

## Abstract

With an increase in global warming awareness, a clear shift of the world toward clean and sustainable processes can be seen. Specially, renewable energy-based electricity generation has gained the importance. With intermittent renewable energy in mind, chemical-based energy storage might be required and applied. Among several options, ammonia seems a promising carbon-neutral energy carrier. The power-to-ammonia concept allows for the production of ammonia from air, water and renewable energy. In principle, the subsequent ammonia synthesis loop is similar to the fossil fuel-based ammonia process, which has been developed over a period of one century. However, the operation and production flexibilities of ammonia synthesis reactor systems and loops have not yet been analysed and understood systematically, as the classical process is operated at its optimal steady state.

The objective of this dissertation is to analyse and understand the ammonia synthesis loop and autothermal reactor system with regard to flexible operation and production. Among several synthesis loop and autothermal reactor system possibilities, two synthesis loops and five autothermal three-bed ammonia synthesis reactor systems are considered. The synthesis loops vary in terms of ammonia separation unit allocations, *i.e.* after and before a synthesis reactor system. The reactor system configurations differ in inter-stage cooling methods, which are based on either a direct cooling by quenching, a combination of indirect and direct cooling, direct and indirect cooling, or indirect cooling by heat exchange between process streams.

In the first part of this dissertation, the impact of the six process variables: operational pressure, process feed temperature, process feed composition ( $H_2$ -to- $N_2$  ratio,  $NH_3$  and inert gas concentration) and feed flow rate on the flexible operation of an autothermal reactor system is quantified. Among them,  $H_2$ -to- $N_2$  ratio, inert gas concentration and feed flow rate provide high flexibilities in operation and production. Then, the effect of these process variables on flexibility is compared among five variants of autothermal reactor systems. All the reactor systems showed their feasibility for power-to-ammonia.

In the second part of this dissertation, multi-variable optimisation is applied for enhancing the load ranges of the reactor systems in the synthesis loop. Beside the reactor systems, the two synthesis loop configurations are also compared for hydrogen intake, ammonia production

and recycle load flexibilities. With the multi-variable optimisation, the load range of all the synthesis loop and reactor system configurations drastically increases.

From this work it is concluded that all the ammonia synthesis reactor system and loop configurations allow operation for a large load range span and therefore are in principle suitable for power-to-ammonia.

## Kurzfassung

Motiviert durch die Folgen der globalen Erwärmung kann ein deutlicher Umschwung in Richtung einer sauberen und nachhaltigen Energiegewinnung wahrgenommen werden. Hierbei rückt besonders Elektrizität aus z.B. Sonnen-, Wind- oder Wasserkraft in den Fokus. Aufgrund des fluktuierenden Charakters dieser erneuerbaren Energiequellen stellt die chemisch-basierte Energiespeicherung einen essentiellen Bestandteil der sogenannten Energiewende dar. Aus der Menge möglicher chemischer Energieträger sticht Ammoniak als vielversprechendster Kohlenstoffdioxid-neutraler Energieträger hervor. Das Konzept Power-to-Ammonia beschreibt eine umweltfreundliche Variante der Ammoniakproduktion aus Luft, Wasser und erneuerbarer Energien. Diese ähnelt grundsätzlich der klassischen Ammoniakproduktion aus fossilen Ressourcen, welche im Zuge des letzten Jahrhunderts ausgiebig erforscht und weiterentwickelt wurde. Da klassische Ammoniaksyntheseanlagen stets für eine optimale Ausbeute und somit für einen optimalen stationären Betriebspunkt ausgelegt sind, wurde bei diesen nicht auf einen dynamischen sowie flexiblen Betrieb eingegangen, weshalb sie nicht für Power-to-Ammonia eingesetzt werden können.

Das Ziel dieser Dissertation ist die Analyse und das Verständnis von autothermen Reaktorsystemen und deren Verhalten im Ammoniaksyntheseprozess mit dem Anspruch einer flexiblen Produktion. In einer Reihe von unterschiedlichen Konfigurationsmöglichkeiten werden zwei Synthesekreisläufe und fünf Reaktorsysteme mit jeweils drei Katalysatorbetten berücksichtigt. Das Prozesslayout unterscheidet sich hauptsächlich in der Lokalisierung der Ammoniakkabscheidung, z.B. vor oder nach dem Reaktorsystem. Die Reaktorkonfigurationen variieren in der Art der Zwischenkühlung, welche durch direkte Einspritzung (Quenching), indirekt durch interne Wärmetauscher oder einer Kombination aus Quenching und indirekter Kühlung erfolgt, wobei es verschiedene Kombinationsmöglichkeiten von indirekter Kühlung und Quenching gibt.

