

Energy and economic assessment of LH₂, NH₃, TOL/MCH and H0-DBT/H18-DBT for large-scale hydrogen transport

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ABSTRACT

The transport of hydrogen from regions rich in renewable energy resources, where green hydrogen can be produced at a low cost, to countries with high energy demand, but limited resources, requires its conversion into a "hydrogen carrier", a substance capable of efficiently storing it. Techno-economic analyses are carried out on the value chains of ammonia (NH₃), liquefied hydrogen (LH₂), toluene/methylcyclohexane (TOL/MCH), and dibenzyltoluene/perhydro-dibenzyltoluene (H0-DBT/H18-DBT) for H₂ transportation. A case study is examined in which hydrogen is transported from North Africa to Italy. The value chain includes H₂ conversion into a carrier, storage, maritime transport, distribution, and reconversion back to H₂. The conversion and reconversion processes correspond to liquefaction and regasification for LH₂, synthesis and cracking for NH₃, and hydrogenation and dehydrogenation for TOL/MCH and H0-DBT/H18-DBT. NH₃ emerges as the most cost-effective and energy-efficient carrier when hydrogen is delivered to a hydrogen valley to serve nearby industries. The synthesis of ammonia, starting from green hydrogen, stands out as the primary cost driver of the value chain, followed by the ammonia cracking process. Ammonia cracking is the main source of energy inefficiency, highlighting the advantage of using ammonia directly where possible to avoid this step. For H₂ application in the road transport sector, which involves its distribution to multiple refuelling stations operating at high pressure, LH₂ is the most cost-effective and energy efficient carrier, provided that reconversion to hydrogen occurs at the refuelling stations. In this value chain, the liquefaction process represents the main cost driver and source of energy inefficiency.

1. Introduction

Hydrogen is a promising sustainable energy vector, as its production through water electrolysis powered by renewable electricity and its combustion generate no greenhouse gas emissions. This makes it a potential solution for decarbonising various sectors, including transportation, industry, power generation, and those where direct electrification is not feasible such as steelmaking industries [1]. Moreover, hydrogen can act as a buffer for intermittent renewable energy sources like wind and solar, storing excess energy produced during periods of high generation and releasing it when demand peaks occur. This capacity to balance supply and demand further underscores hydrogen's potential in the transition to a decarbonised energy system.

It can be efficiently produced in regions rich in renewable energy, which are often remote and far from major industrial centres. For

international hydrogen trade to be cost-effective, the production cost of green hydrogen in the exporting region must be significantly lower than in the importing region, enough to offset transportation expenses [2]. Therefore, establishing a robust transportation infrastructure to move this clean energy vector across continents is essential.

One of the main drawbacks of hydrogen is its low mass density, which is 0.08987 kg/m³ at standard conditions [3]. To enable cost-effective transport, hydrogen can be converted to a "hydrogen carrier", a substance capable of efficiently storing it. Widely considered hydrogen carriers are compressed hydrogen, liquefied hydrogen, ammonia (NH₃), methane (CH₄), methanol (CH₃OH), dimethyl ether (CH₃OCH₃), formic acid (HCOOH), liquid organic hydrogen carriers, and solid-state systems [4]. Compressed and liquefied hydrogen involve physical transformations, while the other mentioned carriers all involve an exothermic reaction to chemically bond hydrogen to another

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compound and an endothermic reaction to release the stored hydrogen.

Compressed hydrogen is the simplest way to store hydrogen, although its hydrogen density is low ($20.5 \text{ kg}_{\text{H}_2}/\text{m}^3$ at 300 bar). Hydrogen compression to high-pressure levels requires a significant energy consumption. Compressed hydrogen is typically stored in cylindrical tanks made of steel, aluminium or composite materials and characterised by a high length-to-diameter ratio. For road transportation, compressed hydrogen is carried in tube trailers, large trailers equipped with multiple high-pressure cylinders that typically transport hydrogen at pressures of 200–500 bar. These trailers can deliver sufficient hydrogen for small industrial applications or to supply refuelling stations. In hydrogen vehicles, hydrogen is stored in a high-pressure tank operating at about 700 bar, which is necessary to store enough hydrogen to achieve a driving range similar to that of conventional vehicles [5]. Moreover, as hydrogen is a very light and small element, leakage at high pressure can easily occur, in addition to the problem related to hydrogen embrittlement. Due to these limitations, compressed hydrogen is used only for small-scale hydrogen storage.

Liquefied hydrogen (LH_2) is considered a promising option for hydrogen storage because of its high hydrogen density ($70.8 \text{ kg}_{\text{H}_2}/\text{m}^3$), which is approximately 800 times that of uncompressed hydrogen [6]. However, in order to bring hydrogen into the liquid phase, refrigeration to a very low temperature (-253°C , at atmospheric pressure) is required, leading to high energy consumption [7]. Additionally, well-insulated tanks are necessary to minimise boil-off losses. On the other hand, the regasification process for converting liquid hydrogen back into gas is relatively simple.

Among chemical hydrogen carriers, liquid ammonia offers the highest hydrogen density ($121 \text{ kg}_{\text{H}_2}/\text{m}^3$), calculated as the product between its hydrogen capacity (17.8 wt% H_2) and its mass density ($680 \text{ kg}/\text{m}^3 \text{ NH}_3$). Ammonia is produced by reacting hydrogen with nitrogen, which can be sourced from air separation, thus avoiding the involvement of carbon-based compounds. Ammonia liquefaction occurs at a milder temperature of -33°C compared to hydrogen liquefaction, resulting in a less energy intensive process. The advantage of using ammonia as a hydrogen carrier lies in its widespread use, along with the availability of existing infrastructure for its transport and handling [8]. However, the main drawback is that the process for decomposing ammonia to release hydrogen is not yet fully developed and requires further research.

Methane, methanol, dimethyl ether, and formic acid can all be produced from fossil fuels or by reacting green hydrogen with CO_2 , typically sourced from carbon capture systems. The use of these carriers either undermines efforts towards sustainability or ties hydrogen storage to carbon capture technologies, which may present both an opportunity and a limitation, depending on the availability of CO_2 sources and the economic feasibility of carbon capture.

Liquid Organic Hydrogen Carriers (LOHCs) are liquids that can be reversibly hydrogenated and dehydrogenated at elevated temperatures in the presence of a catalyst. The initial structure of the LOHC compounds remain unchanged after the stored hydrogen is released, which eliminates the need to produce new carrier material in every cycle. Examples of LOHC pairs are: toluene (TOL)/methylcyclohexane (MCH) [9] and dibenzyltoluene (H0-DBT)/perhydro-dibenzyltoluene (H18-DBT) [10]. The hydrogen density of LOHC pairs is: $48 \text{ kg}_{\text{H}_2}/\text{m}^3$ for TOL/MCH (6.2 wt% H_2 , $770 \text{ kg}/\text{m}^3$ MCH [11]) and $56 \text{ kg}_{\text{H}_2}/\text{m}^3$ for H0-DBT/H18-DBT (6.2 wt% H_2 , $910 \text{ kg}/\text{m}^3$ H18-DBT [11]). Their main advantage is that they are stored and transported at ambient temperature and pressure. However, a drawback of LOHCs is that the organic carriers are typically derived from fossil sources, which raises concerns regarding sustainability.

