Systems & Control Transactions

Research Article - Peer Reviewed Conference Proceeding
ESCAPE 35 - European Symposium on Computer Aided Process Engineering
Ghent, Belgium. 6-9 July 2025
Jan F.M. Van Impe, Grégoire Léonard, Satyajeet S. Bhonsale,
Monika E. Polańska, Filip Logist (Eds.)

PSE PRESS

Green Hydrogen Transport across the Mediterranean Sea: A Comparative Study of Liquefied Hydrogen and Ammonia as Carriers

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ABSTRACT

Green hydrogen is widely recognized as a key player in the decarbonization of the energy system. To transport it efficiently, hydrogen must be converted into a carrier, such as liquefied hydrogen or ammonia, to increase its volumetric density. The supply chain of these carriers includes hydrogen conversion into the carrier, overseas transport, and carrier reconversion back to hydrogen. A case study involving hydrogen transportation across the Mediterranean Sea is used to evaluate the carrier efficiency. The processes involved in the supply chain are simulated in Aspen Plus® V11 to determine material and energy balances, and the "net equivalent hydrogen" method is applied to calculate the equivalent amount of hydrogen needed to supply thermal or electric power. The efficiency, defined as the ratio of net hydrogen delivered (after accounting for consumption and boil-off losses) to the initial hydrogen input, is higher for ammonia than for liquefied hydrogen (73% vs 60%, respectively). This advantage lies in the lower overall hydrogen consumption for ammonia synthesis and cracking compared to liquefaction.

Keywords: green hydrogen, green ammonia, liquefied hydrogen, hydrogen carrier, energy efficiency

INTRODUCTION

Green hydrogen is commonly regarded as a key player in the transition towards a low-carbon future [1]. It can be efficiently produced in regions with abundant renewable resources, which are often remote and distant from major consumption centers. Therefore, the efficient and cost-effective transportation of H_2 from production hubs to end users is essential. However, H_2 has an extremely low volumetric density at ambient conditions. To overcome this issue, hydrogen carriers, such as liquefied hydrogen (LH_2) and ammonia (NH_3), are being explored for its transportation on a large-scale [1].

This study assesses the energy consumption involved in the supply chain of these carriers, focusing on the processes of converting hydrogen into the carrier and reconverting it back to hydrogen. For LH_2, these processes involve hydrogen liquefaction and regasification, while for NH_3, they include ammonia synthesis and cracking. The simulations are conducted using Aspen Plus® V11 [2] to determine the material and energy balances. The analysis adopts the "net equivalent hydrogen" method, which is analogous to the widely used "net equivalent methane" method [3]. This approach assesses the equivalent amount of hydrogen that would need to be burned to power specific equipment. By using this unified energy basis, the method allows for a fair comparison between different processes.

METHODS

The case study considered is for green hydrogen transportation across the Mediterranean Sea [1]. The feed hydrogen conditions are assigned in terms of temperature (T_{in} = 25 °C), pressure (P_{in} = 20 bar) and flowrate (F_{in} = 1,800 kg/h), which resemble the conditions at the outlet of an alkaline electrolyzer. The H_2 is converted into the considered carrier, transported overseas covering a distance of 2,500 km, and finally reconverted to H_2 at the utilization site. The conditions of the delivered hydrogen are selected based on the requirements for industrial application. Therefore, the H_2 purity is 99.9 mol% and the pressure is 30 bar.

The energy analysis is based on the "net equivalent hydrogen" (NEH) method, which evaluates the equivalent amount of hydrogen that would need to be burned to power specific equipment. The Net Equivalent Hydrogen Delivered (*NEHD*) is then calculated by subtracting both the Net Equivalent Hydrogen Consumed (*NEHC*) and the hydrogen lost due to the boil-off phenomenon during shipping (F_{lost}) from the total hydrogen fed into the plant:

$$NEHD = F_{in} - NEHC - F_{lost} \tag{1}$$

The energy interactions can be categorized in:

- heating below ambient temperature,
- cooling above ambient temperature,
- heating above ambient temperature,
- cooling below ambient temperature,
- supplying of electrical power.

