

# High Purity Hydrogen from Liquid NH<sub>3</sub> – Proposal and Evaluation of a Process Chain

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This study proposes a process chain to gain high purity hydrogen from liquid ammonia. The utilization of the stored hydrogen requires the endothermic decomposition of ammonia



and the subsequent purification of H<sub>2</sub>. A process model from liquid NH<sub>3</sub> to high purity hydrogen was developed. The process model includes the reaction kinetics for the catalytic decomposition of NH<sub>3</sub> using a catalyst, such as Ni-Pt/Al<sub>2</sub>O<sub>3</sub>, and the necessary purification steps. Based on the simulation, a final process chain is proposed. Finally, heat integration calculations were performed to optimize the energy efficiency of the process.

The application of a polyimide membrane system is proposed. The performed calculations show that using membrane separation, a H<sub>2</sub> purity of around 97 wt% can be achieved. For a final NH<sub>3</sub> content of < 1 ppm, the study found acidic or adsorptive removal of remaining NH<sub>3</sub> necessary even for high decomposition conversion rates. To achieve even higher H<sub>2</sub> purity, the application of an additional pressure swing absorption separation is proposed. This application can ensure H<sub>2</sub> purities of > 99 wt% suitable for PEM fuel cells.

## 1. Introduction

Energy storage has been the focus of research and industries as global energy demand is rising and zero-carbon and renewable systems are of interest. In this scenario, the hydrogen economy has undeniable potential (Oliveira et al. 2021). Nevertheless, the handling of H<sub>2</sub> still poses substantial hazards and difficulties such as high flammability, complex storability, and a high specific volume (Tashie-Lewis and Nnabuife 2021). Therefore, ammonia, methane, and methanol are options for indirect storage. Among these, ammonia has been (well-)investigated and utilized globally on an industrial scale with established infrastructure. Due to its high volumetric hydrogen density (higher than hydrogen itself) and moderate conditions to liquefy (-33.4 °C at atmospheric pressure or 20 °C at 0.8 MPa), liquid ammonia allows (cost-)efficient storage of hydrogen.

Despite the knowledge in ammonia handling, recovering high purity hydrogen is still under investigation - separation and purification of hydrogen being the main challenge (Makhloufi and Kezibri 2021). The required purity of hydrogen for proton exchange membrane (PEM) fuel cells is a minimum mole fraction of 99.97 %, according to (DIN EN 17124), with limits for individual contaminants, some of which are reported in Table 1.

Many researchers focus on enabling green ammonia production, making the whole process sustainable and carbon-free. Ammonia from fossil fuels (brown ammonia) contains impurities such as CH<sub>4</sub> and hydrocarbons, which are not present in green ammonia. However, the shift from brown to green ammonia will be continuous. Therefore, the authors propose an process chain from low purity brown ammonia to high purity hydrogen: (1) pre-treatment, (2) catalytic NH<sub>3</sub> decomposition, (3) pre-separation purification, (4) H<sub>2</sub> separation via membranes and (5) post-separation purification. As the impurities decrease with the share of green ammonia in the mix, some pre-treatment and purification steps will grow unnecessary. Since Membranes are considered to serve as

a separation unit with a comparably low complexity and energy demand, they have also been implemented into the product purification chain.

*Table 1: Maximum allowable content of individual contaminants in hydrogen for an application in PEM FC*

Contaminant	Max. content ( $\mu\text{mol/mol}$ )
Water H <sub>2</sub> O	5
Hydrocarbons (excluding methane)	2
Methane CH <sub>4</sub>	100
Nitrogen N <sub>2</sub>	300
Argon Ar	300
Carbon dioxide CO <sub>2</sub>	2
Ammonia NH <sub>3</sub>	0.1

## 2. Methods

The foundation of the proposed process chain is a comprehensive literature study of applicable technologies as well as a process simulation of the individual process steps and a final flowsheet calculation for the proposed process chain. The calculations were performed using the sequential modular simulation tool Aspen Plus® V10 and the open source simulation environment DWSIM Version 6.6. The following chapters describes the methods used for every process step in detail.