Solid-state systems are also considered a potential hydrogen storage method, as they can reversibly adsorb and release hydrogen. Hydrogen storage in these systems occurs through two mechanisms: physisorption and chemisorption [12]. In physisorption, hydrogen molecules are adsorbed on the surface of an adsorbent due to the intermolecular force

that exists between the adsorbate (hydrogen) and adsorbent. However, achieving high storage capacities requires either low temperatures or high pressures. In chemisorption, hydrogen reacts chemically with solids to form hydrides. While these materials offer high hydrogen density, their hydrogenation and dehydrogenation processes are highly complex, and their reversibility is relatively limited [12].

Techno-economic assessments of the hydrogen carriers value chain have been widely explored in the literature, particularly in comparative analyses of different carriers [1,10,13–18]. The novelty of this work lies in its comparison of LH_2 , NH_3 , TOL/MCH and H0-DBT/H18-DBT, as the currently considered most promising hydrogen carriers for large-scale hydrogen transport, from both economic and energy efficiency perspectives. Compressed hydrogen is excluded from the analysis, as it is more suitable for small-scale or short-distance transport, as previously discussed. Methane, methanol, dimethyl ether, and formic acid are also excluded due to the co-release of CO_2 during H_2 recovery from these carriers, which compromises sustainability goals. Although CO_2 recirculation after reconversion is theoretically possible, similarly to what is done with LOHCs, this approach is considered uncompetitive. Indeed, the separation of two gases (H_2 and CO_2 , both gaseous at ambient conditions) is significantly more energy-intensive than separating a gas and a liquid (H_2 and LOHC, with the latter being liquid at ambient conditions). Additionally, solid-state materials are not included in the comparative analysis, as they are better suited for stationary application or mid-scale transport [19]. To the authors' knowledge, no other studies provide a comparative analysis that accounts for both economic and energy performance across various hydrogen carriers, while also distinguishing between different end-use applications of hydrogen, such as in industrial or road transport sectors. A key contribution is the introduction of the Net Equivalent Hydrogen method for energy assessment, which converts the energy consumption of processes within the hydrogen carrier value chain into product consumption by quantifying the equivalent hydrogen required to power specific equipment. The results of the comparative analysis are discussed in relation to potential hydrogen applications, using Levelized Cost of Hydrogen (LCOH) as a cost metric and Net Equivalent Hydrogen Delivered (NEHD) as a measure of energy efficiency. This dual-criteria approach facilitates informed decision-making and supports the selection of the most appropriate hydrogen carrier for a given application, providing guidance for planning future hydrogen infrastructure and supply chains.

2. Case study definition

The hydrogen carrier's value chain includes: H_2 production, conversion of H_2 to the considered carrier at the export terminal, storage of the carrier at the export terminal, maritime transport from the export to the import terminal, reconversion of the carrier to H_2 at the import terminal and H_2 utilisation. The following hydrogen carriers are selected for a comparative techno-economic analysis: liquefied hydrogen (LH_2), ammonia (NH_3), toluene/methylcyclohexane (TOL/MCH), and dibenzyltoluene/perhydro dibenzyltoluene (H0-DBT/H18-DBT). Their value chains are depicted in Fig. 1.

For LH_2 , the conversion and reconversion processes correspond to liquefaction and regasification. Liquefaction involves cooling hydrogen to extremely low temperatures to turn it into a liquid state. Indeed, at atmospheric pressure, the H_2 saturation temperature is -253°C . This process requires significant electric power to drive the compressors in the refrigeration cycles. Regasification, on the other hand, involves reheating liquid hydrogen to convert it back into a gaseous form for end use. The infrastructure for storing and transporting LH_2 shares similarities with that of Liquefied Natural Gas (LNG) since both are stored under cryogenic conditions. However, due to LH_2 's lower normal boiling point temperature and lower volumetric energy density compared to LNG, higher-performance insulation is necessary. LH_2 is stored in spherical tanks at slightly above atmospheric pressure [20]. These tanks feature a double-wall design: the inner vessel walls, in contact with the

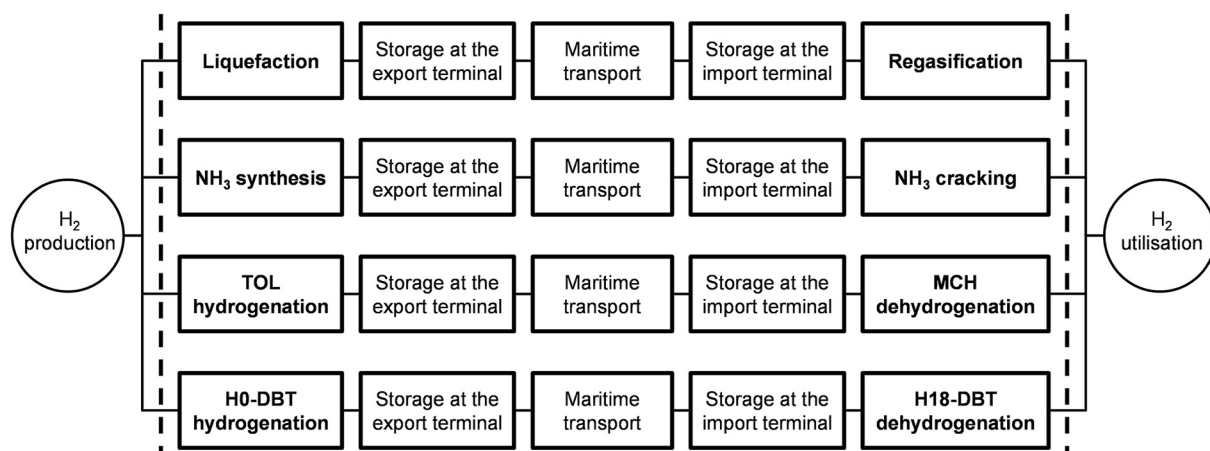


Fig. 1. – Value chain of hydrogen carriers.

low-temperature hydrogen, are made of stainless-steel alloys, while the outer vacuum shells are made of carbon steels [20]. The space between the double walls is filled with insulation materials such as perlite or glass bubbles [21], with a vacuum applied to minimise heat transfer and prevent the freeze-out of air components.