According to the methodology described by Pellegrini et al. [3], heating below ambient temperature (< 25 °C) and cooling above ambient temperature (> 25 °C) do not consume hydrogen since service water can be used to provide or remove heat, respectively. In the studied processes, heating above ambient temperature is achieved, where feasible, by coupling process streams. When this is not possible, heating is supplied by burning the hydrogen carrier (hydrogen, ammonia, and their mixtures) as a fuel with air in a furnace. In this case the Net Equivalent Hydrogen Consumed for heating ($NEHC_{he}$) is related to the hydrogen content of the fuel mixture and is computed as:

$$NEHC_{he} = F_{fuel} \cdot w_{hydrogen} \tag{2}$$

where F_{fuel} is the flowrate of the carrier used as fuel, and $w_{hydrogen}$ is the weight fraction of hydrogen in the fuel. Cooling below ambient temperature is accomplished through heat exchange with fluids flowing in refrigeration cycles. Therefore, the hydrogen consumed is indirectly linked to the electric power required to operate the compressors in these cycles. The Net Equivalent Hydrogen Consumed for supplying electric power ($NEHC_{el}$), used for driving compressors and pumps, is computed assuming hydrogen utilization in fuel cells with an efficiency η_{FC} of 60%:

$$NEHC_{el} = \frac{W}{\eta_{FC} \cdot LHV} \tag{3}$$

where *W* is the electric power consumption, and *LHV* is the lower heating value of hydrogen.

The efficiency of the value chain (η) is then computed as the ratio between the *NEHD* and the hydrogen feed flow rate:

$$\eta = \frac{NEHD}{F_{in}} \tag{4}$$

A schematic of the hydrogen carrier supply chain is depicted in Figure 1.

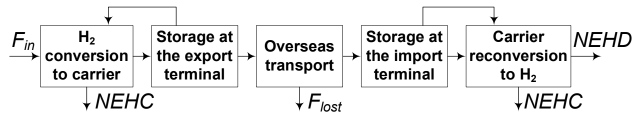

Figure 1. Schematic of the hydrogen carrier supply chain.

PROCESS SIMULATION

The processes involved in the LH_2 and NH_3 value chains are simulated using Aspen Plus® V11 [2] to obtain material and energy balances, necessary for the NEH assessment. It is supposed that the impurities in the hydrogen feed have been removed before the hydrogen enters the processes. Heat exchangers' pressure drops are neglected. An isentropic efficiency of 0.8 is assumed for pumps, compressors and turbine expanders, unless otherwise stated.

Liquefied hydrogen supply chain

Hydrogen liquefaction process

The hydrogen liquefaction process involves cooling hydrogen gas to extremely low temperatures until it transitions from gas to liquid. This happens at about -250 °C at atmospheric pressure. The process typically includes a precooling section, where nitrogen or other refrigerants are used to remove heat, and a cryogenic section, where further cooling happens using Joule-Thomson expansion or other cryogenic methods until hydrogen reaches its liquefaction point. Various process configurations have been explored in the literature. Among them, the process described by Cardella [4], which employs a mixed refrigerant Joule-Thomson cycle for precooling and a dual-pressure hydrogen Claude cycle for cryogenic cooling, stands out as the most balanced in terms of complexity and specific electricity consumption for the small-capacity plant under consideration [5]. For simulating this process, the Peng-Robinson thermodynamic package, modified as detailed in [6], is used to account for the behavior of equilibrium hydrogen and to model continuous ortho-para hydrogen conversion, which is achieved by packing a suitable catalyst within the tubes carrying the processed hydrogen. The Process Flow Diagram (PFD) is depicted in Figure 2a. The hydrogen stream (H2 in Figure 2a) undergoes precooling to -173 °C in the multi-stream heat exchanger HX-1, where it flows counter-currently to a mixed refrigerant. The composition of this refrigerant, optimized by Cardella [4] to minimize temperature differences between the cold and hot composite curves in HX-1, is 14 mol% nitrogen, 30 mol% methane, 31 mol% ethane and 25 mol% iso-butane. The mixed refrigerant is

