitrate and/or urea. Besides these, ammonia finds applications in the production of nitric acid, soda ash, cleaning agents, leather tanning, petroleum refining, pulp and paper industry, textiles, refrigeration, rubber & synthetic resin industries, explosives and food & beverages, and as energy carrier for hydrogen[1].

Ammonia is produced by the reaction between nitrogen (N_2) and hydrogen (H_2)

$$N_2 + 3H_2 \rightarrow 2NH_3 \qquad (2.1)$$

Source of Nitrogen is atmospheric air and following hydrocarbons are generally used as the source of hydrogen.

- Natural gas
- Naphtha
- Heavy Oil

Other sources of hydrogen which were used earlier for manufacture of Ammonia are:

1) Semi-water gas made by gasification of coke/ coal with steam.

2) Hydrogen produced by electrolysis of water.

3) By product Hydrogen from chlorine production.

2.1 Ammonia Properties

Physical Properties		Chemical Properties	
Molecular Mass	17.03 g/mol	**Chemical Formula**	NH_3
Color	Colorless	**Type Of Base**	Weak
Odor	Sharp, Irritating	**Affinity(Water)**	High
Physical State	Gas (at room temperature)	**Corrosiveness**	Corrosive to Some Metals
Melting Point	-77.7°C	**Oxidation Power**	Strong Reducing Agent
Boiling point	-33.35°C	**Reactivity**	Quite Reactive
Flash Point	11°C	**Volatility**	Increases with increase in pH
Decomposition Point	500°C		
Density (Gas)	0.7710 g/L		
Density (Liquid)	0.6818 g/L		
Critical Temperature	132.4°C		
Critical Pressure	111.3atm		
Heat Of Fusion	58.1 kJ/mol		
Heat Of Vaporization	23.3 kJ/mol		
Heat Of combustion	-316 kJ/mol		

Table2.1: Physical and Chemical Properties of Ammonia [12].

2.2 History of Ammonia

The history of ammonia cannot be detached from the large subject of nitrogen supply to the fertilizer and chemical industry. In the early days of chemical industry dependence was placed on natural and waste products of various kinds. Ammonia is the most stable form of "fixed nitrogen" which is used as an essential part of almost all types of fertilizers.

Before 1800, the principle sources of nitrogen were by product, organic material of various types which include manure, seed, meals, fish scraps, leather scraps and slaughter wastage.

First of all 'Priestly' produced ammonia in 1754 by heating "sub-ammonia (ammonium chloride) with lime. The new compound was named for Egyptian god arm mow, because ammonium chloride was first made fourth century (B.C) from camel dung near the temple of arm mow.

In 1975, Hildebraud tried to synthesize ammonia from nitrogen and hydrogen at atmospheric pressure. In 1923, Dobernier realized that a catalyst would be needed for practical method. Between 1850 &1900, the general development of physical chemistry, the new concept of mass action chemical equilibrium did much to pave the way for ammonia synthesis.

First full plant scale was placed on stream in Badishe Aniline – und soda Fabric A.G. (BASF) by Fritz Haber and Carl Bosch at Oppau. Germany.

The process became commercial Haber-Bosch process. Although several processes have developed since 1913.The main differences were the methods for the preparation of synthesis gas, the purification of synthesis gas, the design of ammonia convertor and method of receiving ammonia from converted flue gas.

Prior to 1945, coat and coke oven gas was the major raw material used for the production of hydrogen required for ammonia synthesis. During the past 35 years, there has been a trend towards the use of petroleum products. Most of the plants built during the past 25 years,

throughout the world designed for the use of a natural gas, heavy oil as feed material. During last 15 years, Naphtha has become the most popular feed material in the areas where natural gas is not present. At present almost all of the ammonia plants in world are based on natural gas [12].

2.3 Ammonia most common production processes

2.3.1 Haber Bosch process

The currently adopted ammonia production process basically employs the system invented by Fritz Haber and Carl Bosch about 100 years ago. Therefore, this system is well known as Haber–Bosch process. About 85% of total production of ammonia worldwide is produced by this process. The ammonia synthesis occurs according to reaction (12).

$$3\ H_2 + N_2 \leftrightharpoons 2\ NH_3 \qquad \Delta H°_{27\ °C} = -46.35\ \text{kJ/mol} \quad (2.1)$$

Ammonia synthesis is an exothermic reaction (negative enthalpy change), and it occurs spontaneously at low temperatures (negative entropy change). Although it is favored at room temperature, the reaction rate at which the reaction occurs at room temperature is too slow to be applicable for at an industrial scale. In order to increase the kinetics of the reaction to achieve the targeted conversion rate, high pressure and temperature are required. To effectively synthesize ammonia from its main components (hydrogen and nitrogen), the reaction should be performed at a relatively high temperature and pressure of 400–500 °C and 10–30 MPa, respectively, with the assistance of an iron-based catalyst. This condition is demanded due to the high dissociation energy (941 kJ/mol) of triple-bonded nitrogen. However, to bring the reaction under this high temperature and pressure, about 30 MJ/kg-NH3 of energy is required [13].

The production of ammonia from natural gas is conducted by reacting methane (natural gas) with steam and air, coupled with the subsequent removal of water and CO_2. The products of this process are hydrogen and nitrogen, which are the feedstock for the main ammonia synthesis. During the process, the removal of sulfur and other impurities is important, because they can reduce and damage the performance of the catalyst during synthesis. In the ammonia synthesis process, both nitrogen and hydrogen are compressed to relatively high pressure to be fed to the

synthesis reactor, where the catalyst is immersed inside. The produced ammonia, together with the unreacted hydrogen, argon and other impurities, is then cooled down for ammonia condensation in order to separate the ammonia from the other gases. The unreacted hydrogen and nitrogen are then recycled back and mixed together with the new feedstock. To avoid a build-up of impurities, such as argon, a small part of the gases is purged from the process. Ammonia synthesis produces a small amount of heat, which is released from the reactor; therefore, it can be recovered and utilized for other processes, such as steam and power generation. In general, about 88% of hydrogen's calorific value can be conserved.

Another challenge in the Haber–Bosch process is its low conversion rate; therefore, the process must be recycled to achieve the expected production flow rate. However, at pressure of 30 MPa, the conversion rate from the reaction is still low, no more than 25%. This stream recirculation causes some problems, including the need for an additional recirculation system and a larger reactor, leading to high investment and operation costs.

The energy consumed during ammonia production, including conversion from primary sources, typically ranges from about 28 to 37 GJ/t. An ammonia production system from any primary source, such as natural gas, is considered complex, as it includes many combined processes [13].

The process for converting hydrocarbon feed into ammonia consists of following main sections [14]:

2.3.1.1 Natural gas reforming

Methane is mixed with steam and passed over a nickel catalyst at high temperatures (700-1000 °C).

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad (2.3)$$

This step produces carbon monoxide and hydrogen gas.

2.3.1.2 Carbon monoxide conversion

The resulting carbon monoxide is mixed with more steam and passed over a second catalyst at a lower temperature (200-450 °C).

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (2.2)$$

This produces more hydrogen and carbon dioxide.

2.3.1.3 Hydrogen purification

- The carbon dioxide is removed from the synthesis gas (a mixture of H_2, CO, and CO_2) through a water wash or by using amines.

2. 3.1.4 Ammonia synthesis

- Pure hydrogen gas is combined with nitrogen in a 3:1 ratio.
- The gas mixture is introduced into a reactor at high pressure (15-30 Mpa) and high temperature (400-500 °C) in the presence of an iron catalyst.

$$N_2+3H_2 \rightarrow 2NH_3 \qquad (2.1)$$

2.3.1.5 Process conditions

- Pressure: 15-30 Mpa.
- Temperature: 400-500 °C.
- Catalyst: Commonly iron with promoters such as potassium and aluminum.

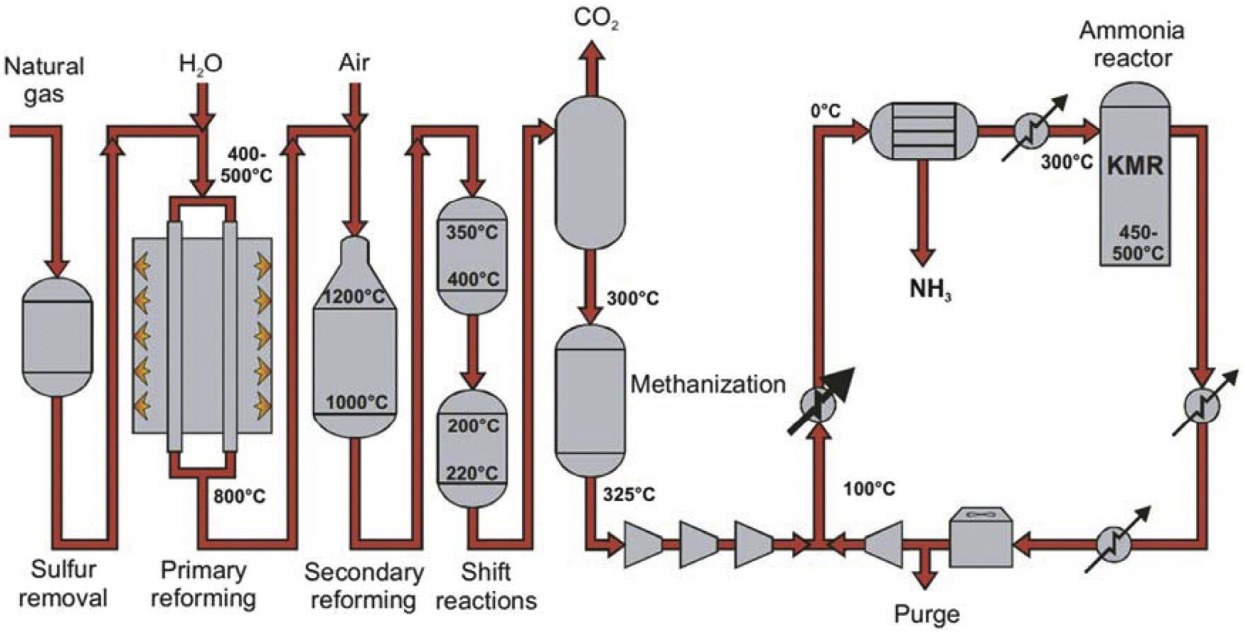


Figure 2.1: Process scheme of steam methane reforming-based ammonia synthesis [15].