For NH_3 , the conversion and reconversion processes correspond to ammonia synthesis and cracking. The Haber-Bosch ammonia synthesis process is well-established and widely applied on a large scale. It is typically carried out starting from the reforming of light hydrocarbons. However, if hydrogen is produced exploiting renewable sources, the reformation step is avoided, and a nitrogen feed must be supplied. The reaction is carried out under a pressure of 200 bar and a temperature of about 350 °C, in the presence of an iron-based catalyst [22]. Downstream of the reaction section, the produced ammonia is separated from the unreacted hydrogen and nitrogen, which must be recycled back to the reactor, while simultaneously reaching the low temperature necessary for ammonia liquefaction at atmospheric pressure. The ammonia cracking process is a strongly endothermic reaction that generally takes place at high temperatures, which is the main drawback for its industrial-scale application. Ongoing research is exploring alternative methods to provide the required energy for activating the reaction. These methods include the application of electric current, microwaves, plasma, or solar energy [23]. The thermocatalytic process involves carrying out the reaction at high temperatures (about 900 °C) in the presence of a nickel-based catalyst [24]. The required heat for the reaction can be supplied by burning part of the fed ammonia along with waste streams. Downstream of the reactor, hydrogen is purified via adsorption. The process is not yet commercially available on a large scale. Currently, only small-scale ammonia crackers are on the market, and, due to their limited size, they are heated by electrical resistances [25]. The NH_3 storage and transport infrastructure is compatible with that of Liquefied Petroleum Gas (LPG) since they have similar physical properties. Ammonia transport infrastructure is already well-established, as ammonia is a key commodity and one of the world's most widely produced chemicals. Generally, there are three methods for liquefied ammonia storage: pressure storage (about 10 bar) at ambient temperature, suitable for small storage capacities; atmospheric storage at -33 °C in insulated tanks, used for large storage capacities; reduced pressure storage at about 0 °C [8]. Ammonia's corrosiveness is a significant factor that impacts the durability, safety, and cost of transportation systems, requiring corrosion-resistant materials (e.g., stainless steel) and frequent maintenance [8].

LOHCs are organic compounds that remain liquid at ambient conditions and can be reversibly hydrogenated and dehydrogenated at elevated temperatures in the presence of a catalyst. For LOHCs, the conversion and reconversion processes correspond to LOHC hydrogenation and dehydrogenation. Storage and transportation occur at

atmospheric conditions. The selection of LOHC species involves balancing cost and energy consumption for dehydrogenation. Toluene (TOL) is already a commercial product with a relatively low cost. It is hydrogenated to methylcyclohexane (MCH). However, by-products such as benzene and cyclohexane may form during its dehydrogenation [26]. Dibenzyltoluene (H0-DBT) is hydrogenated to perhydro dibenzyltoluene (H18-DBT). It has a lower hydrogenation enthalpy and a higher boiling point than toluene due to its molecular structure, but it is more expensive as there is no large-scale market for it yet [11]. The LOHC hydrogenation process is exothermic. The reaction takes place under moderate pressure and at a temperature of 200–250 °C, in the presence of nitrogen, acting as a thermal diluent, and a Pt-based catalyst [10]. The conversion and selectivity of the hydrogenation reaction are higher for dibenzyltoluene than for toluene [11]. Downstream of the reaction section, the hydrogenated compound, must be separated from unreacted hydrogen, which is recycled back to the reactor, and nitrogen, which must be purged to prevent inert gas accumulation. The LOHC dehydrogenation process is endothermic. It occurs under near-atmospheric pressure and at a temperature of 320–350 °C, in the presence of a noble metal-based catalyst [11]. The heat required for the reaction can be supplied by burning part of the produced hydrogen along with the waste streams. Downstream of the reaction section, hydrogen is separated from the organic species. This separation is simpler for perhydro dibenzyltoluene than for methylcyclohexane because H18-DBT's dehydrogenation reaction has a high selectivity toward the desired products. LOHCs are stored at atmospheric conditions. Unlike liquefied hydrogen and ammonia, no refrigeration is needed. They are compatible with existing fuel infrastructure and can be stored in standard industrial chemical storage tanks, such as atmospheric or low pressure (2.5–15 psig) cylindrical vessels, with fixed or floating roofs [27]. Since the export/import terminals must accommodate storage of both hydrogenated and dehydrogenated LOHC, the required storage capacity is effectively doubled.

To perform the techno-economic assessment of the hydrogen carriers, a case study is considered: the hydrogen, produced through renewable energy-driven electrolysis, is available at a flow rate ($F_{\text{H}_2, \text{in}}$) of 1800 kg/h, a pressure of 20 bar, and a temperature of 25 °C. The hydrogen is transported from North Africa to Northern Italy, covering a harbour-to-harbour distance of approximately 2500 km [28]. Two options for the hydrogen's final destination are investigated: a Hydrogen Valley (HV), operating at 30 bar, where all the hydrogen is conveyed for its end use in the industrial sector (requiring a H_2 purity of 99.9 mol%), and Hydrogen Refuelling Stations (HRS), with each station having a hydrogen demand of 500 kg/d, to serve the road transport sector (requiring a H_2 purity of 99.97 mol%, according to ISO 14687:2019). The pressure of the H_2 delivered to the HRS is 900 bar, required to fill the car tanks, typically at 700 bar. The distance from the port to the end user

(HV or HRS) is 100 km, with inland transport carried out by trucks. It is assumed that conventional fuels are used for ships and trucks. Hydrogen production and final utilisation are outside the battery limits.

Regarding hydrogen delivery to multiple HRS, it is essential to evaluate whether it is more cost-effective and efficient to reconvert the carrier to gaseous hydrogen at the import terminal (centralised reconversion) or at the end user's location (decentralised reconversion). These two options are compared for LH_2 and NH_3 carriers. However, for LOHCs, reconversion at the import terminal is predetermined, as it is considered more practical. Indeed, decentralised reconversion would require each end user to have one or more dedicated trucks to transport the dehydrogenated carrier back to the port for recirculation to the export terminal, making the process less feasible.

3. Methodology

The simulations of the conversion and reconversion processes performed in Aspen Plus® V11 [29] have already been discussed in previously published works of the authors [28,30–32]. Building upon these simulation results, this study introduces two key metrics for the techno-economic assessment of the hydrogen carriers' value chain: the Levelized Cost Of Hydrogen (LCOH) and the Net Equivalent Hydrogen Delivered (NEHD). The former is used for evaluating the economic performance of the hydrogen carriers, as detailed in Section 3.1, while the latter is applied to assess their energy efficiency (η), as outlined in Section 3.2.

3.1. Economic assessment

The Levelized Cost Of Hydrogen (LCOH), which is computed according to Eq. (1), is used to assess the H_2 transport cost, overall and for each step of the value chain, for the investigated cases.

$$\text{LCOH} = \frac{\sum_{t=0}^{N-1} \frac{\text{CAPEX}(t) + \text{OPEX}(t)}{(1 + \text{WACC})^t}}{\sum_{t=0}^{N-1} \frac{F_{\text{H}_2, \text{out}}}{(1 + \text{WACC})^t}} \quad (1)$$

In Eq. (1), $\text{CAPEX}(t)$ and $\text{OPEX}(t)$ are the capital and operating expenditures, respectively, at time t . It is assumed to spread the CAPEX among the first 3 years of the project. At the end of the project, the decommission cost is assumed to be 5 % of the total CAPEX. $F_{\text{H}_2, \text{out}}$ is the mass flow rate of hydrogen delivered yearly. The base year ($t = 0$) is 2023, and the project lifetime (N) is set to 25 years. A plant availability of 95 % is considered. The Weighted Average Cost of Capital (WACC) is assumed to be 5 %.