### 2.1 NH<sub>3</sub> feed and pressure input

The input feed is liquid ammonia. Liquid ammonia comes with impurities, which must be considered when designing a process chain to produce highly purified hydrogen. According to experts, the following impurities are present in ammonia coming from hydrogen produced from natural gas reforming:

- H<sub>2</sub>O: 0.15 mass%
- Oil: 10 mg/kgNH<sub>3</sub>
- Dissolved gas containing H<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>, and Ar: max. 450 ml/100gNH<sub>3</sub>

The oil was calculated as C<sub>15</sub>H<sub>23</sub> in the process simulation. The liquid ammonia was assumed to be stored at 10 bar and 15 °C. The expansion was calculated at 1.4 bar and 15 °C. From the expansion until the compressor before the membrane, a total pressure loss of 0.4 bar was assumed, leading to a final pressure of 1 bar at the scrubber outlet. The flowsheet (see figure 1) was designed for a hydrogen output of around 45 kg/h.

### 2.2 Pretreatment

As water and oil in the feed stream can influence the catalyst performance and harm the process, pre-treatment is necessary to reduce their content before entering the catalytic reactor. The effect of cooling the feed stream for purification was assessed by calculating the thermodynamic equilibrium using a flash calculation in AspenPlus.

### 2.3 Catalytic decomposition reaction

The performance of the decomposition is highly dependent on the catalyst choice. Following Wang et al. (2017) the catalyst Ni-Pt/Al<sub>2</sub>O<sub>3</sub> was chosen to model the decomposition due to its high activity. The catalytic reactor was calculated as a kinetic reactor in AspenPlus. The reaction kinetics for the catalyst Ni-Pt/Al<sub>2</sub>O<sub>3</sub> are given by Chellappa et al. (2002). The reaction rate was implemented according to the power-law expression on a partial pressure basis:

$$r = k_0 * e^{-\frac{E}{RT}} * p_{\text{NH}_3} \quad (2)$$

According to Chellappa et al. (2002) the activation energy E is 46.9 kcal/mol and the reaction rate constant is 3.639\*10<sup>11</sup> kmol/(h\*kg\*bar). The decomposition of NH<sub>3</sub> is an endothermic reaction and produces an increased number of molecules. Following Le Châtelier's principle, high temperature and low pressures are required for the reaction to proceed. The decomposition reactor was calculated at a reaction temperature of 600 °C. The conversion rate is strongly dependent on the catalyst loading of the reactor. When designing the reactor, the catalyst loading choice is a trade-off between conversion rate and catalyst costs. In this work, two scenarios were calculated: One with a catalyst loading of 5 g/(mol/h) NH<sub>3</sub> and one with 40 g/(mol/h) NH<sub>3</sub>.

## 2.4 NH<sub>3</sub> removal

Since the reactor does not achieve complete conversion of NH<sub>3</sub>, NH<sub>3</sub> in the outlet gas needs to be removed. NH<sub>3</sub> can cause hydrolysing effects at the membrane. Therefore, it needs to be removed before separating N<sub>2</sub> and H<sub>2</sub> via a membrane. Lamb et al. (2019) reviewed several purification steps. This work investigates the removal of NH<sub>3</sub> by water or acidic scrubbing with subsequent cool drying. To calculate the NH<sub>3</sub> theoretical removal potential by water scrubbing and subsequent cool drying, flash calculations were performed in AspenPlus. For the scrubbing, a liquid/gas ratio of 3.9 l/m<sup>3</sup>(std) was considered.

## 2.5 Membrane separation

Various available publications lay the groundwork for a multi-stage membrane model that can separate gaseous mixtures with multiple components (Coker et al. 1998).