The main sections for Ammonia production are:

- Hydrofining or desulphurization.
- Steam Reforming.
- Shift CO conversion.
- CO_2 removal.
- Final purification,
- Ammonia synthesis.
- Recovery.
- Cracking.
- Liquefaction & Storage.

2.3.2 Electrochemical processing

Although electrochemical processing is significantly under-developed compared to the Haber–Bosch process, it is expected to realize higher energy performance. The energy consumed by this process is about 20% lower than the Haber–Bosch process .the Figure below shows the schematic flow diagram of electrochemical ammonia synthesis. The process is considered simple; therefore, its application is considered to potentially reduce system configuration and control complexity. In addition, the investment cost can be lower compared to currently adopted ammonia synthesis systems [16].

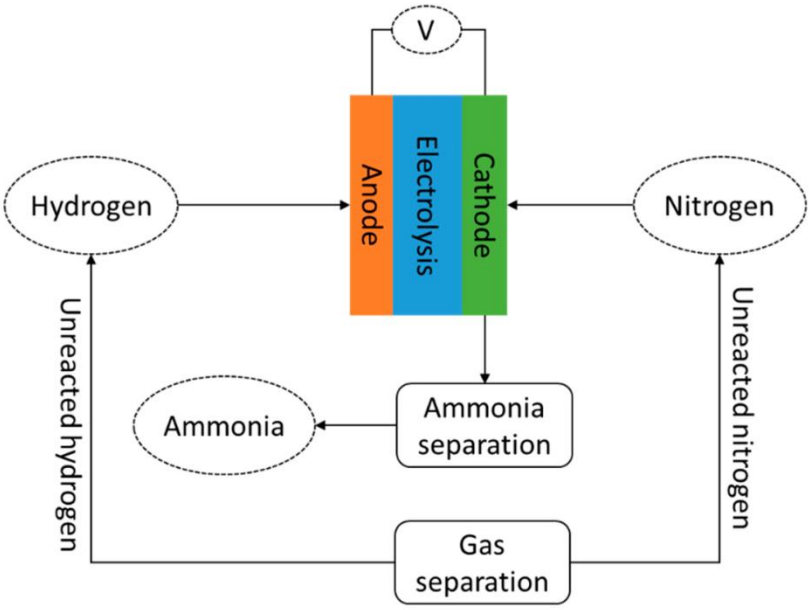


Figure 2.2: Schematic diagram of electrochemical ammonia synthesis.

The reactions at both cathode and anode in proton conducting cells are shown in reactions (2) and (3), respectively. The reactions at each cathode and anode are basically reversible.

$$N_2 + 6\,H^+ + 6\,e^- \rightleftharpoons 2\,NH_3 \qquad (2.4)$$

$$3\,H_2 \rightleftharpoons 6\,H^+ + 6\,e^- \qquad (2.5)$$

Four different types of electrolytes are currently available:

(a) Liquid electrolytes.

(b) Molten salt.

(c) Composite membranes.

(d) Solid state electrolytes.

Liquid electrolytes can operate under atmospheric temperature and pressure. There are some potential liquid electrolytes, including $LiClO_4$ (0.2 M) in tetrahydrofuran, $LiClO_4$ in ionic liquid, $LiClO_4$ in H_2SO_4 and Li_2SO_4 in H_2SO_4. Ammonia production of 3.68×10^{-10} mol/cm^2·s could be obtained, while the system efficiency can reach about 58%, indicating that about 58% of the current supplied to the system is converted into ammonia. However, the research related to this issue is still limited to lab experiments, in small dimensions of cells and limited operation times.

A molten salt type electrolyte is generally operated at a temperature range of 300–500 °C. There are some potential chemicals for use as electrolytes, such as LiCl, KCl and CsCl, with dissolved Li_3N. The reported ammonia production rate is 3.3×10^{-9} mol/cm^2·s, and the efficiency is about 72%.

The system with composite electrolytes also includes solid electrolytes, which are combined with low melting salt, and have an operating temperature of 300–700 °C. The electrolytes comprise the main ionic conducting phase and an additional phase that is attached to the main phase to improve the electrical, mechanical and thermal properties. As the representative of composite electrolytes, alkali metal carbonate (such as $LiCO_3$) and oxide (such as $LiAlO_2$) and CeO_2 doped with Sm_2O_3 have shown the expected properties, including oxygen ion, carbonate ion and proton conductivity.

The system with solid electrolytes generally operates in very wide operating temperatures, from room temperature to about 800 °C. There are different materials which can be included in this type of electrolyte. These include perovskites (such as cerate and zirconate) , fluorites (such as doped zirconia, ceria and thoria), pyrochlores (such as calcium doped lanthanum zirconate) and other materials (including brown millerite, eulytite and monazite). The challenges of this type of electrolyte include their structural stability and the high sintering temperature (up to 1700 °C)

which is required to achieve a high density. By adopting this kind of solid state electrolyte, the ammonia production rate of 3.1×10^{-9} mol/cm^2·s could be achieved under the temperature of 570 °C, with an efficiency of about 75% [16].

2.3.3 Thermochemical Cycle of Ammonia Production

As an alternative process for ammonia production, a process employing the thermochemical cycle has been developed. The system consists of two circulated processes: reduction (nitrogen activation) and steam-hydrolysis (ammonia formation). Both reactions are summarized as follows:

$$Al_2O_3 + 3C + N_2 \rightarrow 2\,AlN + 3\,CO \quad \Delta H°_{25\,°C} = 708.1\ kJ/mol \qquad (2.6)$$

$$2AlN + 3\,H_2O \rightarrow Al_2O_3 + 2\,NH_3 \quad \Delta H°_{25\,°C} = -274.1\ kJ/mol \qquad (2.7)$$

Figure 3 shows the schematic diagram of the thermochemical cycle of ammonia production. The primary energy sources are pre-treated and converted to carbon before being fed to the thermochemical cycle process. In the first reduction process (reaction (6)), the AlN is produced through the carbothermal reduction of Al2O3 and nitrogen. This reaction is endothermic and occurs under a reaction temperature of about 1500 °C. Moreover, in the second reaction, which is steam-hydrolysis (reaction (7)), the AlN produced in the first reduction process is reacted with steam (H2O) producing Al2O3. The produced Al2O3 from this second reaction is then circulated to the first reduction process.

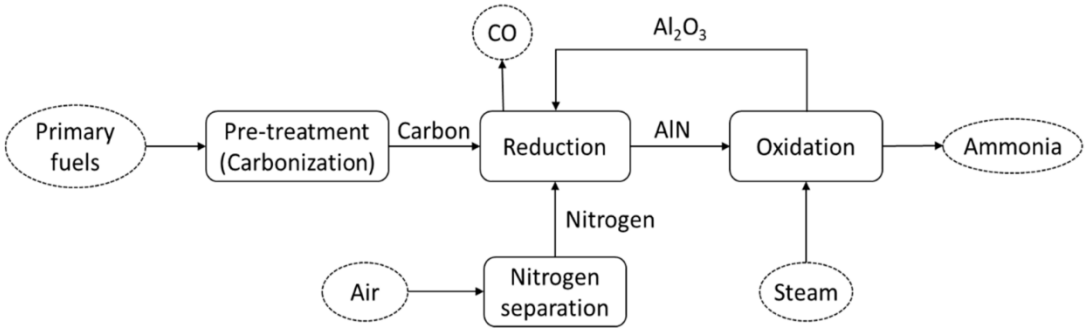


Figure 2.3: Schematic diagram of the thermochemical cycle of ammonia production.

Unlike the Haber–Bosch process, this thermochemical cycle can be carried out at atmospheric pressure and without a catalyst. The process allows independent reaction control for nitrogen activation (reaction (6)) and ammonia formation (reaction (7)). Furthermore, as could be

observed from reaction (6), the system can produce ammonia directly from carbonized material, instead of pure hydrogen. Therefore, this system is expected to be able to reduce the energy consumption during ammonia production. However, this system has the biggest challenge related to its very high operating temperature, leading to limited heat sources and materials. Various ideas have been suggested for the heat supply, including the utilization of concentrated solar heat [16].

2.4 Ammonia uses and applications

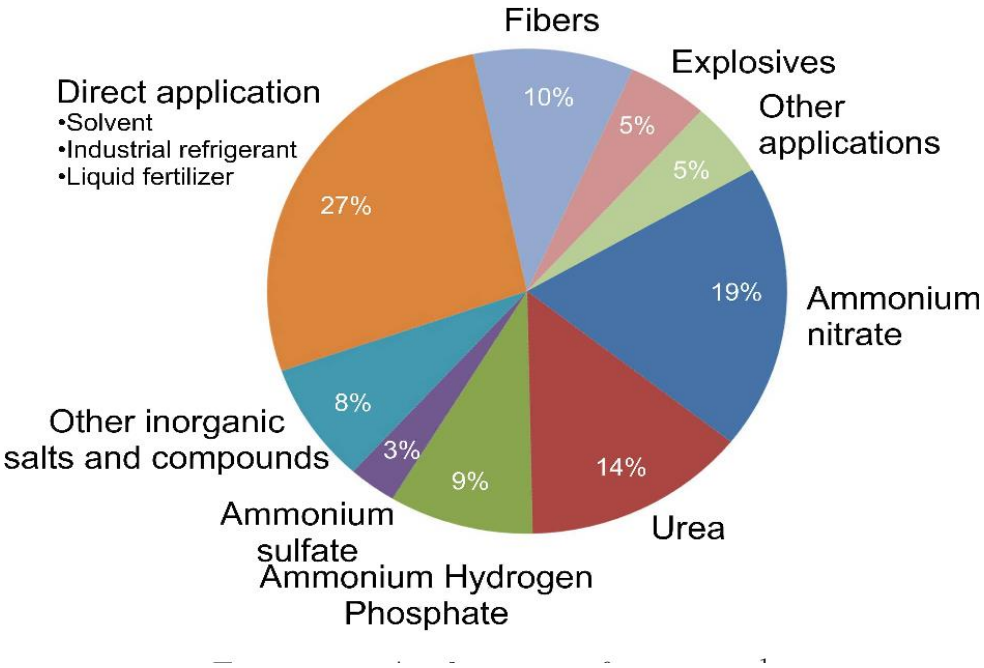


Figure 4: Ammonia uses and applications [7].