For the economic evaluation of the cost drivers of each value chain (liquefaction and regasification of hydrogen, synthesis and cracking of ammonia, hydrogenation and dehydrogenation of LOHCs), the capital and operating costs are estimated using the Turton methodology [33], starting from the process simulations detailed in the next Sections. The approach employed is intended for a preliminary feasibility study and provides a rough estimation of the plant expenses with an accuracy of ± 30 %. On the other hand, the economic evaluation for storage and transport is based on data found in the literature, as explained in Refs. [28,30,31]. It is assumed that the cost of marine fuel is 500 €/t [34], while that of diesel is 1.79 €/L (average retail price of diesel fuel in Italy in 2023 [35]).

The following briefly summarises the methodology proposed by Turton et al. [33]. The estimation of capital expenditures requires the calculation of the purchased base cost $C_{p,i}^0$ referred to the year 2001, for each piece of equipment through the equation:

$$\log_{10}(C_{p,i}^0(2001)) = K_{1,i} + K_{2,i} \log_{10}(A_i) + K_{3,i} [\log_{10}(A_i)]^2 \quad (2)$$

where $K_{1,i}$, $K_{2,i}$, $K_{3,i}$ are constants specific to the equipment type and A_i is

the equipment characteristic size. The constants to be used in Eq. (2) are reported in Ref. [33]. To obtain an up-to-date cost estimate, the following expression is considered:

$$C_2 = C_1 \left(\frac{I_2}{I_1} \right) \quad (3)$$

where C represents the purchased cost, I stands for a cost index and the subscripts denote different times. In this analysis, the chosen cost index is the Chemical Engineering Plant Cost Index (CEPCI), with $\text{CEPCI}_{2001} = 397$ and $\text{CEPCI}_{2023} = 797.9$.

To account for the effects of operating pressure and construction material on the equipment cost, the bare module cost ($C_{BM,i}$) is introduced and calculated using the following equation:

$$C_{BM,i} = C_{p,i}^0 F_{BM,i} = C_{p,i}^0 (B_{1,i} + B_{2,i} F_{M,i} F_{P,i}) \quad (4)$$

where $F_{BM,i}$ is the bare module factor, function of the material factor $F_{M,i}$, which depends on the material of construction, the pressure factor $F_{P,i}$, which accounts for the equipment's operating pressure, and $B_{1,i}$ and $B_{2,i}$, which are equipment-specific constants. The bare module cost for atmospheric pressure and carbon steel construction material ($C_{BM,i}^0$) is computed by setting $F_{M,i}$ and $F_{P,i}$ equal to unity. The total module cost (C_{TM}) is computed increasing by 18 % the bare module cost of the equipment, to take into account contingency costs and fees. The CAPEX, as in Eq. (5), take into account the cost for auxiliary buildings, site development, off-sites and utilities (grassroots cost) by appropriately increasing the total module cost.

$$\text{CAPEX} = C_{TM} + 0.5 \sum_{i=1}^n C_{BM,i}^0 = 1.18 \sum_{i=1}^n C_{BM,i} + 0.5 \sum_{i=1}^n C_{BM,i}^0 \quad (5)$$

The operating expenditures of the plant can be categorised into: direct manufacturing costs, which are expenses that vary according to production rate, fixed manufacturing costs, which remain constant irrespective of variations in production rate and include property taxes, insurance, and plant overhead expenses, and general expenses, which are expenses that rarely change according to production rate and include sales, management, financing and research functions. Neglecting for the considered processes the cost of waste treatment, the OPEX are computed by adding up the direct and fixed manufacturing costs, as well as the general expenses, which are accounted by properly factorising the cost of raw materials (C_{RM}), the cost of utilities (C_{UT}), the cost of operating labour (C_{OL}), and the CAPEX:

$$\text{OPEX} = \frac{C_{RM} + C_{UT} + 2.215 \cdot C_{OL} + 0.146 \cdot \text{CAPEX}}{0.76} \quad (6)$$

C_{RM} accounts for the costs of organic species make-up, with toluene estimated at 850 €/t and dibenzyltoluene at 3000 €/t [28]. C_{UT} involves the costs associated with the consumption of electricity and cooling water (CW), operating from 20 °C to 30 °C. Table 1 reports the specific utility costs utilised in this work for the different countries involved. Utility consumption is determined from the energy balances obtained through process simulation. C_{OL} is calculated based on the number of operators required per shift (N_{OL}), computed according to Eq. (7) [33], and the average annual wage per operator, which is reported in Table 1 for each country involved in this study. It is assumed that a single operator works for five 8-h shifts a week, for a total of 45 weeks in a year.

Table 1

– Specific cost of utilities and average annual wage per operator (chemical plant operator) for the involved countries.

Country	Electricity [€/MWh]	CW [€/t]	Average annual operator wage [€/y/operator]
North Africa	32 [36]	0.015	11968 [37]
Italy	111 [38]	0.015	45716 [39]

In Eq. (7), N_u is the number of process units (excluding valves and pumps).

$$N_{OL} = \text{round up}[(6.29 + 0.23 \cdot N_u)^{0.5}] \quad (7)$$

3.2. Energetic assessment

The “net equivalent hydrogen” method, akin to the widely used “net equivalent methane” method [40], is applied to convert energy consumption into product consumption. This approach estimates the amount of hydrogen that would need to be burned to power specific equipment. By adopting this unified energy basis, the method facilitates a fair comparison across different processes.

Energy interactions are categorised as follows: heating below ambient temperature, cooling above ambient temperature, heating above ambient temperature, cooling below ambient temperature, and supplying electrical power. According to the methodology outlined by Pellegrini et al. [40], heating below ambient temperature and cooling above ambient temperature do not require hydrogen consumption, as service water can be used to provide or remove heat, respectively.

In the processes analysed, heating above ambient temperature is achieved, where possible, by coupling process streams. When this is not feasible, heating is supplied either by burning hydrogen (or ammonia in the NH_3 value chain) with air in a furnace for large-scale processes, or by using electrical resistances (Joule effect) for small-scale processes. In the former case the Net Equivalent Hydrogen Consumed ($NEHC$) depends on the hydrogen content of the fuel mixture and is calculated according to Eq. (8), where F_{fuel} represents the fuel flow rate, and w_{H_2} is the hydrogen weight fraction in the fuel. In the latter case, $NEHC$ is indirectly tied to the electric power required.

$$NEHC = F_{fuel} \cdot w_{H_2} \quad (8)$$

Cooling below ambient temperature is achieved via heat exchange with fluids circulating in refrigeration cycles. Consequently, hydrogen consumption is indirectly related to the electric power needed to operate the compressors in these cycles. The $NEHC$ for supplying electric power, used to drive compressors, pumps, and for small-scale heating using electrical resistances, is determined using Eq. (9), assuming power generation through hydrogen fuel cells.

$$NEHC = \frac{W}{\eta_{FC} \cdot LHV_{H_2}} \quad (9)$$

In Eq. (9), W denotes the electric power consumption, η_{FC} is the fuel cell efficiency, assumed equal to 60 %, and LHV_{H_2} is the lower heating value of hydrogen.