Im ersten Abschnitt dieser Dissertation wird der Einfluss der sechs wichtigsten Prozessvariablen Betriebsdruck, Materialzufuhr-Temperatur, Materialzufuhr-Komposition ( $H_2$ - $N_2$ -Verhältnis,  $NH_3$ - und Inertgaskonzentration) und Materialzufuhr-Massenstrom auf die mögliche Flexibilität des autothermen Reaktorsystems quantifiziert. Unter diesen Variablen stellen sich ins-



besondere das H<sub>2</sub>-N<sub>2</sub>-Verhältnis, die Inertgaskonzentration sowie der Massenstrom als effektive Stellgrößen heraus. Anschließend wird der Einfluss dieser Variablen auf die Prozessflexibilität der fünf untersuchten Prozesskonfigurationen untersucht und die jeweiligen Ergebnisse verglichen. Hierbei können alle Systeme die Anforderungen an einen effizienten und flexiblen Prozess erfüllen.

Im zweiten Abschnitt dieser Dissertation wird eine multidimensionale Optimierung durchgeführt, um das Betriebsfenster und die Produktionskapazität der Reaktorsysteme zu maximieren. Zusätzlich zu den Reaktorsystemen werden ebenfalls die Prozessvarianten in Bezug auf Wasserstoffverbrauch, Produktionskapazität und Umlaufmassenstrom verglichen. Mit Hilfe der multidimensionalen Optimierung konnte das Betriebsfenster aller untersuchten Systeme deutlich erweitert werden.

Diese Arbeit zusammenfassend kann gesagt werden, dass alle betrachteten Prozesskonfigurationen Produktionsflexibilität für ein weites Durchsatz-Betriebsfenster ermöglichen und somit für Power-to-Ammonia geeignet sind. Die Ergebnisse dieser Dissertation helfen autotherme Reaktorsysteme und Power-to-Ammonia weiterzuentwickeln und somit eine flächendeckende Nutzung erneuerbarer Energiequellen zu ermöglichen.

# 1. Introduction<sup>1</sup>

In the twenty-first century, along with a rise in global warming awareness, zero-emission processes have gained substantial attention. Therefore, instead of fossil or nuclear energy fuelled power plants, the world is shifting toward renewable energy generation parks. A problem with renewable energy, however, is that it is seasonal, intermittent and decentralised when harvested. Thus, backup energy storage is required for uninterrupted and regulated power supply.

## 1.1. Ammonia as energy carrier

Chemicals-based storage is capable of high power and high capacity storage (see figure 1.1a) at low cost (see figure 1.1b) for longer seasonal time duration.<sup>[1,2]</sup> From figure 1.1a, chemical-based energy storage consisting of methane, methanol and ammonia seems promising with regard to large capacity storage over a longer period of time. Among these three options, ammonia is the only carbon free fuel. Ammonia is not just a carbon free fuel, it also provides higher energy densities than hydrogen, high round trip efficiency, scalability, availability of transport grid, maintained safety record and its production and consumption may be done CO<sub>2</sub>-emission free.<sup>[3,4]</sup> As an energy carrier, ammonia has clear advantages over pure hydrogen, although hydrogen is considered to be a noble energy carrier, as it only produces water and energy. 1 mol of ammonia contains 1.5 mol of hydrogen, which is 17.8 wt % or 108 kg H<sub>2</sub>/m<sup>3</sup> in liquid ammonia at 20 °C and 8.6 bar. Liquid ammonia contains 1.77 times more H<sub>2</sub> per unit volume than liquid hydrogen itself and even 4 times more than the most modern hydrogen storage methods in metal hydrides *i.e.* up to 25 kg H<sub>2</sub>/m<sup>3</sup>.<sup>[5]</sup>

Ammonia is the second most produced industrial chemical, and the production process has been intensively developed over a period of a century. Ammonia is used as a raw material for the production of various nitrogen compounds, including nitric acid, and a variety of fertilisers and polymers. Also, ammonia is used as refrigerant and neutraliser for NO<sub>x</sub> emission from fuel combustion.<sup>[6]</sup> Moreover, ammonia has been tested and applied as fuel in compression ignition

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<sup>1</sup>Part of this chapter has been published in I. I. Cheema and U. Krewer. *RSC Adv.*, 8:34926–34936, 2018.