Approximately 80% of ammonia used in agricultural industry as fertilizer (ammonium nitrate, urea, ammonium sulfate, ammonium hydrogen phosphate, inorganic salts ...) also ammonia can be used as energy carrier for transportation and storage of hydrogen [17].

2.5 Ammonia storage and transportation

Ammonia is usually handled in liquid form, but in some cases delivery of ammonia vapor to downstream consumers on site may have some advantage due to savings of refrigeration energy in the ammonia plant [8]. It is important to note that storage of gaseous ammonia would require larger tanks to store the same amount of ammonia as liquid storage as the density of ammonia gas is lower than that of the liquid. For instance, liquid ammonia expands to 850 times its liquid volume at atmospheric pressure. Currently, the main methods for storing ammonia are [18]:

• Atmospheric storage at -33 °C in insulated cylindrical tanks for around 50,000 tons each tank.
• Pressure storage at ambient temperature in spherical or cylindrical pressure vessels with capacities up to 1,500 tons per vessel.
• Semi-refrigerated storage at about 0 °C in insulated, usually spherical pressure vessels for quantities up to about 2,500 tones.
• Solid-state storage

The first three forms of storage are mature technologies widely used throughout the world and even combinations of these methods can be found in practice [19]. However, the solid-state storage is still under development.

In atmospheric pressure storage, ammonia is stored as a liquid at its boiling point of -33°C under atmospheric pressure. This technology is highly economical and ideal for large-scale storage facilities, accommodating up to 50,000 tons. Tanks require advanced insulation and refrigeration systems to maintain the low temperature, making it energy-intensive and susceptible to temperature fluctuations, causing ammonia vaporization.
Pressurized storage maintains ammonia at ambient temperatures under high pressure, eliminating refrigeration needs and reducing energy costs. Specialized pressurized tanks, such as spheres or cylinders, handle pressures up to 250 PSIG to ensure ammonia remains in liquid form. However, this process requires materials resistant to stress corrosion cracking, increasing infrastructure complexity.
Semi-refrigerated storage combines refrigeration with lower pressures, storing ammonia at around 0°C. This hybrid approach balances infrastructure demands and is suitable for medium-

scale operations, requiring moderate refrigeration systems and tanks designed for reduced pressures.

Underground storage in salt caverns is used for strategic reserves, making use of natural insulation and security against environmental hazards. This method is highly reliable but requires specific geological conditions and substantial upfront investment, making it less commonly implemented compared to other methods [20].

Ammonia as a global commodity is widely traded and transported through various distances. Between 25 and 30 million tons of ammonia is transported annually [21].

Plants located in areas with abundant natural gas and low population density may transport close to 100% of their ammonia production or 40-60% if combined with some capacity to produce fertilizers [22]. Therefore, there is a large network of ports, ships, pipelines and dedicated storage facilities in ammonia producing and consuming countries and a high level of maturity regarding transport infrastructure. Most common ways for transportation ammonia are:

- Pipeline transportation
- Ocean and barge transportation
- Rail transportation
- Truck transportation

Chapter 3

Thermodynamic Analysis of Ammonia Synthesis and Decomposition

3. Ammonia Synthesis

3.1 The Synthesis Reaction

The industrial synthesis of ammonia is achieved through the Haber-Bosch process, which is centered on the following reversible reaction:

$$N_{2\,(g)} + 3H_{2\,(g)} \rightleftharpoons 2NH_{3\,(g)} \qquad (3.1)$$

This reaction is exothermic, releasing heat, and is accompanied by a negative change in entropy, meaning the products are more ordered than the reactants. A thorough understanding of the reaction's thermodynamic functions—enthalpy (ΔH), entropy (ΔS), and Gibbs free energy (ΔG), as well as the equilibrium constant (K_p) is crucial. This knowledge forms the basis for designing and optimizing industrial reactors and related chemical processes. While the literature contains data on this reaction, it is often incomplete, focusing on specific temperatures and pressures without providing a full thermodynamic profile (23).

3.2 Thermodynamic Principles and Mathematical Formulation

3.2.1 Thermodynamic Functions

The spontaneity and energy changes of the ammonia synthesis reaction are governed by key thermodynamic functions.

- **Enthalpy of Reaction (ΔH):** The enthalpy change is the difference between the sum of the bond enthalpies of the products and the reactants. The temperature dependence of reaction enthalpy is given by Kirchhoff's law (24).

$$\Delta H = \sum_j b_j \,.\Delta h_j - \sum_i b_{ji} \,.\Delta h_i \qquad (3.2)$$

Where:

- bi is the number of kilomoles of the i-th reactant.
- bj is the number of kilomoles of the j-th product.
- Δhi is the bond enthalpy of the i-th component.
- Δhj is the bond enthalpy of the j-th component.

The effect of temperature on the reaction enthalpy is described by Kirchhoff's law:

$$\Delta HT = \Delta H_{298} + \int_{298}^{T} \Delta C_{mp}(T)dT \qquad (3.3)$$

Here, ΔC_{mp} represents the sum of the specific molar heat capacities of the components, calculated as:

$$\Delta C_{mp} = \sum_j b_j \ . C_{mpj} - \sum_i b_i \ . C_{mpi} \qquad (3.4)$$

The temperature dependence of the molar heat capacity can be expressed by the empirical polynomial:

$$C_{mp}\ (\mathrm{T}) = \mathrm{a} + \mathrm{b}\cdot 10^{-3}\cdot \mathrm{T} + \mathrm{c}\cdot 10^{5}\cdot \mathrm{T}^{-2} \qquad (3.5)$$

- **Entropy of Reaction (ΔS):** The entropy change is the difference in the specific entropies of the products and reactants. A negative value, as seen in ammonia synthesis, indicates a decrease in disorder (24).

$$\Delta S = \sum_j b_j \ . s_j - \sum_i b_i \ . s_i \qquad (3.6)$$

Where:

- si represents the specific entropies of the i-th component.
- sj represents the specific entropies of the j-th component.

The change in reaction entropy with temperature is given by:

$$\Delta S_T \ = \Delta S_{298} \ + \int_{298}^{T} \frac{\Delta C_{mp}(T)}{T} dT \qquad (3.7)$$

Gibbs free energy (ΔG): The Gibbs free energy determines the direction of a spontaneous reaction and is defined by the Gibbs-Helmholtz equation: $\Delta G = \Delta H - T\Delta S$. For a reaction to be spontaneous, ΔG must be negative. If ΔG is positive, the reaction favors the reactants.

$$\Delta G = \sum_j b_j \ . \Delta g_j - \sum_i b_i \ . \Delta g_i \qquad (3.8)$$

Where:

- Δgi are the specific free enthalpies of the i-th component.
- Δgj are the specific free enthalpies of the j-th component.

The relationship between free enthalpy, enthalpy, and entropy is given by the Gibbs-Helmholtz equation:

$$\Delta G = \Delta H - T\cdot \Delta S \qquad (3.9)$$

3.2.2 Chemical Equilibrium

For the ammonia synthesis reaction, Le Chatelier's principle is fundamental to understanding how to maximize yield. The principle states that a system at equilibrium will shift to counteract any imposed change (25).

- **Effect of Temperature:** As the reaction is exothermic ($\Delta H<0$), a decrease in temperature shifts the equilibrium to the product side, favoring the formation of more ammonia.
- **Effect of Pressure:** The reaction involves a reduction in the number of moles of gas (from 4 moles of reactants to 2 moles of product). Therefore, an increase in pressure shifts the equilibrium towards the side with fewer moles, significantly favoring the formation of ammonia.

For a chemical reaction: $\sum_i a_i \times A_i = \sum_j b_j \times B_j$

The chemical equilibrium constant, expressed in terms of partial pressures (Kp) is:

$$K_p = \frac{\prod_j (P_{Bj})^{bj}}{\prod_i (P_{Ai})^{ai}} \qquad (3.10)$$

The reduced chemical equilibrium constant (K_p') at a standard pressure is determined by:

$$K_p' = e^{\frac{\Delta G}{Ru.T}} = K_p . P_0^{-(\sum_j b_j - \sum_i a_i)} \qquad (3.11)$$

3.2.3 Calculation of the Composition of the Equilibrium Mixture of the Synthesis Reaction

Balance equations of reactants in the reaction:

$$N_{2\,(g)} + 3H_{2\,(g)} = 2NH_{3\,(g)} \qquad (3.1)$$

Can be written as follows:

Nitrogen	$\eta_{N2\,(g)} = a-y$, (Kmol)
Hydrogen	$\eta_{H2\,(g)} = b-3y$, (Kmol)
Ammonia	$\eta_{NH3\,(g)} = 2y$, (Kmol)

a represent the number of kilomoles of nitrogen entering the reaction .

b represent the number of kilomoles of hydrogen reacting .

2y represent the number of kilomoles of ammonia in the mixture after establishing chemical equilibrium (25).