Finally, the Net Equivalent Hydrogen Delivered ($NEHD$) is calculated by subtracting both the $NEHC$ and the hydrogen lost due to boil-off during shipping (F_{BOG}) from the total hydrogen fed into the plant:

$$NEHD = F_{H_2, in} - NEHC - F_{BOG} \quad (10)$$

The energy efficiency (η) of the value chain is defined as the ratio between the $NEHD$ and the hydrogen feed flow rate:

$$\eta = \frac{NEHD}{F_{H_2, in}} \quad (11)$$

4. Results and discussion

The results of the economic and energetic assessments are presented and discussed considering H_2 final application in the industrial sector (Section 4.1) and in the road transport sector (Section 4.2).

4.1. HV case

Regarding the H_2 application to the industrial sector (HV case), the $LCOH$ for each investigated carrier is presented in Table 2 and Fig. 2.

Table 2

– $LCOH$ [€/kg] for each step of the hydrogen carriers' value chain.

	LH_2	NH_3	TOL/MCH	H0-DBT/H18-DBT
Initial loading	–	–	0.16	0.57
Conversion	2.56	2.27	2.17	0.51
Storage	1.21	0.45	1.50	1.31
Maritime transport	0.92	0.64	0.65	0.53
Distribution	0.25	0.31	0.65	0.62
Reconversion	0.14	1.15	1.05	1.25
Overall	5.09	4.82	6.18	4.79

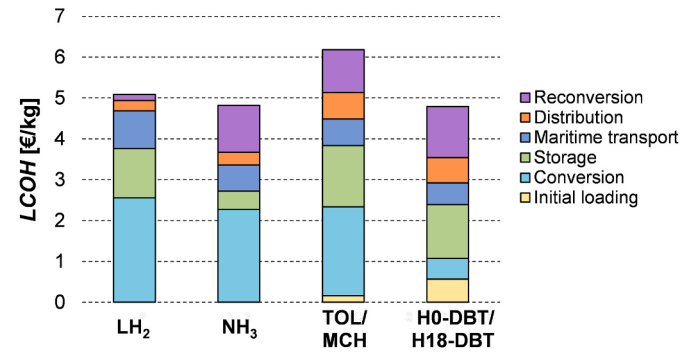


Fig. 2. – $LCOH$ [€/kg] for the hydrogen carriers in the HV case.

For the LH_2 value chain, the overall $LCOH$ is 5.09 €/kg. The cost driver of the value chain is the liquefaction process, followed by storage and transport, while the regasification process has a negligible impact on the total $LCOH$. The high cost of the conversion process arises from the significant electricity demand required to operate the compressors. The total $LCOH$ for the NH_3 value chain is 4.82 €/kg, with the synthesis of ammonia being the primary cost driver of the value chain, followed by the centralised cracking. The lower transport and storage costs for NH_3 compared to LH_2 stem from its higher hydrogen density (121 kg/m^3 vs 70.8 kg/m^3), which implies smaller storage tanks, and its less advanced insulation requirements, as a consequence of its milder storage temperature (-30°C vs -250°C). While the reconversion process is less costly for LH_2 than for NH_3 , this is insufficient to offset the higher costs in the other stages of the value chain. LH_2 regasification involves only pumping and vaporisation, whereas ammonia cracking requires a reaction section where the high-temperature endothermic decomposition process is carried out. For the TOL/MCH value chain, the overall $LCOH$ is 6.18 €/kg, with toluene hydrogenation being the step with the highest cost. The major factor contributing to this is represented by the make-up cost, which accounts for approximately 50 % of the hydrogenation costs. The overall $LCOH$ for the H0-DBT/H18-DBT value chain is 4.79 €/kg. For both the considered LOHC pairs, TOL/MCH and H0-DBT/H18-DBT, storage costs are significant. This is because the LOHC species present a lower gravimetric hydrogen density ($48 \text{ kg}_{H_2}/\text{m}^3$ for TOL/MCH and $56 \text{ kg}_{H_2}/\text{m}^3$ for H0-DBT/H18-DBT), compared to LH_2 ($70.8 \text{ kg}_{H_2}/\text{m}^3$) and NH_3 ($121 \text{ kg}_{H_2}/\text{m}^3$), which leads to larger storage tanks, and, in addition, both the hydrogenated and dehydrogenated organic species need to be stored at each terminal, entailing doubling the number of storage tanks. For both the TOL/MCH and H0-DBT/H18-DBT value chains, dehydrogenation costs are substantial due to the high energy demands of the endothermic dehydrogenation processes.

The ranking of hydrogen carriers based on their cost-effectiveness is as follows: H0-DBT/H18-DBT (4.79 €/kg), NH_3 (4.82 €/kg), LH_2 (5.09 €/kg), and TOL/MCH (6.18 €/kg). H0-DBT/H18-DBT and NH_3 are the most cost-effective hydrogen carriers for H_2 application to the industrial sector (HV case), with H0-DBT/H18-DBT having slightly better performance than NH_3 due to its lower costs for hydrogen conversion to the carrier. In the future, when the cost of electricity is expected to decrease

due to the increasing deployment of renewable energy and technology development, liquefied hydrogen has greater potential for cost reduction as the process relies almost entirely on electricity.

Fig. 3 presents the results of the energetic assessment for the considered hydrogen carriers using Sankey diagrams, for the case in which hydrogen application is envisaged in the industrial sector.