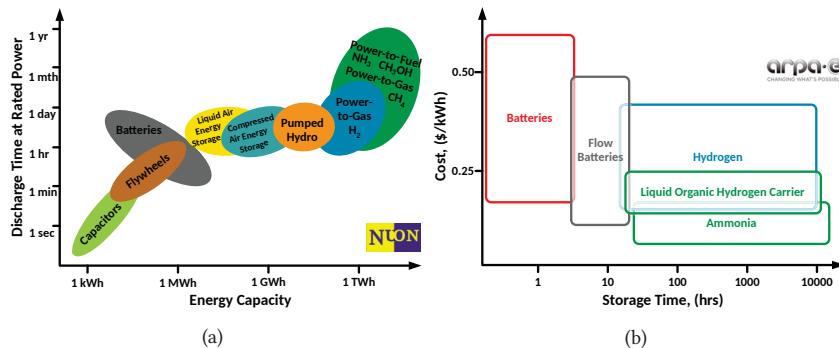


Figure 1.1.: Comparison between energy carriers for (a) capacity of energy storage<sup>[1]</sup> and (b) cost of energy storage.<sup>[2]</sup>

engines<sup>[7–9]</sup>, spark ignition engines<sup>[10–12]</sup>, gas turbines<sup>[13–15]</sup> and fuel cells<sup>[16,17]</sup> over a period of time. Despite its toxicity, ammonia has an excellent safety record in the fertiliser industry and a well established transportation network.<sup>[18,19]</sup> Thus, an ammonia economy would be low in cost and easier to apply than hydrogen in the energy sector.

Currently, about 1.6 % of fossil fuel, such as coal and natural gas, is used worldwide for the manufacturing of ammonia.<sup>[6]</sup> The classical production method, the Haber-Bosch process, relies heavily on natural gas<sup>[20]</sup>, whereas ammonia has also the capability of being produced from renewable energy sources e.g. solar<sup>[21]</sup> and wind.<sup>[3,4,22]</sup>

## 1.2. Conventional ammonia production

### ***versus power-to-ammonia***

The conventional ammonia production process consists of three major sections: the steam and/or air based reforming of natural gas for producing H<sub>2</sub>, CO<sub>2</sub> and the desired H<sub>2</sub>-to-N<sub>2</sub> molar ratio, afterwards the removal of CO<sub>2</sub> and CH<sub>4</sub>, and eventually the conversion of H<sub>2</sub> with N<sub>2</sub> to NH<sub>3</sub> in the Haber-Bosch reactor. In total, the conventional ammonia process consists of seven gas-solid catalytic steps: desulphuriser unit, primary reformer, secondary reformer, high temperature shift converter, low temperature shift converter, methanator and finally ammonia synthesis reactor.<sup>[6]</sup> An option for a CO<sub>2</sub> neutral production process is power-to-ammonia, which relies on H<sub>2</sub> production by splitting of water *via* electrolysis, where N<sub>2</sub> will be sepa-



rated from air e.g. by pressure swing adsorption (PSA) and cryogenic distillation.<sup>[4]</sup> Energy requirements of pressure swing adsorption are up to 35 % less than the cryogenic distillation<sup>[23]</sup>, therefore the air separation process based on pressure swing adsorption is considered in figure 1.2. The Haber-Bosch ammonia synthesis loop itself has shown to be similar to the conventional one.<sup>[4,21,22]</sup> The overview of the conventional *versus* the power-to-ammonia process is given in figure 1.2.

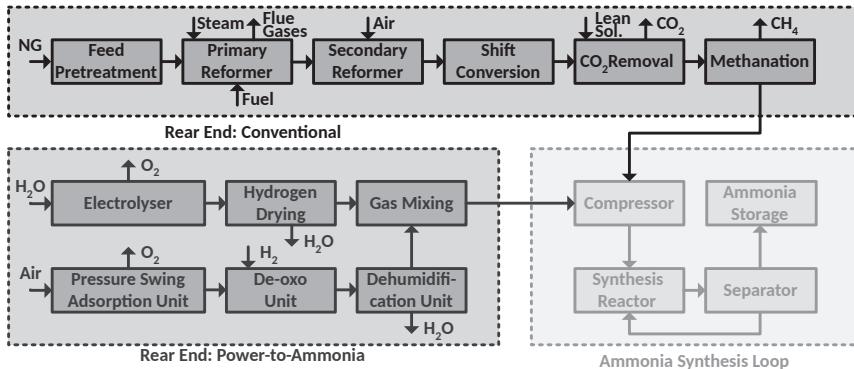


Figure 1.2.: Block diagram of the conventional ammonia production process and the power-to-ammonia process.