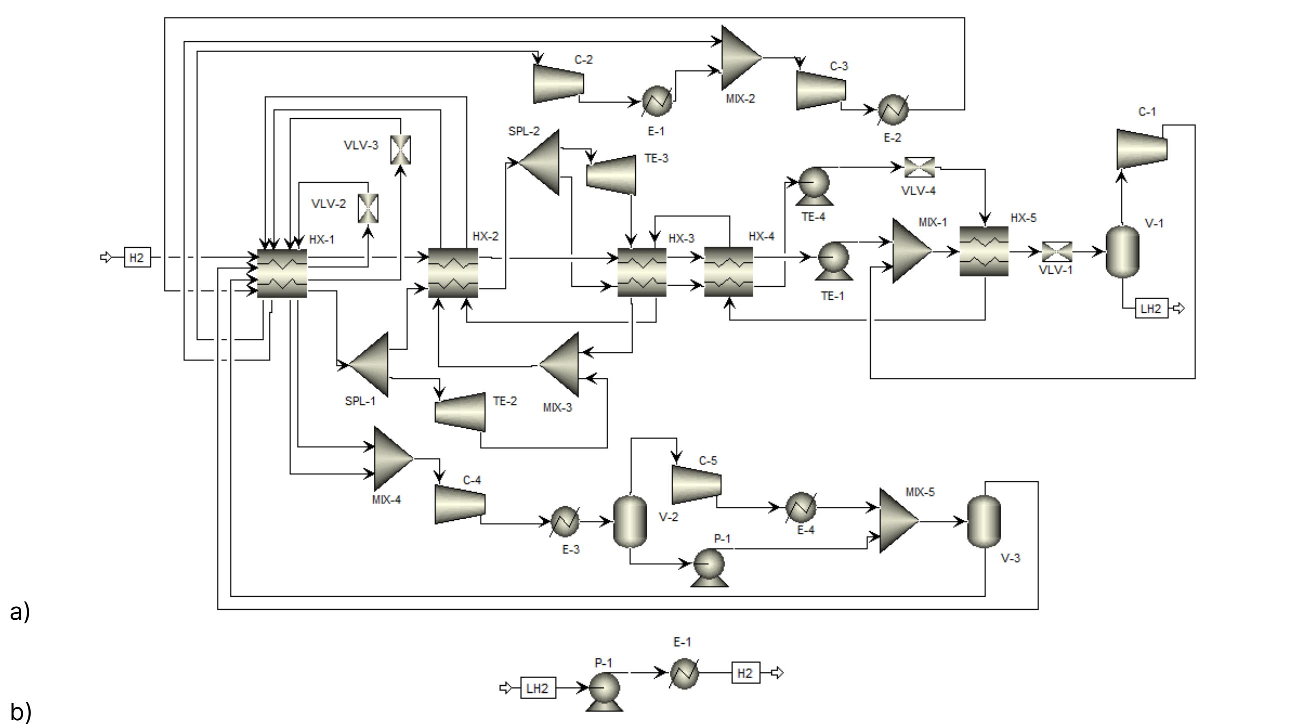

Figure 2. PFD of the processes involved in the LH_2 supply chain: a) H_2 liquefaction and b) LH_2 regasification.

