

Ammonia as hydrogen carrier for transport application

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Abstract. As the interest in hydrogen to help the decarbonization of the transport sector is growing fast, the interest in new methods for its storage is a key point to improve its diffusion in many contexts, investigating innovative methods. Ammonia is a promising solution, as its hydrogen content per volume unit is higher than hydrogen stored in liquid form; furthermore, ammonia does not require cryogenic temperature nor high amounts of energy for liquefaction. In this study, two different plant layouts have been investigated, considering as a case study an ammonia-to-hydrogen conversion plant to feed a bus station composed of ten hydrogen buses (106 kg H₂/day). In the end, a techno-economic analysis is performed to investigate the Levelized Cost of Hydrogen production from ammonia for the two cases and evaluate the most feasible solution. For both the plant layouts, the following results are obtained: (i) the optimal size of the main components; (ii) the global energy efficiency; (iii) the purity of H₂ obtained; (iv) the H₂ production cost. Finally, the size effect is investigated to evaluate the economic feasibility of the best plant solution for large-scale hydrogen refuelling stations (2000 kg H₂/day), which are a more representative case for future implementations.

1 Introduction

The transport sector and electricity producers are responsible for the more than 22 Gtons of CO₂ emission on a total of 36 Gtons in 2021 [1]. Then, making decisions for decarbonization is essential, and hydrogen (H₂) is a promising alternative being a carbon free fuel [2-3]. One of the issues related to H₂ utilization is its transport and storage [4-5]. The three main storage methods available today are i) high-pressure as compressed gas, ii) cryogenic method for liquid H₂ and iii) solid-state storage in metal hydrides [6-8]. Further options are based on the chemical storage of H₂ by using compounds, such as methanol [9-11] and ammonia (NH₃), which need less harsh storage conditions (temperature and pressure) [12]. NH₃ is a strong candidate as H₂ carrier because it provides a higher H₂ volumetric density (120 kg_{H2}/m³) than other methods (e.g. compressed H₂ at 700 bar is 38 kg_{H2}/m³) and compounds (e.g. for CH₃OH is 99 kg_{H2}/m³) [12]. Moreover, the risk management associated with its high toxicity is based on worldwide well-consolidated know-how in production, transport and storage, being NH₃ one of the top products of the basic chemical industry. Then, such deep knowledge about

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NH_3 represents a strength for designing optimized processes for on-demand H_2 production based on ammonia. The final use of H_2 , obtained by NH_3 decomposition, strongly affects the whole process configuration, which must satisfy the purity grade required by the application [13][14]. Two different plant layouts have been considered for H_2 production from NH_3 , for transport application based on a polymer electrolyte membrane fuel cell (PEMFC) system.

2 Case study

Two different plant configurations have been proposed for H_2 production from NH_3 for a fuel station dedicated to the public transport. The main difference between the two case studies is the technology employed for H_2 separation after the cracking reactor, which affects the H_2 purity, the energy/material loops recovery, and the energy efficiency. For both cases, the operating conditions of all the equipment have been set, as well as the compositions of all the fluxes involved have been calculated to evaluate energy and mass process balances. Dataset used for evaluating the H_2 daily production for the aforementioned application are based on projects about green mobility [15]. Each bus has an average H_2 consumption of $8.7 \text{ kg}_{\text{H}_2}/100 \text{ km}$ ($0.11 \text{ kg}_{\text{H}_2}/\text{km}$), a daily driving time of 5.25 hours/day, and an average speed of 18.4 km/h. Then, the overall daily consumption for one bus is $10.6 \text{ kg}_{\text{H}_2}/\text{day}$.