### Membrane characteristics

The purification of H<sub>2</sub> with a membrane demands a comparably high selectivity of H<sub>2</sub> over any other compound and good industrial applicability.

Both of these requirements are fulfilled by the Polyimide Membrane Matrimid 5218. Shalygin et al. (2015) reports a high H<sub>2</sub>/N<sub>2</sub> selectivity of > 800 as well as a relatively high H<sub>2</sub> permeability of > 100 Barrer. The permeances of CO, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub> and CO<sub>2</sub> are also documented. Table 2 gives an insight into the permeances of the most relevant compounds of the membrane separation step.

Table 2: Membrane permeance

Compound	Permeance Nm <sup>3</sup> /m <sup>2</sup> sPa	Reference
H <sub>2</sub>	5,87E-10	(Shalygin et al. 2015)
N <sub>2</sub>	7,07E-13	

Liemberger et al. (2017) separated H<sub>2</sub>/CH<sub>4</sub> gas mixtures using a polyimide membrane while achieving a stage cut of 0.7 and an H<sub>2</sub> permeate purity of > 95 % when applying a feed with 70 % H<sub>2</sub> and a pressure of 21 bar. The selectivity of H<sub>2</sub>/CH<sub>4</sub> is > 100 and consequently lower than the selectivity of H<sub>2</sub>/N<sub>2</sub> (> 800) (Shalygin et al. 2015). Based on these studies found in literature, it is expected that the polyimide membrane performs very well when separating H<sub>2</sub> and N<sub>2</sub> is therefore chosen for the calculations.

### Membrane calculation

Alongside the illustrative model for the mass transfer through the membrane, which was chosen to be the solution diffusion model, further preliminary assumptions must be specified:

- Negligible radial pressure variation.
- Minor pressure loss from the feed to the retentate side.
- Perfect mixing of the feed, permeate and retentate streams.
- Negligible radial concentration variation.
- The difference between components' permeance in a mixture or as a pure compound through a membrane is negligible.
- The permeance of a compound is independent of temperature and pressure.

The calculation routine is derived from the solution diffusion model. The mass transfer is driven by the logarithmic mean pressure difference and must overcome the resistance consisting of a series of adsorption, diffusion, and desorption (Davis 2002). The molar flux  $J_i$  of each component  $i$  is calculated over the product of its permeance  $Pm_i$ , the total area of the membrane  $A$  and the logarithmic-mean trans-membrane partial pressure for counter current flow, where  $p_{xf}$  and  $p_{xr}$  describe the partial pressure of the feed and retentate components and  $p_{yp}$  the partial pressure of the permeate components:

$$J_i = Pm_i * A \frac{(p_{xf_i} - p_{yp_i}) - (p_{xr_i} - p_{yi_i})}{\ln \frac{p_{xf_i} - p_{yi_i}}{p_{xr_i} - p_{ye_i}}} \quad (3)$$

### 3. Results and discussion

Figure 1 shows the proposed process chain to gain high purity H<sub>2</sub> from liquid NH<sub>3</sub>.