compressed to 25 bar in compressor C-4, cooled to 30 °C in heat exchanger E-3 using service water, and separated in flash vessel V-2 to avoid the presence of liquid at the inlet of the second compressor. The separated vapor is compressed to 50 bar in C-5, cooled to 25 °C in E-4, and mixed with the liquid from V-2 after it is pumped to 50 bar in pump P-1. This mixture is separated in V-3, with liquid and vapor streams sent to the hot side of HX-1. The former is precooled to -110 °C and expanded to 2.9 bar through Joule-Thomson valve VLV-2. The latter is precooled to -193 °C and expanded to 2.9 bar through VLV-3. These low-pressure streams are directed to the cold side of HX-1 and are mixed at its outlet in mixer MIX-4. The design of the dual-pressure H_2 Claude cycle has been optimized by Cardella [4] to reduce temperature differences in the heat-exchangers HX-2, HX-3, HX-4, and HX-5. The low-pressure H_2 refrigerant is compressed to 8.3 bar in C-2, cooled to 30 °C in E-1 using service water, and mixed with the intermediate-pressure H_2 refrigerant in MIX-2. The mixture is compressed to 49.9 bar in C-3, and cooled to 25 °C in E-2. The resulting high-pressure H_2 refrigerant is precooled to -173°C in HX-1 and then split in splitter SPL-1, directing 38.8 % of the flow to turbine expander TE-2, where it is expanded to an intermediate pressure of 8.3 bar. This stream is mixed with a recycle stream in MIX-3 and routed to the cold side of HX-2. The remaining flow from SPL-1 passes at the hot side of HX-2, reaching an outlet temperature of -213 °C, and is then split in SPL-2. Of this, 73.8 % is directed to TE-3, where it expands to 8.3 bar, then passes at the cold side of HX-3 to cool the processed hydrogen stream. The remaining flow from SPL-2 passes at the hot side of HX-3, reaching -237 °C at the outlet. The processed hydrogen and the high-pressure hydrogen refrigerant are further cooled in HX-4 to -249 °C. At the outlet of HX-4, the processed hydrogen is expanded in TE-1 to 5 bar, then mixed with the vapor from the flash separator V-1 and cooled in HX-5 to -251 °C. The high-pressure refrigerant is expanded to 3 bar in TE-4 and then to 1.4 bar in VLV-4, then passes as cold stream through HX-5, HX-4, HX-3, HX-2, and HX-1. The processed hydrogen is finally throttled to the storage pressure (1.3 bar) in VLV-1. A minimum approach temperature of 3 °C is maintained in all heat exchangers, except for the exchanger where hydrogen undergoes a phase change (HX-5), where the minimum approach temperature is set to 1 °C.

Liquefied hydrogen storage and transport

The produced liquid hydrogen is stored in properly insulated tanks. The boil-off gas is assumed to be reliquefied at the export terminal and sent to the regasification process at the import terminal. During overseas transport, the boil-off gas is lost with a rate of 0.2 % per day [1]. The total hydrogen loss during transport is calculated based on the travel distance and an average shipping speed of 30 km/h [1].

Liquefied hydrogen regasification process

Regasification involves converting liquid hydrogen back into its gaseous state. This process is relatively straightforward, involving the pumping of liquefied hydrogen followed by heating it to ambient temperature.

The PFD of the process is depicted in Figure 2b. The discharge pressure of the pump (P-1) is set to 30 bar to meet the pressure requirements for industrial application. The pump is assumed to have an efficiency of 0.6, and service water is used as the heating medium in the vaporizer (E-1).

Ammonia supply chain

Ammonia synthesis process

NH_3 is synthesized from nitrogen and hydrogen, according to the reaction:

$$3H_2 + N_2 \rightarrow 2NH_3 \tag{5}$$

The simulation utilizes the Redlich-Kwong-Soave equation of state with the alpha function modification proposed by Boston and Mathias (RKS-BM). The PFD of the process is shown in Figure 3a. The nitrogen required for the synthesis is determined by the stoichiometric ratio given in Eq. (5). Nitrogen is produced from air using the process scheme proposed in [7]. Air (AIR in Figure 2a) is compressed to 9.9 bar and then precooled to its dew point in the multi-stream heat exchanger HX-6. The resulting stream is sent to the high-pressure rectification column T-1, which consists of 50 theoretical stages. This column separates the air into two streams: a nitrogen-rich vapor (residual oxygen content of 2 ppm) as the top product and a bottom product comprising an approximately equimolar mixture of oxygen and nitrogen. The bottom stream is expanded to 3.3 bar and fed into the low-pressure stripping column T-2, which separates the feed into a top stream resembling the composition of air and an oxygen-enriched bottom stream. The oxygen-