The *NEHD* for the LH_2 value chain is 1070 kg/h, reflecting an overall energy efficiency of 59 %. Among the processes, hydrogen liquefaction has the highest *NEHC* (712 kg/h), used to supply electric energy for driving the compressors. This process consumes approximately one-third of the total hydrogen input to the value chain. The *NEHC* for regasification is negligible (2 kg/h) and is related to the electricity required for driving the pumps. For NH_3 , the *NEHD* is 1277 kg/h, reflecting a η of 71 % for the value chain. Among the processes, ammonia cracking has the highest *NEHC* (366 kg/h), used to provide the heat required to sustain the endothermic reaction. This is achieved by burning part of the fed ammonia together with the waste streams from the hydrogen purification section. The *NEHC* for supplying electric power to the process accounts for 1 kg/h. The ammonia cracking process involves a hydrogen consumption of approximately one-fifth of the total hydrogen input to the value chain. The *NEHC* for ammonia synthesis is 148 kg/h, used to supply electric power for driving the compressors, as the reaction section operates at a pressure of 200 bar. Hydrogen losses due to boil-off occur during maritime transport both in the LH_2 and NH_3 value chains. While boil-off losses are higher for LH_2 than NH_3 , their impact do not significantly affect the overall results. Among LOHC pairs, H0-DBT/H18-DBT is more energy efficient than TOL/MCH. The *NEHD* is 934 kg/h for H0-DBT/H18-DBT, corresponding to η of 52 %, and 896 kg/h for TOL/MCH, reflecting a η of 50 %. TOL hydrogenation stage has a higher equivalent hydrogen consumption than that of H0-DBT: this is due to the higher *NEHC* for supplying electric power to drive the H_2 recycle compressor (72 kg/h for TOL/MCH vs 32 kg/h for H0-DBT/H18-DBT), as well as to the product losses in purge streams, which accounts for 98 kg/h for TOL/MCH. Purge streams are necessary to avoid the build-up of nitrogen, used as thermal diluent, and by-products, as methane and benzene, formed during toluene hydrogenation. Due to by-

products formation and the need for purge streams in both the hydrogenation and dehydrogenation of the LOHC species, a make-up stream is required. For H0-DBT/H18-DBT, the make-up flow-rate is negligible because no by-products form during its hydrogenation and dehydrogenation, and H0-DBT and H18-DBT are heavy components and, hence, their losses through the vents are negligible. In contrast, for TOL/MCH, the make-up flow rate is significant, representing approximately 6 % of the total toluene flow rate entering the hydrogenation process. As opposite to LH_2 or NH_3 , no H_2 losses because of the carrier boil off occur during storage and maritime transport, as they are stable under ambient temperature and pressure. For both LOHC species, dehydrogenation requires significant energy input to cope for the endothermicity of the reaction. This energy is supplied by burning part of the hydrogen product, possibly combined with purge streams, thereby reducing the overall efficiency. This contribution amounts to 603 kg/h for MCH dehydrogenation and 647 kg/h for H18-DBT dehydrogenation.

The efficiency ranking of hydrogen carriers is as follows: NH_3 (71 %), LH_2 (59 %), H0-DBT/H18-DBT (52 %), and TOL/MCH (50 %).

Given its low *LCOH* and high η , NH_3 results the best hydrogen carrier for hydrogen application to the industrial sector. The significantly higher NH_3 efficiency compared to the other considered carriers suggests that it would become even more economically favourable as utility prices rise. Indeed, a higher efficiency implies a lower utility consumption, which translates to reduced *OPEX*. Consequently, as utility prices increase, the cost gap between the different carriers widens in proportion to their respective efficiencies.

4.2. HRS case

The *LCOH* for the hydrogen carriers in case of H_2 application to the road transport sector (HRS case) is reported in Table 3 and graphically in Fig. 4.

As regards the LH_2 value chain, the overall *LCOH* is 11.75 €/kg and 9.61 €/kg for the centralised and decentralised configurations, respectively. Therefore, it is more cost-effective to distribute liquefied hydrogen and perform decentralised regasification at the refuelling

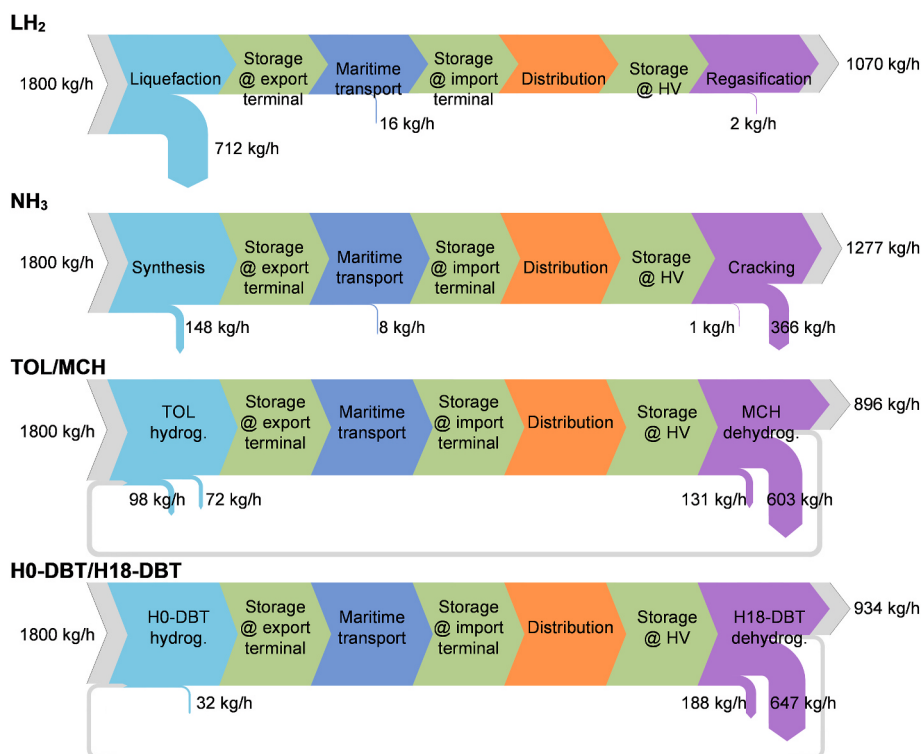


Fig. 3. – *NEHD* [kg/h] for the hydrogen carriers in the HV case.

Table 3– *LCOH* [€/kg] for each step of the hydrogen carriers' value chain.

	LH ₂		NH ₃		TOL/ MCH	H0-DBT/ H18-DBT
	centr.	decentr.	centr.	decentr.		
Initial loading	–	–	–	–	0.11	0.38
Conversion	2.53	2.53	2.30	2.12	2.17	0.51
Storage	0.80	1.00	0.30	0.31	1.00	0.87
Maritime transport	0.91	0.91	0.65	0.60	0.65	0.53
Distribution	1.44	0.25	1.44	0.29	1.46	1.44
Reconversion	0.19	4.92	1.16	4.84	1.05	1.25
Compression	5.88	–	6.33	3.92	6.38	6.37
Overall	11.75	9.61	12.17	12.08	12.81	11.35