The total number of kilomoles in the mixture at any conversion time is equal to:

$$\eta\Sigma = \eta N_{2(g)} + \eta H_{2(g)} + \eta NH_{3(g)} \qquad (3.12)$$

$$\eta\Sigma = (a-y)+(b-3y)+2y = a+b+2y \qquad (3.13)$$

The mole fraction of the components in the mixture after the establishment of chemical equilibrium amounts to:

$$y_{N2\,(g)} = \frac{\eta N2(g)}{\eta\Sigma} = \frac{a-y}{a+b-2y} \qquad (3.14)$$

$$y_{H2\,(g)} = \frac{\eta H2(g)}{\eta\Sigma} = \frac{b-3y}{a+b-2y} \qquad (3.15)$$

$$y_{NH3\,(g)} = \frac{\eta NH3(g)}{\eta\Sigma} = \frac{2y}{a+b-2y} \qquad (3.16)$$

The partial pressures of the components in the equilibrium mixture are:

$$P_{N2\,(g)} = y_{N2\,(g)}.p = \frac{a-y}{a+b-2y}.p \ , \ p(Pa) \qquad (3.17)$$

$$P_{H2\,(g)} = y_{H2\,(g)}.p = \frac{a-3y}{a+b-2y}.p \ , \ p(Pa) \qquad (3.18)$$

$$P_{NH3\,(g)} = y_{NH3\,(g)}.p = \frac{2y}{a+b-2y}.p \ , \ p(Pa)$$

Of which:

P is total pressure in the reactor space after equilibrium is established, (Pa). The chemical equilibrium constant of the reaction is determined using the expression:

$$K_p = \frac{p^2_{NH3(g)}}{p_{N2}.p^2_{H2(g)}} \ , (Pa^{-2}) \qquad (3.19)$$

The numerical values of the mole fractions of the components in the equilibrium mixture are obtained. Degree of responsiveness of reactants $N_2(g)$ and $H_2(g)$ is determined using the expression:

$$\eta_{N2} = \frac{a-(a-y)}{a} = \frac{y}{a} \qquad (3.20)$$

$$\eta_{H2} = \frac{b-(b-3y)}{b} = \frac{3y}{b} \qquad (3.21)$$

The results of the calculation of the composition of the equilibrium mixture at the stoichiometric ratio of reactants, at T = 400 K and pressure p = 1.013×105 Pa are shown in the table below: (26)

T (K)	yN2 (kmol/kmol)	yH2 (kmol/kmol)	yNH3 (kmol/kmol)	ηN2 (kmol/kmol)	η_{H2} (kmol/kmol)
400	0.1218	0.3654	0.5128	0.6779	0.6779
500	0.2269	0.6808	0.0922	0.1690	0.1690
600	0.2464	0.7393	0.0143	0.0282	0.0282
700	0.2492	0.7475	0.0033	0.0066	0.0066
800	0.2498	0.7493	0.0010	0.0020	0.0020
900	0.2499	0.7496	0.0005	0.0010	0.0010
1000	0.2499	0.7486	0.0005	0.0010	0.0010

Table 3.1: Composition of the equilibrium reaction $N_2(g) + 3H_2(g) = 2NH_3(g)$ mixture at the stoichiometric number of moles of reactants (a =1 kmol , b = 3 kmol) at pressure 1.013 × 105 Pa.(26).

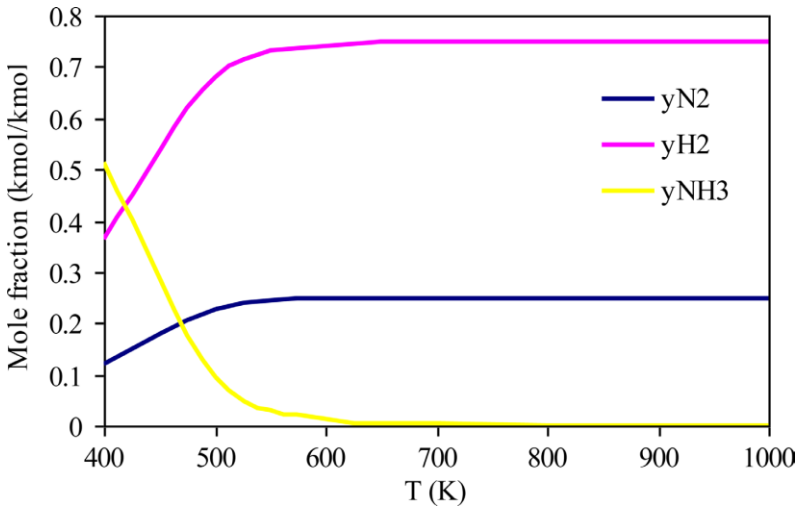


Figure 3.1: Mole fraction of components in the equilibrium reaction mixture $N_2(g) + 3H_2(g) = 2NH_3(g)$ depending on the temperature.(5)

It can be seen that ammonia synthesis starts at lower temperatures. At 400 K, the mole fraction of ammonia in the equilibrium mixture is 0.5128 kmol/kmol. At higher temperatures, the mole fraction of ammonia decreases, while at 900 K, the mole fraction of ammonia is equal to 0.0005 kmol/kmol. The degree of conversion (reaction) N2(g) and H2(g) depending on the temperature Apparently, the increase in the reaction temperature and mole fraction shares N2(g) and H2(g) in the equilibrium reaction $N_{2(g)} + 3H_{2(g)} = 2NH_{3(g)}$ mixture, the degree of conversion of the reactants decreases. At 400 K, the degree of conversion of reactants is as much as 0.6779 kmol/kmol, and at 900 K, the degree of conversion is 0.0010 kmol/kmol. This practically means that the synthesis process NH3(g) at 900 K is completed because it amounts to only 0.0005 kmol/kmol. (27).

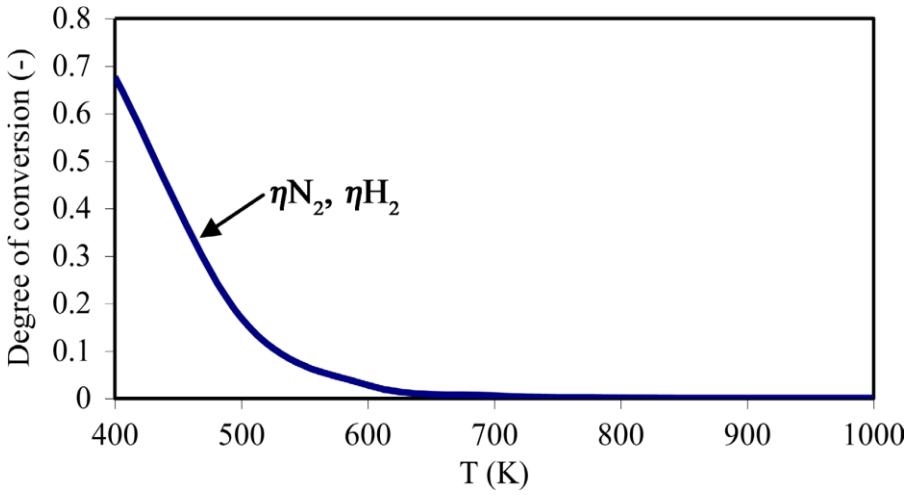


Figure 3.2: Degree of conversion N_2 (g) and H_2 (g) in the equilibrium reaction mixture N_2 (g) + 3H_2 (g) = 2NH_3 (g) depending on the temperature. (5)

3.3 Industrial Application: The Haber-Bosch Process

To resolve the conflict between kinetics and thermodynamics, the Haber-Bosch process employs a combination of high pressure, moderate temperatures, and a catalyst. (28)

- **Catalysts:** The process is critically dependent on a catalyst to increase the reaction rate at industrial operating temperatures. The most common catalysts are iron-based, often with promoters like potassium oxide, aluminum oxide, and calcium oxide to enhance activity and stability. Ruthenium-based catalysts are also used as they show high activity, especially at lower pressures. The catalyst provides an alternative reaction pathway with lower activation energy but does not alter the final equilibrium position.

- **Operating Conditions:** A compromise temperature, typically between 400°C and 450°C (673 K to 723 K), is used. Industrial plants operate at very high pressures, typically between 150 and 250 atmospheres, to shift the equilibrium towards ammonia production.
- **Recycling:** Even under these optimized conditions, the conversion to ammonia per pass through the reactor is only about 15%. To achieve a high overall yield, the gas mixture leaving the reactor is cooled to liquefy and remove the ammonia. The unreacted nitrogen and hydrogen are then recycled back into the reactor, ensuring an overall conversion rate of approximately 97%.

3.4 Ammonia Decomposition for Hydrogen Production

3.4.1 Introduction: Ammonia as a Hydrogen Vector

The global transition towards a sustainable energy future has intensified the search for efficient and safe methods of hydrogen (H_2) storage and transportation. Hydrogen, with its high energy density per unit mass and zero-carbon emission profile at the point of use, is a promising energy carrier. However, its low volumetric energy density in its gaseous state and the challenges associated with its liquefaction and high-pressure storage present significant logistical hurdles.

In this context, ammonia (NH_3) has emerged as a superior hydrogen vector. With a high hydrogen content by mass (17.6%), a high volumetric hydrogen density, and a well-established global infrastructure for its production, storage, and transport, ammonia offers a practical solution to the challenges of a hydrogen economy. The release of hydrogen from ammonia is achieved through a process known as **ammonia decomposition or cracking**, a thermochemical process that breaks down ammonia into its constituent elements, nitrogen (N_2) and hydrogen.(29)

A fundamental understanding of the thermodynamics of ammonia decomposition is paramount for the design, optimization, and operation of efficient ammonia cracking reactors. Thermodynamic principles govern the feasibility of the reaction, predict the maximum achievable conversion of ammonia at different conditions, and dictate the energy requirements of the process. This chapter provides a detailed thermodynamic analysis of the ammonia decomposition reaction, exploring the key parameters of enthalpy, entropy, and Gibbs free energy, and their profound implications for practical applications.