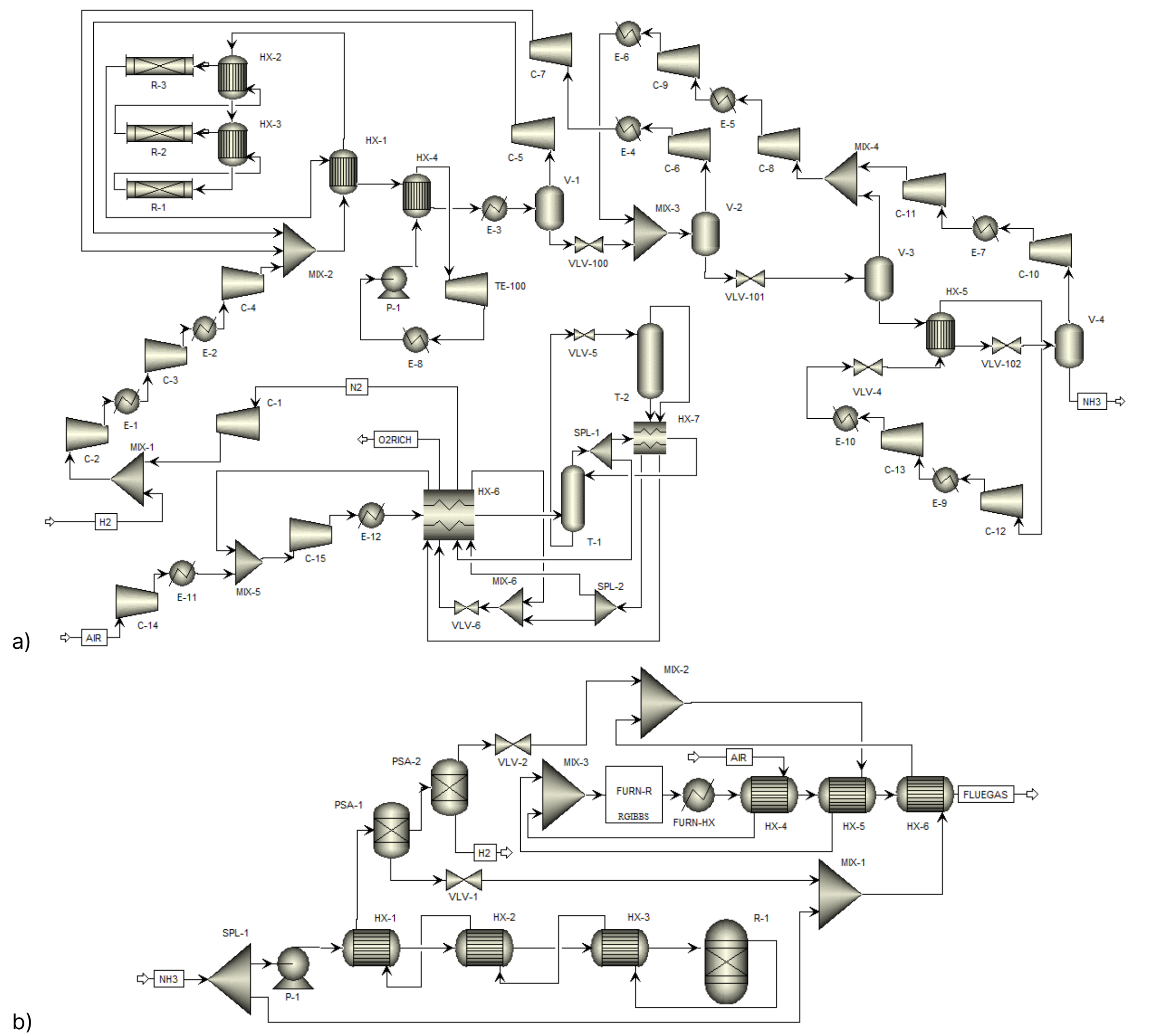

Figure 3. PFD of the processes involved in the NH_3 supply chain: a) NH_3 synthesis and b) NH_3 cracking.