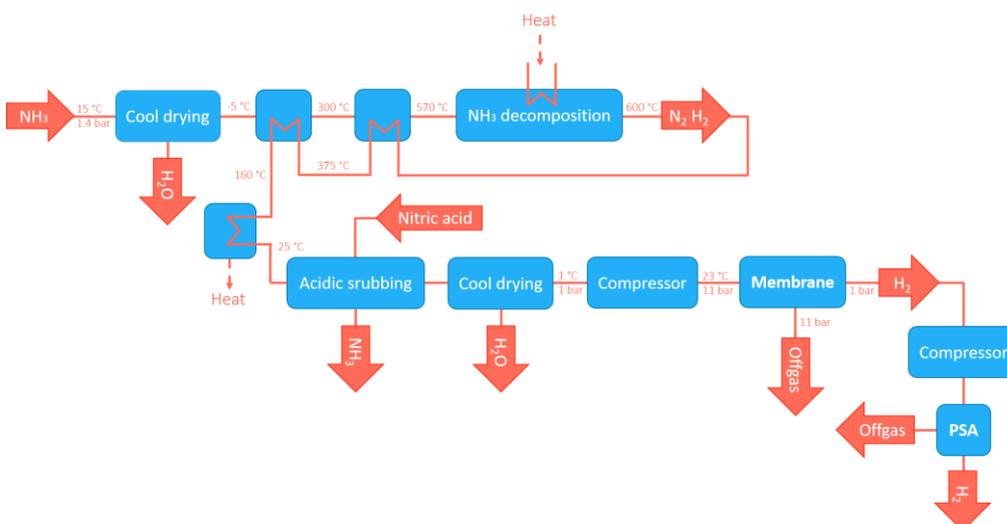


Figure 1: Proposed flowsheet for high purity H<sub>2</sub> production from liquid NH<sub>3</sub>

The following summarizes and discusses the single process steps in detail.

#### 3.1 Pretreatment

Finding the right cooling temperature is a trade-off between H<sub>2</sub>O removal, NH<sub>3</sub> losses in the condensate, and energy demand. With the considered pressure of 1.3 bar at the cool dryer, cooling down to -5 °C can reduce the water content to around 290 ppm and leads to an NH<sub>3</sub> loss of 0.16 mass%. Lowering the temperature reduces the water content even more: Cooling down to -20 °C results in a water content of 16 ppm in the gas and leads to an NH<sub>3</sub> loss of 0.45 mass%. However, the technical demand for such low-temperature drying is excessive. The technical demand could be lowered by utilizing the cooling effect of the expansion of the gas after exiting the liquid tank. This work suggests cool drying to -5 °C. The necessity of more extensive drying depends on the water content of the used ammonia and the applied catalyst in the reactor. If lower water concentrations are required, a drying adsorbent can be used (Chiang et al. 2005).

#### 3.2 Catalytic decomposition

The calculations revealed that a catalyst loading of 40 g/(mol/h) achieves a conversion of over 97.1 % NH<sub>3</sub> and a catalyst loading of 5 g/(mol/h) achieves a conversion of over 80.9 % NH<sub>3</sub>. Table 3 summarizes the streams after decomposition for both catalyst loadings.

Table 3: Gas stream before and after catalytic reactor

Catalyst loading		40 g/(mol/h)		5 g/(mol/h)	
		in	out	in	out
Volume flow	Nm <sup>3</sup> /h	390	770	431	778
Mass flow	kg/h	298	298	328	328
NH <sub>3</sub>	mol-%	99.75	1.61	99.75	10.72
H <sub>2</sub>	mol-%	0.01	73.71	0.01	66.87
N <sub>2</sub>	mol-%	0.03	24.58	0.03	22.30
H <sub>2</sub> O	mol-%	0.03	0.01	0.03	0.02
CH <sub>4</sub>	mol-%	0.14	0.07	0.14	0.08
Ar	mol-%	0.03	0.02	0.03	0.02
C <sub>15</sub> H <sub>32</sub>	mol-%	0.00	0.00	0.00	0.00
External heat demand	kW	262		242	
	MJ/kg H <sub>2</sub>	18.5		18.6	

The heat demand for the reactor can be minimized by heat integration: The input stream can be preheated with the hot output stream to 570 °C by using two heat exchangers. The first heat exchanger is used to preheat the stream from – 5 to 300 °C, the second to preheat to 570 °C. After heat integration, the reaction requires an external heat of around 18.5 MJ per kg H<sub>2</sub>. The residual external heat can be provided by electrical heat.