3.4.2 The Stoichiometry and Equilibrium of Ammonia Decomposition

The decomposition of ammonia is a reversible chemical reaction represented by the following stoichiometric equation:

$$2NH_{3(g)} \rightleftharpoons N_{2(g)} + 3H_{2(g)} \qquad (3.22)$$

This equation reveals several critical aspects of the process. Firstly, it shows that for every two moles of gaseous ammonia that decompose, a total of four moles of gaseous products are formed: one mole of nitrogen and three moles of hydrogen. This net increase in the number of moles of gas has significant implications for the entropy of the system and the effect of pressure on the reaction equilibrium. (30)

The double arrow indicates the reversible nature of the reaction. This means that under a given set of conditions, the reaction will proceed until it reaches a state of chemical equilibrium where the rates of the forward (decomposition) and reverse (synthesis) reactions are equal. At this point, the concentrations of reactants and products remain constant. The position of this equilibrium, which dictates the maximum possible conversion of ammonia, is highly dependent on temperature and pressure. While the synthesis of ammonia (the Haber-Bosch process) is favored at high pressures and relatively low temperatures, the decomposition of ammonia is favored at high temperatures and low pressures. (30)

3.4.3 Enthalpy of Reaction: The Endothermic Nature of Decomposition

The enthalpy of reaction (ΔH_r) quantifies the heat absorbed or released during a chemical reaction at constant pressure. For the decomposition of ammonia, the standard enthalpy of reaction ($\Delta H°_r$) at 298.15 K (25 °C) and 1 atm is + 92.4 kJ/mol. (31)

$$2NH_{3(g)} \rightarrow N_{2(g)} + 3H_{2(g)} \quad \Delta H°_r = +92.4 kJ/mol \qquad (3.23)$$

The positive sign of $\Delta H°_r$ signifies that the reaction is **endothermic**. This means that energy must be supplied to the system from the surroundings for the reaction to proceed. This energy input is required to break the strong nitrogen-hydrogen (N-H) bonds within the ammonia molecules. The average bond enthalpy of an N-H bond is approximately 391 kJ/mol. Since there are three N-H bonds in each ammonia molecule and two ammonia molecules in the reaction, a significant amount of energy is needed to initiate the bond-breaking process.

The endothermic nature of ammonia decomposition has profound practical consequences. Reactors for ammonia cracking must be designed to provide a continuous and efficient supply of heat to maintain the high temperatures necessary for a favorable reaction rate and equilibrium conversion. This energy requirement is a key consideration in the overall energy balance and economic viability of ammonia-based hydrogen production systems.

3.4.4 Entropy Change: The Driving Force of Increased Disorder

Entropy (S) is a thermodynamic property that measures the degree of molecular disorder or randomness in a system. The change in entropy for a reaction (ΔS_r) is a critical factor in determining its spontaneity. The decomposition of ammonia leads to a significant increase in the entropy of the system.

The standard entropy change ($\Delta S°_r$) for the decomposition of ammonia is +198.7 J/(mol·K). This substantial positive value can be attributed to the increase in the number of moles of gas during the reaction. As previously noted, two moles of gaseous ammonia produce four moles of gaseous products. This increase in the number of particles leads to a greater number of possible microstates and, consequently, a higher degree of disorder. The system moves from a state of relatively low entropy (a single molecular species) to a state of higher entropy (a mixture of two different molecular species).

This positive entropy change is a key driving force for the decomposition reaction, particularly at elevated temperatures. (32)

3.4.5 Gibbs Free Energy: Predicting the Feasibility and Spontaneity

The spontaneity of a chemical reaction under conditions of constant temperature and pressure is ultimately determined by the change in Gibbs free energy (ΔG). The Gibbs free energy elegantly combines the effects of both enthalpy and entropy into a single state function:

$$\Delta G = \Delta H - T\Delta S \qquad (3.9)$$

Where:

- ΔG is the change in Gibbs free energy
- ΔH is the change in enthalpy
- T is the absolute temperature in Kelvin
- ΔS is the change in entropy

A reaction is spontaneous in the forward direction if ΔG is negative. It is non-spontaneous if ΔG is positive, and it is at equilibrium if ΔG is zero.

For ammonia decomposition at standard conditions (298.15 K), the standard Gibbs free energy of reaction ($\Delta G°_r$) is:

$\Delta G°_r = \Delta H°_r - T\Delta S°_r = 92.4\text{kJ/mol} - (298.15\text{K} \times 0.1987\text{kJ/(mol·K)}) \quad \Delta G°r \approx +33.1\text{kJ/mol}$

The positive value of $\Delta G°_r$ at room temperature confirms that the decomposition of ammonia is not spontaneous under standard conditions. To make the reaction feasible, the temperature must be increased. As the temperature (T) rises, the $-T\Delta S$ term becomes increasingly negative. Because ΔS is positive for this reaction, this term will eventually outweigh the positive ΔH term, causing ΔG to become negative. (32)

The temperature at which the reaction becomes thermodynamically favorable can be estimated by finding the temperature at which ΔG=0:

$T_{eq} = \Delta H / \Delta S = (92400(\text{J/mol})) / (198.7\ \text{J/(mol·K)}) \approx 465\text{K or } 192°\text{C}$

This calculation indicates that above approximately 192℃, the decomposition of ammonia is thermodynamically spontaneous. However, it is crucial to distinguish between thermodynamic feasibility and reaction kinetics. While the reaction may be spontaneous above this temperature, the rate at which it proceeds may be infinitesimally slow. Therefore, in practice, much higher

temperatures (typically > 600°C) and the use of catalysts are necessary to achieve a high conversion of ammonia in a reasonable timeframe. (32)

3.5 The Influence of Temperature and Pressure: Le Chatelier's Principle

Le Chatelier's principle provides a qualitative framework for understanding how a system at equilibrium responds to external changes. For the ammonia decomposition reaction, the principle predicts the following:

- **Effect of Temperature:** As the decomposition of ammonia is an endothermic reaction ($\Delta H > 0$), an increase in temperature will shift the equilibrium position to the right, favoring the formation of products (N_2 and H_2). Therefore, higher temperatures lead to a higher equilibrium conversion of ammonia.

Effect of Pressure: The reaction results in an increase in the total number of moles of gas (from 2 moles to 4 moles). According to Le Chatelier's principle, an increase in pressure will shift the equilibrium to the side with fewer moles of gas. Therefore, high pressures will favor the reverse reaction (ammonia synthesis) and hinder decomposition. Conversely, **low pressures will favor the forward reaction** and lead to a higher equilibrium conversion of ammonia. (33)
These principles are fundamental to the design of ammonia cracking reactors. To maximize the yield of hydrogen, these reactors are typically operated at high temperatures and low pressures.

3.6 Thermodynamic Imperatives for Ammonia Cracking

The thermodynamic analysis of ammonia decomposition reveals a fascinating interplay between enthalpy and entropy. The reaction is endothermic, creating a significant energy barrier that must be overcome with high temperatures. However, it is also characterized by a large positive entropy change, which provides a strong thermodynamic driving force for the reaction at these elevated temperatures.

The key takeaways from this thermodynamic study are:

- Ammonia decomposition is an endothermic process, requiring a continuous input of heat.
- The reaction is favored by high temperatures and low pressures.
- While thermodynamically favorable at moderately high temperatures, the reaction requires catalysts to proceed at a practical rate. (34)

Chapter 4

Ammonia Synthesis and Decomposition simulation with aspen plus

4. Introduction to process simulation

Process simulation plays a vital role in various fields by allowing for the modeling and analysis of complex systems and processes. It helps in optimizing designs, enhancing safety, and improving overall efficiency in areas like chemical engineering, and manufacturing. It covers the entire lifecycle of a process from research and development

through to conceptual design and operational management. It involves creating and experimentingwith an operational model of a system to understand its behavior or assess different strategies forits development or management.

Effective simulation must accurately replicate certain behaviors of the system beingmodeled. Theessence of simulation lies in the creation and refinement of models based on experimental data,enabling the performance of 'virtual experiments.' Modeling, a fundamental component of simulation, often operates behind the scenes within software technologies. It's vital to remember that a simulation is an approximation of reality, capturing it with a certain level of precision, ratherthan being an exact duplicate. Therefore, it's critical for users to assess the reliability of a simulator's outcomes.

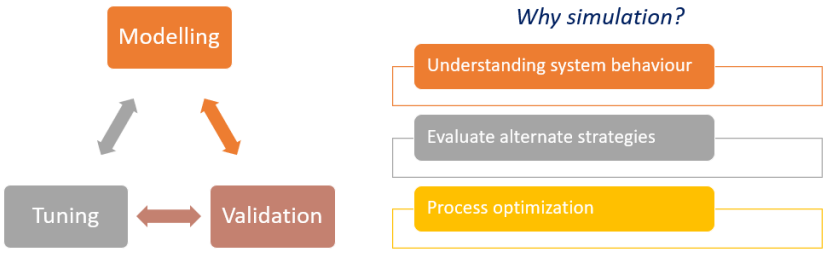


Figure 4.1: Steps in process simulation and its importance.

4.1 Process simulation with Aspen Plus

Aspen Plus (Advanced System for Process Engineering) is process simulation software grounded in techniques initially used for developing flowsheets in the chemical engineering industry years ago. These early methods were suited for designing standalone units, requiring engineers to manually calculate and adjust each unit one by one within a flowsheet. Challenges arose when dealing with recycle streams, as iterative manual adjustments were needed until the output of the last unit matched the input conditions, a process that did not guarantee convergence. The sequential modular simulator approach evolved to addressthis issue by creating individual unit

models, which could be interconnected through software tomanage the recycle loops more effectively.

4.1.1 Background and global significance of ammonia synthesis

Ammonia (NH_3) stands as one of the most critical chemical commodities globally, playing an indispensable role in various sectors. Its primary application lies in the agricultural industry, where over 80% of synthesized ammonia is converted into nitrogenous fertilizers such as urea, ammonium nitrate, and diammonium phosphate. These fertilizers are fundamental to sustaining global food production, feeding a rapidly growing population by enhancing crop yields. Beyond agriculture, ammonia is a vital precursor in the manufacture of a wide array of chemicals, including nitric acid, caprolactam, polyurethanes, and explosives. Emerging applications also highlight ammonia's potential as a carbon-free energy carrier and a sustainable fuel for the maritime industry, further emphasizing its strategic importance in the transition towards a greener economy.