enriched stream is routed through process exchangers HX-7 and HX-6 and exits as a product (O2RICH in Figure 3a). The top stream also passes as a cold stream in HX-7 and HX-6 and is then recycled to mixer MIX-5, where it mixes with the incoming air feed. The cooling required to condense part of the nitrogen-rich vapor from the high-pressure column, providing reflux, is achieved by evaporating the bottom product of the low-pressure column. HX-7 operates with an approach temperature difference of 1 °C. The produced nitrogen stream (N2 in Figure 3a) feeds the ammonia synthesis section. The hydrogen stream (H2 in Figure 3a) is mixed with N2, after being compressed to 20 bar, and then compressed to 200 bar in a three-stage compressor with intercooling. The resulting stream is mixed with the recycle streams, the vapors exiting the V-1 and V-2 separators, suitably compressed, and heated to 347 °C using a series of process-process heat exchangers (HX-1, HX-2, HX-3), which recovers heat from the streams exiting the reactor beds, before being sent to the first catalytic stage R-1. The reaction section comprises three adiabatic catalytic beds (R-1, R-2, R-3) with intermediate cooling. Iron-based catalysts are used to enhance the conversion (Haber-Bosch process). The stream exiting the last reactor stage R-3 contains ammonia along with hydrogen and nitrogen. The unconverted reagents must be separated and recycled to the reactor. The goal is to produce liquid ammonia at near-ambient pressure (1.3 bar), with a purity exceeding 99.95%, as defined by legislation [8]. To achieve this, the stream is first cooled to 50 °C in HX-4, transferring heat to a steam Rankine cycle, and further cooled to 30 °C in heat exchanger E-3 using service water. The resulting biphasic stream is separated in the V-1 separator: the vapor phase is recycled to the reaction section, while the liquid phase undergoes further purification through downstream expansion and cooling stages. Specifically, flash vessels V-2, V-3, and V-4 operate at pressures of 40 bar, 7 bar, and 1.3 bar, respectively. Cooling is achieved in HX-5 using an ammonia refrigeration cycle.

Ammonia storage and transport

Liquefied ammonia storage takes place in properly insulated tanks. The boil-off gas is assumed to be reliquefied at the export terminal and directed to the cracking process at the import terminal. During overseas transport, a boil-off gas loss rate of 0.024 % per day is considered [1].

Ammonia cracking process

The dissociation of ammonia is a highly endothermic process, described by the following reaction:

$$2NH_3 \rightarrow 3H_2 + N_2 \tag{6}$$

Commercially, small-scale ammonia cracking reactors (capacities ranging from 1 Nm^3/h and 1,000 Nm^3/h), operating at temperatures between 800 and 1,000 °C with Ni-based catalysts are available. The endothermic reaction is supported by electricity.

The simulation of the ammonia cracking process assumes the use of the thermocatalytic technology with Ni-based catalysts, as this is the most mature technology. Figure 3b illustrates the PFD of the process. Upon reaching the utilization site, ammonia (NH3 in Figure 3b) is pumped to 30 bar, preheated through a series of heat exchangers (HX-1, HX-2 and HX-3) that recover heat from the reaction products, and fed into the cracking reactor (R-1). The reactor is modeled using Aspen Plus's RGibbs module due to the lack of sufficiently detailed kinetic data. As a result, the ammonia conversion is assumed to follow thermodynamic equilibrium at the reactor's operating conditions of 30 bar and 900 °C. The heat required for the endothermic cracking reaction is supplied by burning a portion of the ammonia, which is mixed with hydrogen-rich waste streams from the purification section. Air (AIR in Figure 3b), used as the oxidizer, is added slightly above the stoichiometric ratio to ensure complete combustion. Following the reaction stage, hydrogen is separated from the unconverted ammonia and nitrogen via pressure swing adsorption units (PSA-1 and PSA-2).