### 3.3 NH<sub>3</sub> removal

The results show that with water scrubbing and subsequent cool drying at 1 °C, the NH<sub>3</sub> content can be reduced from 1.61 mol% to 800 ppm when applying a catalyst loading of 40 g/(mol/h). Water scrubbing and subsequent drying do not sufficiently remove the NH<sub>3</sub> from the gas. A higher catalyst loading in the reactor leads to a higher NH<sub>3</sub> conversion and therefore can minimize the need of subsequent NH<sub>3</sub> removal. However, even with higher catalyst loading, it is expected that an acid scrubbing or adsorptive NH<sub>3</sub> removal operation is necessary to reach the required NH<sub>3</sub> content of < 1 ppm. To show the limitations of water scrubbing, the flowsheet was calculated with the Gibbs reactor. Assuming a GIBBS Equilibrium leads to an NH<sub>3</sub> concentration of 18 ppm after water scrubbing and drying. A commonly applied scrubber fluid for acid scrubbing contains sulfuric acid or nitric acid. When applying nitric acid, the scrubber liquid can be utilized as a product for agricultural use afterwards. Acidic scrubbing towers are expected to reduce the NH<sub>3</sub> concentration with an optimized design down to < 1 ppm. Due to the high removal efficiency, acid ammonia scrubbing is a widely applied method to remove ammonia from gas. Many industrial companies offering ammonia scrubbing towers guarantee removal efficiencies of 99.9 %.

### 3.4 Membrane separation

Table 4 and 5 present the results of the membrane calculation for the permeate and the retentate.

*Table 4: Product permeate streams after membrane separation*

Catalyst loading		40 g/(mol/h)	5 g/(mol/h)
Volume flow	Nm <sup>3</sup> /h	763	501
Mass flow	Kg/h	47.68	44.16
H <sub>2</sub>	mol-%	99.34	99.29
N <sub>2</sub>	mol-%	0.12	0.16
H <sub>2</sub> O	mol-%	0.53	0.54

*Table 5: Product retentate streams after membrane separation*

Catalyst loading		40 g/(mol/h)	5 g/(mol/h)
H <sub>2</sub>	mol-%	27.04	16.03
N <sub>2</sub>	mol-%	71.86	82.97
H <sub>2</sub> O	mol-%	0.85	0.63
CH <sub>4</sub>	mol-%	0.20	0.30
Ar	mol-%	0.05	0.06

Since the processes did not come with a diverse inlet stream composition, also the permeate streams show some similarities. In both calculated cases (high and low catalyst loading) the H<sub>2</sub> concentrations of the permeate streams have a maximum amount of approximately 99.3 %. Impurities that remain in the permeate stream are N<sub>2</sub> with 0.16 % and Ar and CH<sub>4</sub> with below 0.01 %. The retentate stream mainly consists of N<sub>2</sub> and H<sub>2</sub> with a H<sub>2</sub> content of up to 27.04 %.

## 4. Conclusion

The design of the reactor and the resulting reactor conversion decide over the necessary NH<sub>3</sub> removal steps after the reactor. For NH<sub>3</sub>-residues of < 1 ppm, an ammonia-removal step is necessary even for high conversion reactors. If acid scrubbing is chosen for NH<sub>3</sub> removal, subsequent drying is also required. Alternatively, adsorptive removal is an option.

A separation of N<sub>2</sub> and H<sub>2</sub> is necessary after NH<sub>3</sub> removal. In this work, the separation of N<sub>2</sub> and H<sub>2</sub> using membrane technology was calculated. Using a polyimide membrane, a high H<sub>2</sub> purity of around 99.3 mol% can be met while an off-gas stream containing the rest of the H<sub>2</sub> is produced. PSA separation as subsequent separation step after membrane separation is necessary to reach higher H<sub>2</sub> purity.

Future work will investigate the purification steps in more detail to assess the applicability of membranes in specific situations in comparison to other separation technology. An economic analysis will be needed.

Furthermore, we will analyse possible utilization of the off-gas and optimize the membranes and their interconnection to utilize the by-product.

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