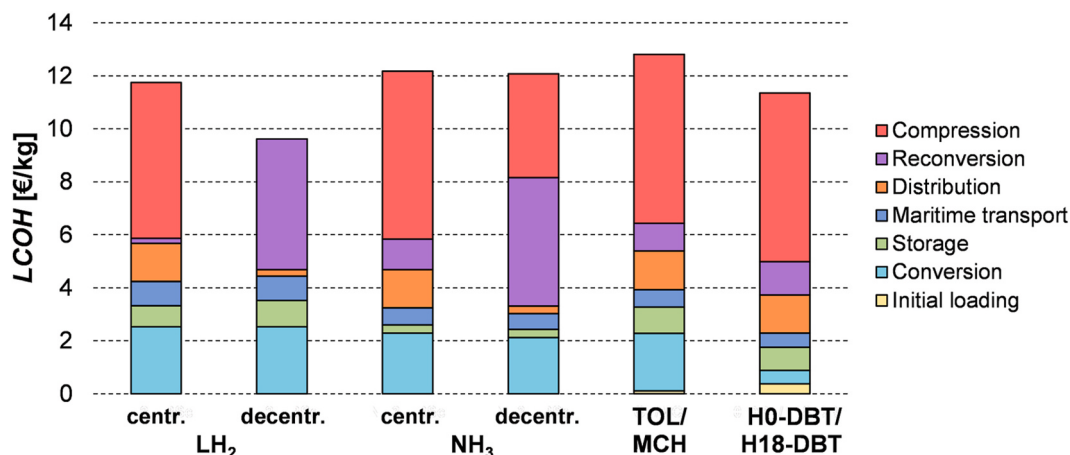
stations rather than performing centralised regasification at the import terminal and distributing compressed gaseous hydrogen, which would then require further compression at the stations. As illustrated in Fig. 4, the decentralised configuration involves slightly higher storage costs (green bar) than the centralised one due to the need for LH₂ storage tanks at each refuelling station to supply the decentralised regasification process. However, these higher storage costs are offset by lower distribution costs (orange bar), owing to the higher density of liquefied hydrogen compared to compressed hydrogen, and by lower reconversion + compression costs, as compressing a liquid requires less mechanical power than compressing a gas. For the NH₃ value chain, the total *LCOH* is 12.17 €/kg and 12.08 €/kg when considering, respectively, the centralised or decentralised ammonia reconversion to hydrogen. In the case of hydrogen delivery to HRS, distributing liquefied ammonia and carrying out decentralised cracking at the refuelling stations is more cost-effective than performing centralised cracking at the import terminal and distributing compressed gaseous hydrogen. In fact, the centralised configuration is disadvantaged by the higher cost associated with road transport of compressed hydrogen. Furthermore, because ammonia is burned to sustain the endothermic cracking reaction, unlike in the decentralised configuration, where small-scale crackers are powered by electricity, a lower hydrogen flow rate is delivered, resulting in fewer refuelling stations being served. For hydrogen application in the road transport sector, it has been determined that decentralised reconversion at the refuelling stations is more cost-effective for both LH₂ and NH₃. In this configuration, LH₂ exhibits a lower *LCOH* than NH₃. The breakdown of *LCOH* across the stages of the value chain differs for these two carriers (see Fig. 4), with NH₃ having higher reconversion costs, but lower conversion, storage, transport, and distribution costs. For the less economical centralised configuration, H0-DBT/H18-DBT has a slightly lower *LCOH* (11.35 €/kg) than the other carriers. In this centralised configuration, distribution costs are roughly equivalent for all the

carriers. The compression costs are roughly equivalent for NH₃, TOL/MCH and H0-DBT/H18-DBT, while LH₂ has lower costs because the centralised pressurisation at the import terminal is achieved through more efficient liquid pumping, rather than gaseous hydrogen compression.

The ranking of hydrogen carriers based on their cost-effectiveness is as follows: LH₂ in the decentralised configuration (9.61 €/kg), NH₃ in the decentralised configuration (12.08 €/kg), H0-DBT/H18-DBT (11.35 €/kg), LH₂ in the centralised configuration (11.75 €/kg), NH₃ in the centralised configuration (12.17 €/kg), and TOL/MCH (12.81 €/kg). This highlights the economic convenience of the decentralised configuration and the advantage of LH₂ over NH₃ in avoiding the compression costs. Since most of the *LCOH* is due to the reconversion costs, which are mostly related to electricity consumption for pumping in the LH₂ value chain, and for heat supply through resistances and compression in the NH₃ value chain, the only way to reduce costs is by lowering the price of electricity.

Fig. 5 compares the results of the energetic assessment for the considered hydrogen carriers for the case in which hydrogen application is envisaged in the road transport sector, in the centralised configuration and in the decentralised configuration (only LH₂ and NH₃).

For LH₂, the *NEHD* is 780 kg/h and 1018 kg/h, reflecting an overall efficiency of 43 % and 57 %, for the centralised and decentralised configurations, respectively. For LH₂, decentralising the reconversion to the refuelling stations is energetically convenient because hydrogen arrives at the user in its liquid state and can be pumped to the HRS operating pressure before vaporisation, to save compression work downstream of regasification. These results indicate that for LH₂ the decentralised configuration is superior to the centralised one, not only from an economic perspective but also in terms of energy efficiency. The *NEHD* for NH₃ is 957 kg/h and 862 kg/h, with associated η of 53 % and 48 % for the centralised and decentralised configurations, respectively. These results indicate that, while the decentralised configuration is economically advantageous, it results in lower energy efficiency. The difference in the energy efficiency of the two configurations arises because the cracking process powered by electricity is less efficient overall than the process conducted in a furnace. This is inherent in the Net Equivalent Hydrogen method, where electricity is generated from hydrogen utilisation in fuel cells, which have an efficiency of 60 %. However, electrically powered cracking could become less demanding in terms of hydrogen consumption if renewable production facilities were available on-site (at the refuelling stations). For the LOHC species, the *NEHD* is 656 kg/h for TOL/MCH and 680 kg/h for H0-DBT/H18-DBT, reflecting overall efficiencies of 38 % and 36 %, respectively. The same considerations discussed for the HV case apply here; however, in this case, the additional *NEHC* for gaseous hydrogen compression at