RESULTS AND DISCUSSION

The Net Equivalent Hydrogen Consumed is calculated from the material end energy balances obtained from process simulations using Eqs. (2)-(3), then the Net Equivalent Hydrogen Delivered is computed using Eq. (1). Figure 4 presents the results through Sankey diagrams, which are particularly effective for visualizing where hydrogen is consumed or lost within the supply chain. Processes characterized by a low efficiency must be the primary targets for future research efforts. The *NEHD* for LH_2 is 1,072 kg/h, reflecting an overall efficiency of 60% for the supply chain. Among the processes, hydrogen liquefaction exhibits the highest equivalent hydrogen consumption, with approximately one-third of the hydrogen input being consumed during the process. This highlights the need to focus research on optimizing the process to minimize electricity consumption. One potential solution is the use of refrigerant mixtures in both the precooling and cryogenic cooling stages, with their composition optimized to achieve a close match between the hot and cold composite curves of the heat exchangers, while ensuring that no components precipitate as solid at the operating temperature of the refrigeration cycle. Another approach is to explore energy integration opportunities with processes that require low-temperature heat, such as liquefied natural gas regasification. The *NEHD* for NH_3 is 1,323 kg/h, corresponding to an overall η of 73% for the supply chain. Ammonia cracking accounts for the highest equivalent hydrogen consumption, utilizing approximately one-fifth of the total hydrogen input during the

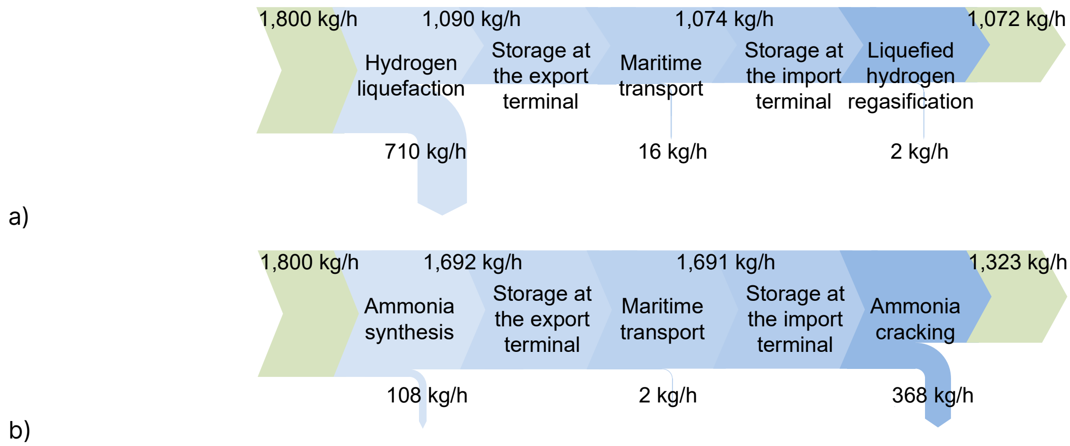

Figure 4. NEH assessment for the a) LH_2 and b) NH_3 supply chains.

process. Therefore, research efforts should focus on improving this process by exploring alternative and sustainable methods for supplying the heat of reaction.

The *NEHD* is higher for NH_3 than LH_2 because the combined hydrogen consumption for ammonia synthesis and cracking is lower than that required for the liquefaction process. The difference in *NEHD* between the two carriers is 251 kg/h, meaning that hydrogen liquefaction would need to consume 459 kg/h, equivalent to one-fourth of the total hydrogen input, to break even with NH_3. In addition, hydrogen losses due to boil-off during maritime transport are smaller for NH_3, even if their contribution does not significantly impact the overall results. Therefore, NH_3 is the most efficient hydrogen carrier for hydrogen delivery considering the final hydrogen application to the industrial sector.

CONCLUSIONS

The processes involved in the liquefied hydrogen and ammonia supply chains for hydrogen overseas transportation have been analyzed from an energy consumption perspective. The ammonia supply chain is more efficient than the liquefied hydrogen supply chain, with efficiencies of 73% and 60%, respectively. This is because the combined equivalent hydrogen consumption for ammonia synthesis and cracking is lower than that required for the liquefaction process. Ammonia would become even more attractive if it could be used directly by end consumers, eliminating the inefficiency associated with its reconversion back to hydrogen.

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