The efficiency of power-to-ammonia is estimated between 50 and 60 %, including hydrogen and nitrogen production<sup>[24]</sup>, which is lower than from the latest classical Haber-Bosch ammonia production plants *i.e.* between 60 and 64 %.<sup>[25]</sup> This is mainly due to the high energy requirements and energy losses in the production of H<sub>2</sub> from electrolysis of water by atmospheric alkaline, high pressure alkaline (HPA - 16 bar) or proton exchange membrane electrolyzers in comparison to energy requirements of the air separation based on cryogenic distillation or pressure swing adsorption and to the Haber-Bosch NH<sub>3</sub> synthesis process with iron, ruthenium or cobalt molybdenum bimetallic nitride based catalyst<sup>[24]</sup>.

### 1.3. Power-to-ammonia-to-power

Fuhrmann *et al.*<sup>[4]</sup> reviewed the electro- and thermo-chemical sustainable ammonia based energy production and usage concepts illustrated in figure 1.3. Among these processes, the combination of a Haber-Bosch NH<sub>3</sub> synthesis loop with the H<sub>2</sub> supply from the electrolysis of water and the N<sub>2</sub> supply from the air separation *via* pressure swing adsorption or cryogenic

distillation seems promising with respect to production capacities. They also discussed the potential for dynamic or flexible operation of the developed Haber-Bosch process concept, and as such, its ability to flexibly store excess renewable energy. With the growth of renewable energy production, power-to-ammonia and ammonia-to-power has gained world-wide interest. The current activities related to renewable ammonia in the U.S., Europe and Japan are comprehensively highlighted by Pfromm.<sup>[26]</sup>

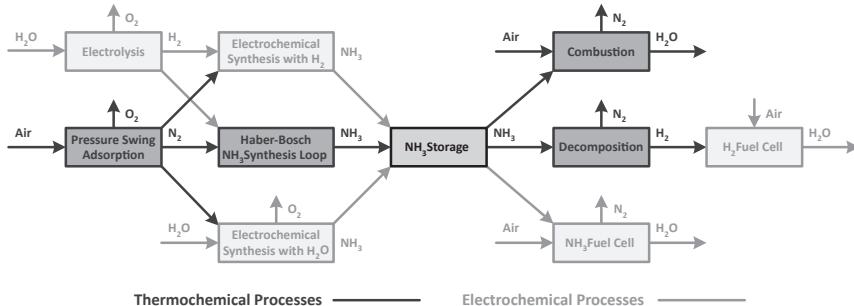


Figure 1.3.: Pathways of sustainable ammonia based energy production and usage concepts.

For the power-to-ammonia concept *via* the Haber-Bosch synthesis loop, a Technology Readiness Level of 6 has already been accomplished by Proton Ventures BV, The Netherlands.<sup>[21]</sup> The first pilot plant has been operating at West Central Research and Outreach Center, Morris, Minnesota, USA since 2013<sup>[22]</sup> and the second demonstrator became operational in June 2018 at Science & Technology Facilities Council's Rutherford Appleton Laboratory, Oxfordshire.<sup>[27]</sup> The operation of a power-to-ammonia plant by West Central Research and Outreach Center, Morris, Minnesota, USA has yet only been studied at steady-state, but not dynamically.

In parallel, simulations of the power-to-ammonia process were carried out for a system consisting of electrolyser, cryogenic separation and Haber-Bosch by Sánchez & Martín<sup>[28]</sup>, whereas Cinti *et al.*<sup>[29]</sup> considered a process based on low temperature and high temperature electrolyzers, pressure swing adsorption and Haber-Bosch. Cinti *et al.* analysed energy performances along with electricity consumption of every individual section. For the Haber-Bosch loop, thermodynamic equilibrium was considered instead of a kinetic approach, which is suitable for design-based analysis only. In contrast, Sánchez & Martín carried out complete system simulation and operational optimisation, including a kinetic approach for Haber-Bosch synthesis reactor. However, they did not consider autothermic operation of the ammonia synthesis reactor, which is of high interest for realising stand-alone power-to-ammonia plants. The question



of how much an autothermal Haber-Bosch reactor system can be operated flexibly outside its standard conditions, is of crucial relevance for the power-to-ammonia concept, but has not been addressed so far. An alternative approach is to realise constant NH<sub>3</sub> production for the proposed power-to-ammonia process, mainly with help of an uninterrupted reactants supply. The uninterrupted supply of the reactants is maintained either by the continuous production of reactants with the help of non-stop supply of electricity or *via* producing excess amount of reactants during surplus energy which are stored and later on used during shortfall times.<sup>[1]</sup> However, storing H<sub>2</sub> reactant in bulk over a day can be up to three times more expensive than ammonia (figure 1.1b); in fact an ammonia storage tank is the cheapest way of storing large amounts of energy, *i.e.* greater than 100 GWh.<sup>[1,2]</sup>