The industrial production of ammonia is predominantly achieved through the Haber-Bosch process, a monumental achievement in chemical engineering developed in the early 20th century by Fritz Haber and Carl Bosch. This process synthesizes ammonia directly from its constituent elements, nitrogen (N_2) and hydrogen (H_2), under high temperature and pressure conditions in the presence of a catalyst. The overall reaction is exothermic:

$$N_{2(g)}+3H_{2(g)}\rightleftharpoons 2NH_{3(g)}\Delta H^{0}_{298K}=-92.4\ \text{kJ/mol} \qquad (4.1)$$

Despite its pivotal role, the Haber-Bosch process is notably energy-intensive. It is estimated to consume approximately 1-2% of the world's total energy supply, primarily due to the high pressures (150-300 bar) and temperatures (400-500^{0}C) required for the reaction, and the significant energy demand for hydrogen production (typically via steam methane reforming) and gas compression. Furthermore, the conventional process relies heavily on fossil fuels, leading to substantial greenhouse gas emissions, primarily carbon dioxide (CO_2), from the syngas production stage. These factors underscore the continuous drive for process optimization, energy efficiency improvements, and the exploration of more sustainable production routes.

4.2 Ammonia Synthesis simulation

4.2.1 Aspen plus simulation steps

- Start Aspen Plus V14.0. Select New on the Start Page, select new and Recent | New Simulation, press the Create button. We choose New for this process because templates have default property methods, unit sets, and databanks selected. When using a specific method, such as RKS-BM, it is best to choose New to ensure that the correct property method is selected.

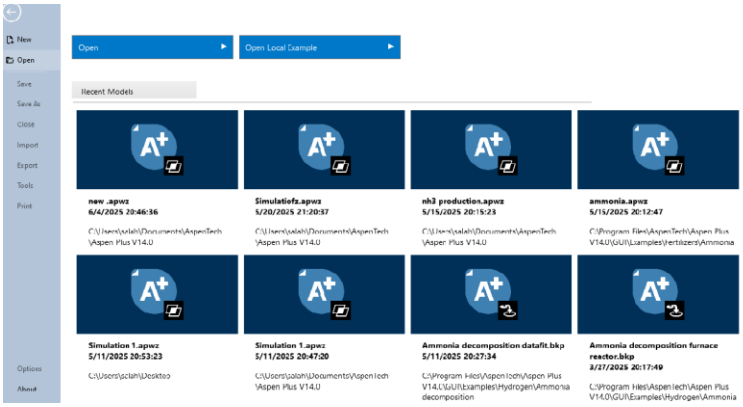


Figure 4.2: Aspen plusV14 interface

- In **Properties** view, go to **Components | Specifications**, select components: **H2**, **N2**, **CH4**, **AR**, **CO**, and **NH3**.

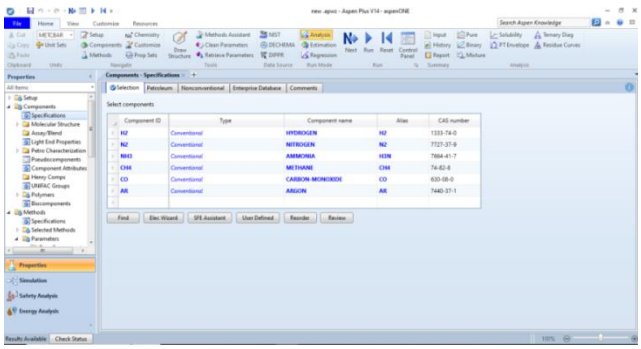


Figure 4.3: Specifications window on Aspen plusV14

- In Methods **| Specifications**. In the drop-down **Method name** combo box, find **RKS-BM** and select it. After that, click on **Methods | Parameters | Binary Interaction | RKSBV-1**, it will retrieve the binary interaction parameters to complete RKS-BM for use in the simulation. If these parameters do not populate, make sure that the databank **EOS-LIT** is selected in the **Databanks** tab under **RKSBV-1**.

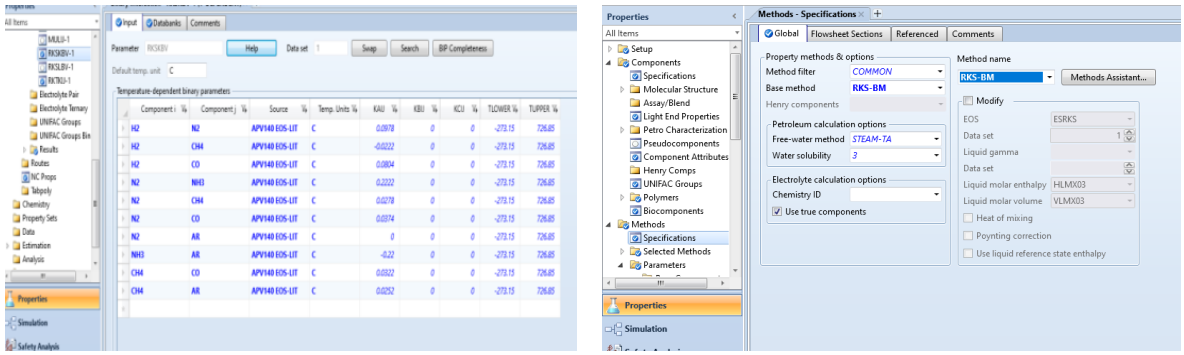
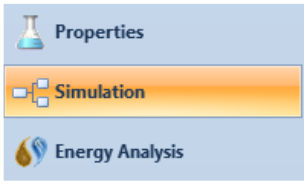


Figure 4.4: choosing RKSBV-1 method from the Database

- Next to the simulation environment. For that, click on the **Simulation** button in the bottom left of the screen. Then find the **Main Flowsheet** tab. The **Main Flowsheet** is the main simulation flowsheet where you will create a simulation.



Adding the following models from the **Model Palette**, and drop them onto the flowsheet.

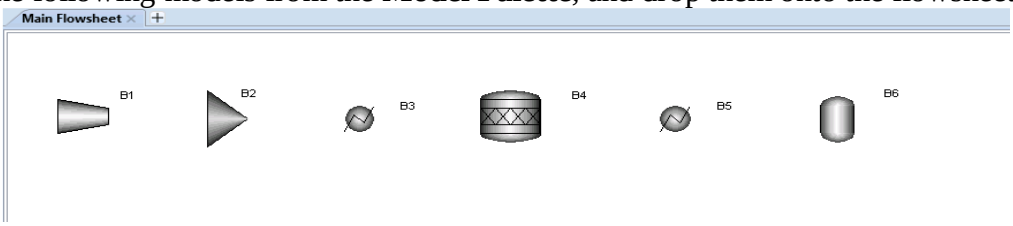


Figure 4.5: Model Palettes for Ammonia synthesis simulation

Diagram Overview

1. **Feed Streams:**

- **N_2** (from air separation)

- **H_2** (from steam methane reforming or electrolysis)

- **Inerts (Ar, CH_4)** typically present in small amounts

2.**Compression:**

- Multi-stage compression (up to 200–300 bar) - Intercooling to minimize work

3. **Reactor Section:**

- **Equilibrium (RGibbs)** or **Kinetic (RPlug)** reactor - Heat management (exothermic reaction)

4. **Separation & Recycle:**

- **Flash separator** to remove unreacted N_2/H_2

- **Recycle compressor** to improve conversion

- Using **Material Stream** from the **Model Palette**, and use it to connect model blocks.

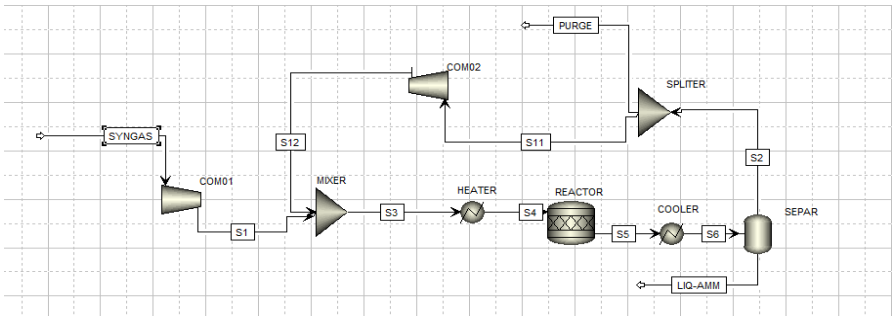


Figure 4.6:Main flowsheet of Ammonia synthesis

- Specify feed stream (**SYNGAS**). Double click on the stream labeled **SYNGAS** on the main flowsheet or navigate to **Streams | SYNGAS | Input**.

  - **T = 250 C, P = 26 Bar**
  - **Component Mole-Fraction:(N_2 from air separation, H_2 from SMR or electrolysis ,AR,CH_4 in small amounts) :**

    H_2 = 0.7365, N_2 = 0.2462, CH_4 = 0.0105, AR = 0.0035, CO = 0.0033

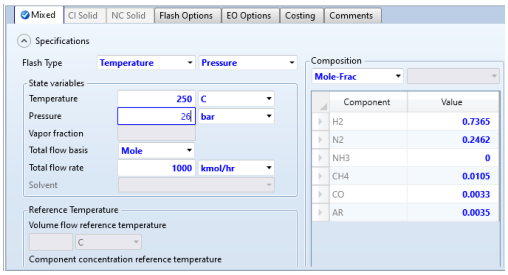


Figure 4.7: Specifying the components by mole fraction

Configure/Specify Compressor. Double click the compressor block or navigate to **Blocks | Compressor | Setup.**

- **Isentropic Compressor**
- **Discharge pressure = 280 bar**

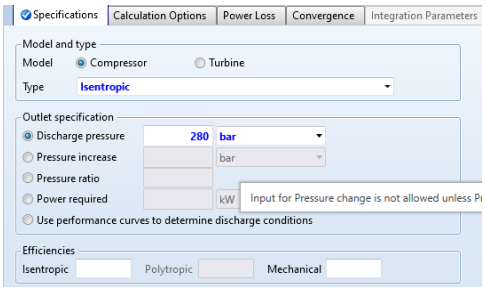


Figure 4.8 : Specifying the compressor parameters

- Configure/Specify Mixer. Double click on the mixer block or navigate to **Blocks | Mixer | Input**.