In the first case (CASE 1 - Fig. 1), liquid NH_3 ($-33 \text{ }^\circ\text{C}$, 1 bar) is compressed and heated in several consecutive steps to reach the conditions for the endothermic decomposition reaction ($450 \text{ }^\circ\text{C}$, 10 bar), allowing an NH_3 conversion of 96% as confirmed by simulation, and in accordance with the literature [13]. The outlet reactor stream is rich in H_2 and cooled up to $25 \text{ }^\circ\text{C}$ by a heat exchanger and a cooler to be fed to the bottom of the countercurrent absorption column while the water is fed from the top.

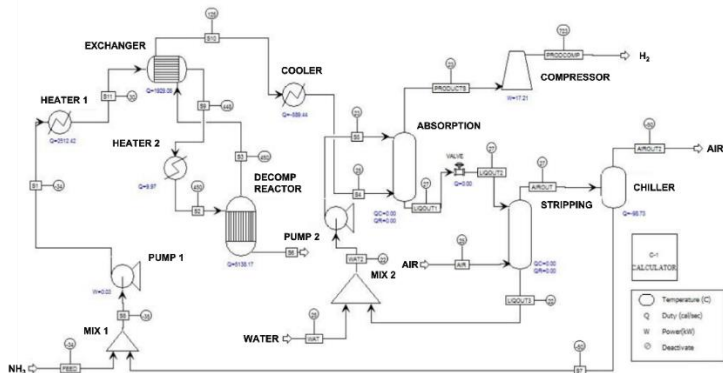


Fig. 1 Plant layout considered in case study 1

H_2 is separated from the unreacted NH_3 using a two steps method. Firstly, the NH_3 is recovered in an absorption column by water, followed by a stripping column with air for water regeneration. The absorption stage produces a gas phase mainly composed of H_2 (74%) and NH_3 , and a liquid phase made of water and NH_3 . The first is compressed to 350 bar, while the latter is treated in a stripping column with air. This last step allows the recovering the water for absorption while the NH_3 -rich stream is fed to a chiller. Here, the temperature is set to $-50 \text{ }^\circ\text{C}$ to condensate NH_3 and clean the air stream. The unreacted NH_3 is then mixed with the fresh NH_3 stream.

In the second plant layout (CASE 2 - Fig. 2), the first steps of the process are similar to those reported for CASE 1, to heat and compress NH_3 from storage ($-33 \text{ }^\circ\text{C}$, 1 bar) to decomposition conditions ($450 \text{ }^\circ\text{C}$, 10 bar). The dashed line, which feeds the decomposition reactor, represents the heat supplied by the combustor.

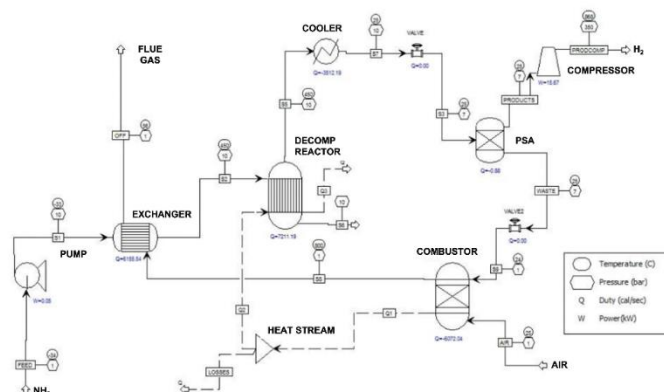


Fig. 2 Plant layout considered in case study 2

The output H₂-rich gas stream from cracking reactor is cooled to 25 °C, and the pressure is decreased by an expansion valve to 7 bar, the value required by the pressure swing adsorption (PSA). Here, the separation of H₂ is carried out by four absorbent beds made of 5A zeolite, with an H₂ recovery of 71.4% and a final H₂ purity of 99.51%. This stream is compressed to 350 bar, while the waste stream from PSA is mainly composed of H₂ and NH₃, then is fed to a combustor producing the heat required by the cracking reaction. The working temperature of the combustor is set at 800 °C; this value has been calculated to guarantee the heating required by the cracking reactor.