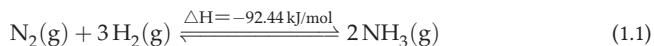
As alternative to the above mentioned power-to-ammonia process, a low pressure reaction-absorption process for power-to-ammonia is suggested by Malmali *et al.*<sup>[30]</sup>, whereas Wang *et al.*<sup>[31]</sup> proposed a power-to-power system design concept of *ca.* 72 % round trip efficiency. Malmali *et al.* used a synthesis loop consisting mainly of three steps: reaction, absorption and compression. They used an absorber instead of a condenser for separating NH<sub>3</sub> from unreacted gas, which allows one to operate the synthesis loop at 10 times lower pressure than the conventional process. This means lower capital and operational cost. However, work on absorbent regeneration still needs to be done.<sup>[30]</sup> Wang *et al.* used a H<sub>2</sub> powered cell in combination with a Haber-Bosch reactor. They divided their proposed ammonia-based energy storage system with respect to operation into two modes *i.e.* charging and discharging modes. During charging mode, heat is released from the NH<sub>3</sub> synthesis process and used in heating feed streams of reversible solid oxide fuel cell whereas waste heat contained by the product streams of reversible solid oxide fuel cell is used in reforming the H<sub>2</sub> during discharging mode.<sup>[31]</sup>

All the above mentioned processes mainly considered the Haber-Bosch design concepts for ammonia synthesis. However, the differences among the processes arise from the preparation of reactants, operational conditions of synthesis loop and/or ammonia separation. In this work, the focus is made on the developed Haber-Bosch process, rather than underdeveloped concepts.



## 1.4. Haber-Bosch ammonia synthesis loops

Ammonia synthesis is an exothermic reaction and is driven by thermodynamic equilibrium: for every 1 mole of N<sub>2</sub>, 3 moles of H<sub>2</sub> are consumed to produce 2 moles of NH<sub>3</sub>, see equation 1.1.



Only partial conversion of the reactant feed (25 to 35 %) takes place in the synthesis reactor system. Therefore, reactants need to be separated from ammonia and recycled back. Ammonia is separated from un-reacted reactants by condensation, and preferably condensation takes place at low temperature and low temperature is achieved by passing through a trail of heat exchangers and coolers. A number of different ammonia synthesis loop configurations are possible, mainly these are classified with regard to the location of the ammonia separator and fresh feed entrance<sup>[6]</sup>, see figure 1.4. Also, these ammonia synthesis loop configurations affect process feed composition and reactor design.<sup>[32]</sup>

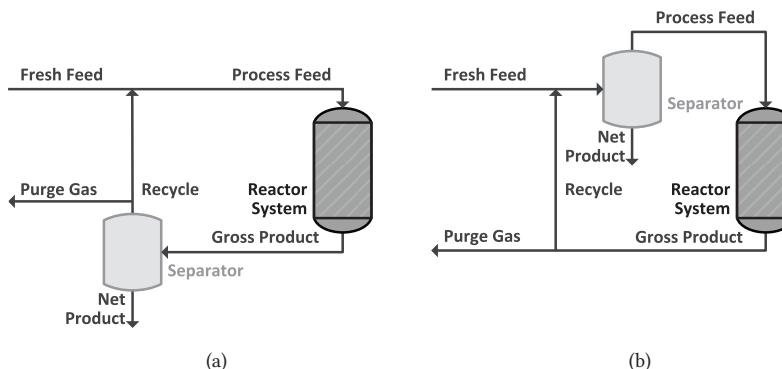


Figure 1.4.: Haber-Bosch ammonia synthesis loop configurations for (a) pure and dry fresh feed and (b) impure and wet fresh feed.

In power-to-ammonia, for a fresh feed two possibilities exist, pure or impure, and dry or wet. For example, for obtaining pure and dry reactants H<sub>2</sub> and N<sub>2</sub>, post-treatment after electrolyser and pressure swing adsorption is required, see figure 1.2, otherwise in addition to argon (Ar), the feed may also contain H<sub>2</sub>O and O<sub>2</sub>. A pure and dry fresh feed is mixed with the recycle stream and is directly sent to the synthesis reactor system; afterwards it is passed through the