- Verify that the input sheet contains a **-0.1**in the **Pressure** spec. Note that in the Pressure field, if you enter a number greater than 0, this will be the discharge or operating pressure. If you enter a number less than or equal to zero, this will be the pressure drop through the unit.

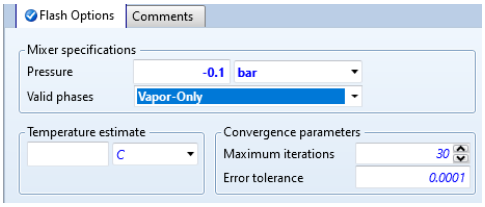


Figure 4.9: Specifying the mixer parameters

- Configure/Specify Heater. Double click on the heater block or navigate to **Blocks | Heater | Input**.
- **Temperature = 450 C**(Outlet temperature)
- Heater with zero pressure drop – enter **0** in the **Pressure** spec

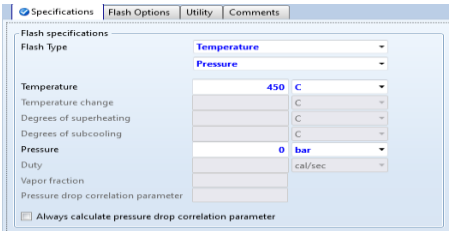


Figure 4.10: Specifying the heater parameters

- Configure/Specify Reactor (**R-Stoic**). Double click the reactor or navigate to **Blocks | R-Stoic| Setup**.
- Reaction temperature and pressure: **450C,280bar**

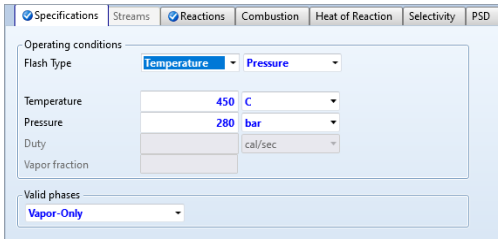


Figure 4.11: Specifying the reactor parameters

Go to the **Reactions** tab and click **New** to specify the reaction.

- Reaction **Stoichiometric Coefficients**: N_2=-1, H_2 = -3, NH_3 = +2

$$N_2 + 3H_2 = 2NH_3$$

- Specify Product Regeneration: **Fractional conversion** = **60%** of the reactant **N_2**

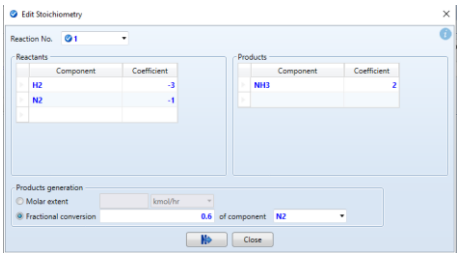


Figure 4.12: Specify the reaction and product regeneration

- Configure/Specify Heater. Double click on the heater or navigate to **Blocks | Heater | Input**.
- Actually, this is a 'cooler', cooling to **25 C**
- Pressure drops – enter **-0.1**for the **Pressure** spec

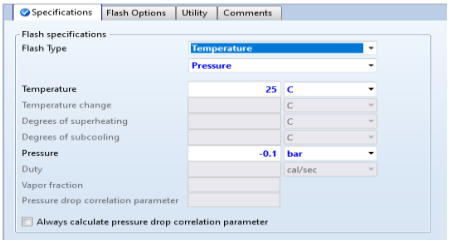


Figure 4.13: Specifying the cooler parameters

- Configure/Specify Flash Drum (**FLSH-2**). Double click the flash drum (**FLSH-2**) or navigate to **Blocks | FLSH-2 | Input**.
- No additional heat; **Heat Duty = 0**
- Pressure drops – enter **-0.1**for the **Pressure** spec

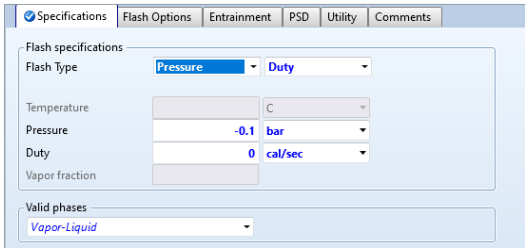


Figure 4.14: Specifying the flash drum parameters

For recycling unite

- Configure/Specify Mixer. Double click on the mixer block or navigate to **Blocks | Mixer| Input**.

Verify that the input sheet contains a **-0.1**in the **Pressure** spec

- Configure/Specify Compressor02. Double click the compressor block or navigate to **Blocks | compressor | Setup.**
  - **Isentropic Compressor**
  - **Discharge pressure = 280 bar**

4.3 Ammonia decomposition (cracking) simulation

The ammonia decomposition method involves the process where ammonia is thermally decomposed into its constituent elements; nitrogen and hydrogen gas . This reaction is classified as endothermic, requiring the input of energy, and it occurs at high temperatures, generally ranging from 500 °C to 900 °C. Typically, a catalyst is employed during this process to accelerate the rate of the reaction. The chemical reaction of the process can be expressed by equation:

$$2NH_3 \rightarrow 3H_2 + N_2 \qquad (4.2)$$

4.3.1 Aspen plus simulation steps

Adding the following models from the **Model Palette**, and drop them onto the flowsheet.

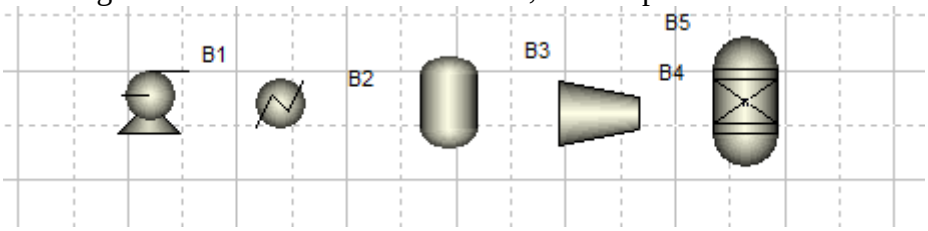


Figure 4.15: Model Palettes for Ammonia decomposition simulation

Diagram Overview

1. **Feed Streams:**

- **NH3** (Liquid phase)

2.**Pump:** (10 to 30 bar)

3. **Separation & Recycle:**

- **Flash separator** to remove liquid phase NH3

4. **Compression:**

- Multi-stage compression (up to 30–50 bar) - Intercooling to minimize work

5. **Reactor Section:**

- **Equilibrium (RGibbs)** Heat management (endothermic reaction)

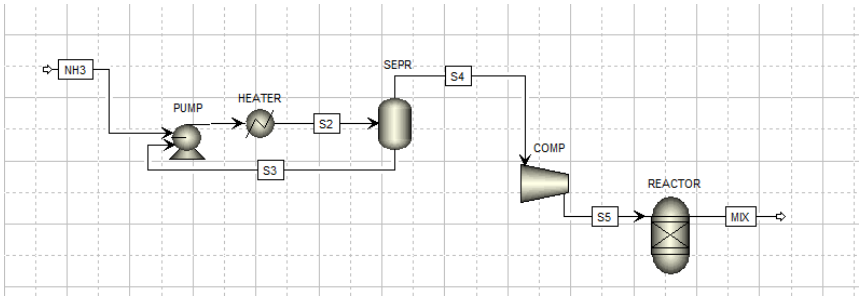


Figure 4.16:Main flowsheet of Ammonia decomposition simulation

- Specify feed stream (**NH_3 liquid)**. Double click on the stream labeled **NH_3**on the main flowsheet or navigate to **Streams | NH_3 | Input**.
  - **T = 25 C, P = 1 Bar**
  - **Component Mole-Fraction: (NH_3 in liquid form, N_2, H_2)**
  - $H_2 = 0$, $N_2 = 0$,$NH_3 = 1$

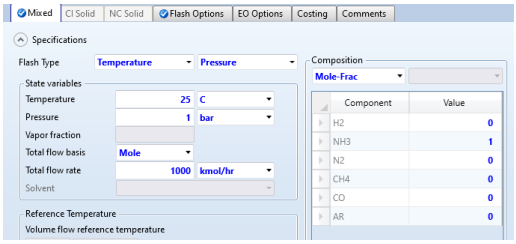


Figure 4.17: Specifying the components by mole fraction

- Configure/Specify pump. Double click the pressure changer block or navigate to **Blocks | pump | Setup.**
  - **Discharge pressure = 25 bar**
- Configure/Specify heater. Double click the heat exchanger block or navigate to **Blocks | heater | Setup.**
  - **Temperature = 700 C . Pressure =-0.1 bar**
- Configure/Specify flash drum.Double click the heat separators block or navigate to **Blocks | flash2 | Setup.**
  - **Temperature = 700 C Pressure =-0.1 bar**
- Configure/Specify Reactors. Click the reactor Blocks **| R-GIBBS | Setup**.
  - Reaction temperature and pressure: **700C,25bar**

Chapter 5

Result and Discussion

5.1 Ammonia synthesis

The ammonia synthesis process was simulated in Aspen Plus v14 at 450 °C and 280 bar, incorporating both recycling and a purge stream to optimize conversion while controlling inert gas accumulation. This design mirrors industrial Haber-Bosch systems, where thermodynamic limitations make recycling essential and inert gases must be purged regularly to maintain process efficiency.

	Unites	AMMONIA Stream	INLETS Stream	PURGE Stream
Mole Flows	kmol/hr	**469.409**	**1000**	**72.72510**
H2	kmol/hr	6.66354	736.5	43.03870
N2	kmol/hr	2.22811	246.2	15.03935
NH3	kmol/hr	451.789	0	4.770802
CH4	kmol/hr	5.72953	10.5	6.075032
CO	kmol/hr	0.77995	3.3	2.520073
AR	kmol/hr	2.21887	3.5	1.281129

Table 5.1: results on mole flow of synthesis simulation

5.1.1 Reactant utilization and system performance

The INLET stream contains mainly hydrogen (736.5 kmol/hr) and nitrogen (246.2 kmol/hr), in a molar ratio of approximately 3:1, which matches the stoichiometry of the ammonia synthesis reaction: $N_2 + 3H_2 \rightleftharpoons 2NH_3$ (5.1)

Based on the total ammonia produced (including both the AMMONIA and PURGE streams), the amount of nitrogen consumed is estimated to be 228.28 kmol/hr, and the hydrogen consumed is 684.83 kmol/hr. This corresponds to conversion rates of 92.7% for nitrogen and 93.0% for hydrogen, indicating that the reactor, in combination with the recycle loop, achieves a high overall conversion of reactants.