**Fig. 4.** – *LCOH* [€/kg] for the hydrogen carriers in the HRS case.

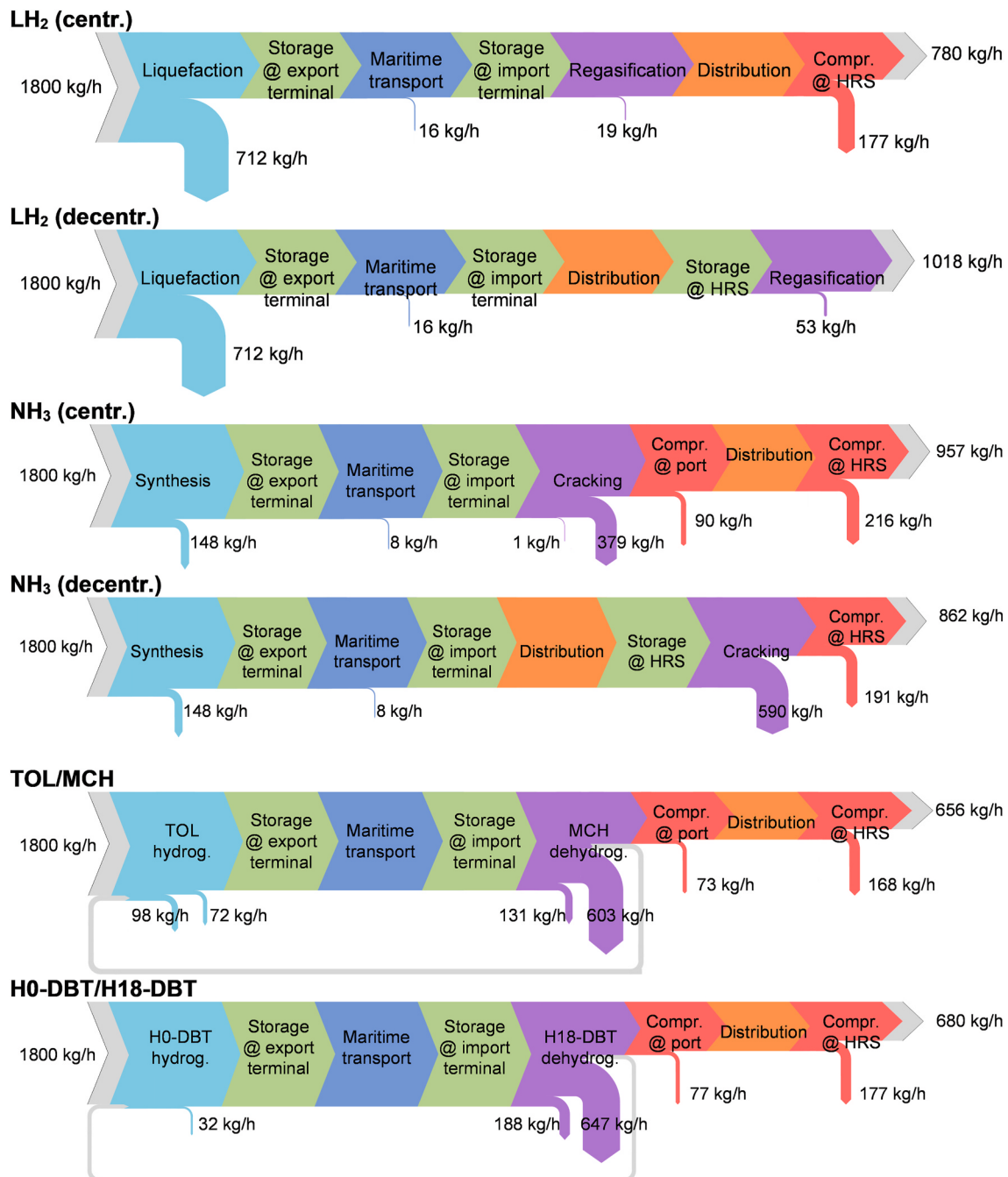


Fig. 5. – NEHD [kg/h] for the hydrogen carriers in the HRS case.

the port and refuelling stations must be accounted.

The ranking of hydrogen carriers based on their energy efficiency is as follows: LH₂ in the decentralised configuration (57 %), NH₃ in the centralised configuration (53 %), NH₃ in the decentralised configuration (48 %), LH₂ in the centralised configuration (43 %), H0-DBT/H18-DBT (38 %), and TOL/MCH (36 %).

Since LH₂ has the lowest *LCOH* and the highest η , it is selected as the preferred option for hydrogen application to the road transport sector, in the decentralised configuration.

5. Conclusions

The conducted techno-economic analysis allowed for a detailed exploration of each step of the hydrogen carriers' value chains, offering

insights into the strengths and weaknesses of the processes involved. For the considered case study, recommendations for selecting the most suitable hydrogen carrier are provided based on the intended end use of the delivered hydrogen, distinguishing between applications in the industrial sector (delivery to a Hydrogen Valley) and the road transport sector (delivery to Hydrogen Refuelling Stations):

- for H₂ application in the industrial sector, NH₃ is the best hydrogen carrier option, as it presents a low cost (*LCOH* of 4.82 €/kg) and a high energy efficiency (η of 71 %);
- for H₂ application in the road transport sector, LH₂ is the preferred carrier, offering a low cost (*LCOH* of 9.61 €/kg) and a high energy efficiency (η of 57 %), provided that reconversion to hydrogen takes place at the refuelling stations.

The economic viability of transporting hydrogen should be evaluated by comparing the cost of hydrogen production at the export location with that at the import location. For international trade to be cost-effective, the combined cost of producing green hydrogen in Africa and transporting it to Italy must be lower than the cost of producing green hydrogen domestically in Italy. This cost advantage is expected to grow with increasing project scale and technological advancements that reduce transport costs.

In conclusion, the key findings of this work are:

- the optimal use of hydrogen involves centralisation at a single hub operating at moderate pressure. This approach enhances safety, as hydrogen is a hazardous substance with risks of flammability and explosion, allowing few, well-trained personnel to manage it, thereby reducing the risk of accidents;
- ammonia would be more economically attractive if it could be used directly by the end consumer, thereby avoiding the additional costs of reconverting it back into hydrogen;
- for hydrogen applications in the road transport sector, where distribution to multiple refuelling stations operating at high pressure is required, it is more cost-effective to distribute the liquid carrier and perform the reconversion to hydrogen at the refuelling stations (decentralised configuration). This approach is more economical than reconverting the carrier at the import terminal and distributing compressed gaseous hydrogen to refuelling stations (centralised configuration), where additional compression is needed after truck discharge. The cost advantage arises from the higher density of liquid carriers compared to compressed hydrogen, allowing for fewer trucks to transport the same quantity of hydrogen.

This study represents a systematic evaluation of the technical and economic aspects of transporting hydrogen overseas. Future research should focus on improving the cost-effectiveness of the cost-driving processes by implementing energy-saving schemes and exploring potential integration with external processes. As the scale increases, operating costs, which increase linearly with the flow rate, become more important than investment costs, which benefit from the economy of scale. Among operating expenses, those related to utilities are the most subject to variability, in particular the cost of electricity. Since electricity prices are generally low in exporting regions and higher in importing regions, it is more impactful to optimise the processes of carrier reconversion to hydrogen. In this perspective, future research efforts should focus on improving the efficiency of ammonia cracking, LOHC dehydrogenation, and liquefied hydrogen regasification. Regarding ammonia cracking, research should focus on developing new catalysts, that can lower the operating temperature of the reactor, or on advancing alternative technologies to the thermocatalytic process. As regards LOHC dehydrogenation, investigating new LOHC pairs with lower dehydrogenation enthalpies is essential to reduce the inefficiencies associated with this step of the value chain. For liquefied hydrogen regasification, research should focus on exploiting cold energy, especially when regasification is carried out in centralised hubs, to generate electric power or produce marketable products that require cryogenic separation. This approach could effectively result in a negative cost for this step in the LH₂ value chain.

CRediT authorship contribution statement

Federica Restelli: Writing – original draft, Visualization, Software, Methodology, Formal analysis, Conceptualization. **Elvira Spatolisano:** Writing – review & editing, Software, Methodology, Formal analysis, Conceptualization. **Laura A. Pellegrini:** Writing – review & editing, Supervision, Resources, Methodology, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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