3 Main results and discussion

A mass and thermal balance for both plant layouts have been investigated. The most relevant results are summarized in **Table 1**. CASE 1 requires a lower amount of NH₃ (36.52 kmol/d) than CASE 2 (51.42 kmol/day) for providing the same daily H₂ production. Nevertheless, CASE 2 provides higher purity hydrogen (99.51% vs 74%), and the flue gas stream from the combustor is mainly composed of N₂ (molar fraction, X_{N2}=0.71), water (X_{H2O}=0.22) and H₂ (X_{H2}=0.07). The molar fractions of nitrogen compounds such as NH₃, NO, and NO₂ are evaluated in an order of magnitude of 10⁻⁶, 10⁻¹³, 10⁻²³, respectively, which are compatible with the emission in the air as well as its final temperature (56 °C). CASE 2 has also lower electrical/thermal energy consumption, but the presence of PSA leads to worse energy efficiency. Indeed, PSA is less performing in H₂ separation than the absorption column used in CASE 1 (separation efficiency PSA = 71.4 %, absorption column = 90%). This drawback is counterbalanced by the higher purity of the obtained H₂ as reported above. Another factor to take into account is the complete process layout. From **Fig. 1** and **Fig. 2** is well evident that the second solution is simpler with a reduced number of equipment.

Table 1: energy comparison between the two plant layouts

FEATURES	CASE 1	CASE 2
NH ₃ feed [kmol/d]	36.52	51.42
NH ₃ cracking reactor	Isothermal (450 °C, 10 bar)	Isothermal (450 °C, 10 bar)
Daily H ₂ production [kg/d]	106.26	106.26
Daily NH ₃ consumption [kg/d]	621.87	875.71

Electrical energy consumption [kWh/d]	415	378
Thermal energy consumption [kWh/d]	770	351
Specific energy consumption [kWh/kgH ₂]	11	6.85
H ₂ purity	74%	99.51%
Energy efficiency [%]	80.5	64.7

The economic analysis is mandatory to complete the feasibility evaluation, determining the hydrogen production cost (COH) for the most promising configuration. The obtained COH is compared to current and expected future hydrogen costs to evaluate the economic feasibility. COH is calculated as follows:

$$COH = (\text{Annual Fixed Costs} + \text{Annual Variable Costs}) / H_2 \text{ annual production} \quad (1)$$

Annual Fixed Costs (AFC) are evaluated starting from Total Capital Investment (TCI), considering the plant lifetime in years n and the interest rate r :

$$AFC = TCI \cdot (r \cdot (1+r)^n) / ((1+r)^n - 1) \quad (2)$$

While Annual Variable Costs (AVC) include ammonia, electrical and thermal energy input costs, which are the most impactful voices. The following assumptions are considered:

- Ammonia price 500 €/ton, based on 2021 market [16];
- Electrical energy price 135 €/MWh, based on average 2021 price for large size industrial users in Italy [17];
- Thermal energy price 50 €/MWh;
- Plant lifetime 30 years, as reported in recent literature [18][19];
- Interest rate 3% [20];
- 350 operative days per year.

To evaluate the Purchased Equipment Cost (PEC), reference value for a similar plant layout used as reference with a capacity of 500 kg H₂/day has been considered. In this case, the PEC_{ref} was equal to 15 M€, as reported in recent literature [18]. Thus, considering the plant size scale-down to 106 kg H₂/day, the correct PEC can be calculated as follows:

$$(PEC / PEC_{ref}) = (\text{Capacity} / \text{Capacity}_{ref})^x \quad (3)$$

Where x is the capacity factor, set equal to 0.65 as reported in literature for industrial plants. The PEC for the lower scale plant has been determined in 5.48 M€. Assuming a TCI/PEC ratio equal to 2 [10], the TCI is estimated in 10.96 M€. Annual costs distribution for this kind of plant is reported in **Fig. 3**.