5.1.2 Product composition and purity

The AMMONIA stream, representing the product output, exhibits a very high purity of ammonia, with a mole fraction of 0.9625 and a total ammonia flow rate of 451.789 kmol/hr. Minor quantities of hydrogen (1.42%), methane (1.22%), argon (0.47%), carbon monoxide

(0.17%), and nitrogen (0.47%) are present. The high ammonia concentration confirms that the separation system downstream of the reactor (typically a cooling or condensation step) is highly effective in isolating ammonia from the unreacted synthesis gas.

Mole Fractions	AMMONIA Stream	INLETS Stream	PURGE Stream
H2	0.014195	0.7365	0.59179
N2	0.004746	0.2462	0.20679
NH3	0.962463	0	0.08353
CH4	0.012205	0.0105	0.06560
CO	0.001661	0.0033	0.03465
AR	0.004726	0.0035	0.01761

Table 5.2: results on mole fraction of synthesis simulation

5.1.3 Recycle and purge role

Due to the equilibrium limitations of the exothermic ammonia synthesis reaction, only a portion of the reactants are converted in a single pass. To improve overall conversion, unreacted hydrogen and nitrogen are recycled. However, inert components such as methane, argon, and carbon monoxide, which do not participate in the reaction, accumulate in the loop. To control their concentrations, a purge stream is included. The PURGE stream contains:

- 43.04 kmol/hr of H_2

-15.04 kmol/hr of N_2

- Significant amounts of CH_4 (6.08 kmol/hr), CO (2.52 kmol/hr), and Ar (1.28 kmol/hr)These values suggest that while some valuable reactants are lost through purging, the purge ratio is carefully optimized to prevent excessive build-up of inerts without incurring large reactant losses. The loss of ammonia in the purge stream is relatively low (4.77 kmol/hr), indicating effective ammonia separation prior to purging.

5.1.4 Effect of temperature and pressure

5.1.4.1 Temperature Effect:

- The forward reaction releases heat, so high temperatures shift the equilibrium backward, reducing NH_3 yield.
- However, low temperatures slow down the reaction kinetics.
- In practice, a moderate temperature (400–500 °C) is chosen to balance rate and yield.

5.1.4.2 Pressure Effect:

- The reaction results in a decrease in total moles of gas (4 → 2), so increasing pressure shifts the equilibrium toward ammonia formation.
- High pressure enhances NH_3 yield, improves condensation, and supports better overall production efficiency.

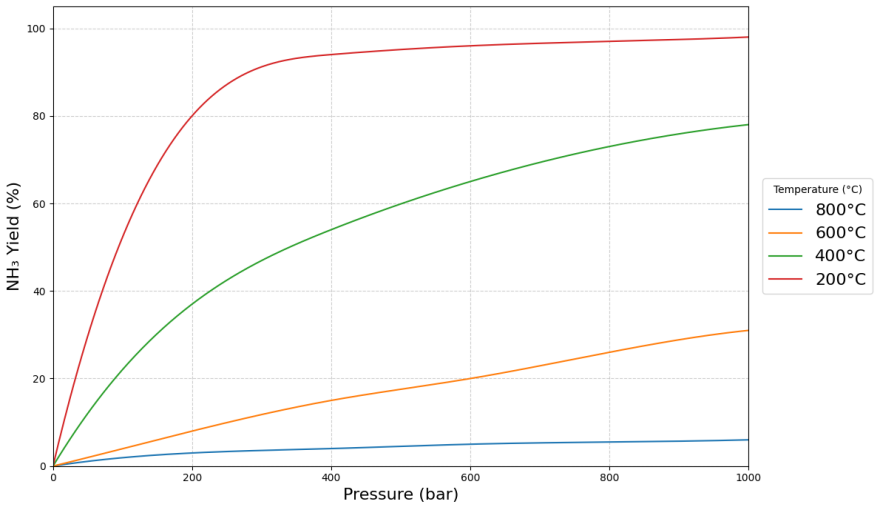


Figure 5.1: NH3 yield rate by pressure and temperature

Therefore, Industrial plants typically operate at **150–300 bar** and **400–500 °C**.
These conditions maximize conversion and rate when supported by catalysts and recycling loops.
These reaction conditions are not the best in terms of the yield but balance a decent yield with a decent rate of reaction and a reasonable production cost. These are called compromise conditions as they are chosen to give a good compromise between yield, rate and cost.

5.2 Ammonia decomposition

Ammonia decomposition into hydrogen and nitrogen is an endothermic reaction and reversible, and its equilibrium is influenced by temperature and pressure. The simulation of ammonia decomposition was carried out under Industrial conditions: a high temperature of **700 °C** and a moderate pressure of **25 bar**, with a feed of **1000 kmol/hr** of pure ammonia (NH_3). The process follows the endothermic reaction: $\mathbf{2NH_3 \rightarrow 3H_2 + N_2}$ (5.2)

5.2.1 Simulation Results

The simulation results showed a near-complete conversion of ammonia, with only **11.23 kmol/hr** of NH_3 remaining in the outlet stream. This corresponds to an **ammonia conversion rate of 98.88%**, calculated by:

$$\text{Conversion} = \frac{1000 - 11.227}{1000} \text{ x } 100 = 98.88\%$$

Mole Flows		**inlet**	**outlet**
	kmol/hr	1000	1988.77217
H2	kmol/hr	0	1483.15826
NH3	kmol/hr	1000	11.2278254
N2	kmol/hr	0	494.386087
Mole Fractions			
H2		0	0.7457658
NH3		1	0.00564561
N2		0	0.2485886

Table 5.3: results on mole flow of decomposition simulation

The total molar flowrate increased from 1000 kmol/hr at the inlet to 1988.77 kmol/hr at the outlet, consistent with the stoichiometry of the reaction, which produces more moles of gas than it consumes (2 mol NH_3 → 4 mol products). The product distribution at the outlet was 1483.16 kmol/hr of hydrogen (H_2) and 494.39 kmol/hr of nitrogen (N_2).

The mole fraction analysis of the outlet stream further confirmed the dominance of hydrogen in the gas mixture (**74.58% H_2**), followed by nitrogen (**24.86% N_2**) and a minor trace of unreacted ammonia (**0.56% NH_3**). These results demonstrate that the operating conditions chosen are

highly effective for driving the reaction toward complete decomposition, maximizing hydrogen production while minimizing residual ammonia.

5.2.2 Effect of Temperature and Pressure

Ammonia decomposition is favored by high temperature and low pressure. The following chart illustrates the effect of temperature (500–800 °C) on NH_3 conversion at different pressures (15, 25, and 35 bar):

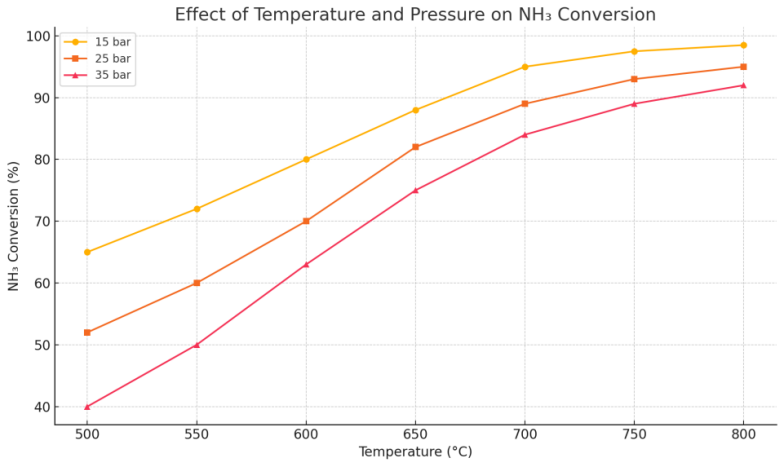


Figure 5.2: Effect of temperature and pressure on ammonia decomposition

Figure shows the effect of varying temperature and pressure on the equilibrium conversion of ammonia. The data clearly demonstrate that **temperature has a strong positive effect**, while **pressure has a negative impact** on the extent of NH_3 decomposition.

Condition	Effect on Decomposition	Reason
High Temperature	Favors decomposition (↑) conversion	Reaction is **endothermic**; heat drives equilibrium forward.
Low Temperature	Limits decomposition (↓) conversion	Not enough thermal energy to shift equilibrium.
Low Pressure	Favors decomposition (↑) conversion	Fewer moles on reactant side; low pressure shifts equilibrium **forward**.
High Pressure	Opposes decomposition (↓) conversion	More gas moles are formed; high pressure shifts equilibrium **backward**.

Conclusion

This work highlights ammonia's dual role: a key industrial product and a potential clean energy carrier.

- Ammonia contains **17.6 wt% hydrogen**, making it one of the most hydrogen-dense liquid carriers. Unlike pure hydrogen, which requires liquefaction at **–253 °C**, ammonia can be stored as a liquid at **–33 °C at 1 bar** or at room temperature under moderate pressure, offering a safer and more practical storage option.

- From the synthesis simulation, it became clear that pressure **[150 to 300 bar]**, temperature **[400 to 500 C°]**, and catalyst performance are the main factors affecting yield and conversion.

- The decomposition study showed that hydrogen can be obtained efficiently, and higher temperatures (above **700C**°) improve the process significantly.

These results underline ammonia's dual importance of modern industry and a potential enabler of future clean energy systems. At the same time, there is still room for progress. Better catalysts, stronger integration with renewable energy, and detailed economic studies will all be crucial in making ammonia-based hydrogen systems more practical and sustainable in the years ahead.

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