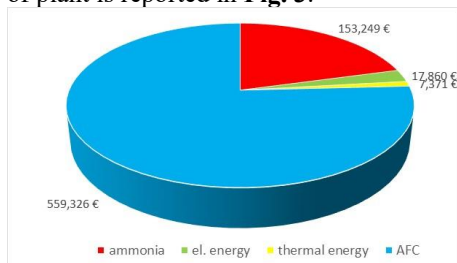


Fig. 3 Annual costs' breakdown for small scale plant

It is worth noting that the largest contribute is due to annual fixed costs for this kind of plants, in particular for the small size analysed for this application. However, the plant complexity is high and the hydrogen production is quite limited (106 kg/day), based on the hydrogen demand for ten buses operations. Therefore, the hydrogen production cost, calculated as reported in Eq. (1), results 19.86 €/kg, which is a high value compared to market ones. A further analysis is carried out considering the influence of plant size. As the target is a refuelling station for vehicles, higher production rates, up to 4,000 kg/day, are analysed. Main economic results are shown in Figs. 4 and 5. **Fig. 4** shows costs' breakdown: as the size increases, specific CAPEX gets lower and OPEX influence gets higher, in particular the ones related to ammonia consumption. Electrical and thermal energy amounts required in the process are limited thus their economic impact is low too.

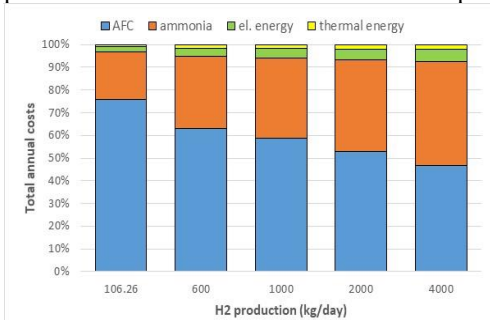


Fig. 4 Annual costs' breakdown for different plant sizes

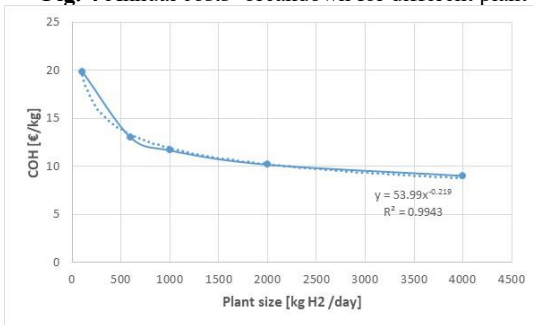


Fig. 5 COH trend vs size

Fig. 5 shows COH trend according to plant size variation. As the size gets higher, the economic feasibility is improved: for 2,000 kg/day COH is 10 €/kg, which is quite close to green H₂ production prices in several present scenarios [21][22]. In this configuration, H₂ production plant is located close to the refuelling station, thus costs for H₂ transport are saved.

4 Conclusions

This study considers ammonia as candidate for hydrogen storage for the mobility sector, evaluating the impact of process design on hydrogen purity, mass and thermal balances, as well as energy efficiency. Two different plant layouts have been presented, and the most relevant difference is related to the H₂ separation system after the cracking reactor. The results show that the H₂ separation by absorption and stripping has a higher energy efficiency and a lower ammonia daily consumption than the solution based on PSA. Nevertheless, this second approach improves the final hydrogen purity and reduces the kWh/kg_{H2} required by the process, and it also has a simpler process layout, making CASE 2 more suitable for the

application. Starting from the energy results, a techno-economic analysis is carried out to evaluate the hydrogen production cost (COH). For the considered application, as the size is very small, investment costs are too high to achieve economic feasibility: COH is about 20 €/kg. However, considering higher sizes, comparable to the ones for a typical refuelling station (I.e. 2000 kg H₂/day), costs would be significantly lower (10 €/kg). Furthermore, it must be noted that this configuration would avoid costs related to hydrogen transportation.

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